ACTA CHEMICA SCANDINAVICA 27 (1973) 1987–2000

Formation of 5-Hydroxy-Δ^2-1,2,3-triazolines, 1,2,3-Triazoles, and Ketohydrazones in Base-catalyzed Reactions of Organic Azides with Methyl Ketones

CARL ERIK OLSEN

*Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark and Organic Chemical Laboratory, Royal Veterinary and Agricultural University, Thorvaldsenvej 40, DK-1871 Copenhagen, Denmark**

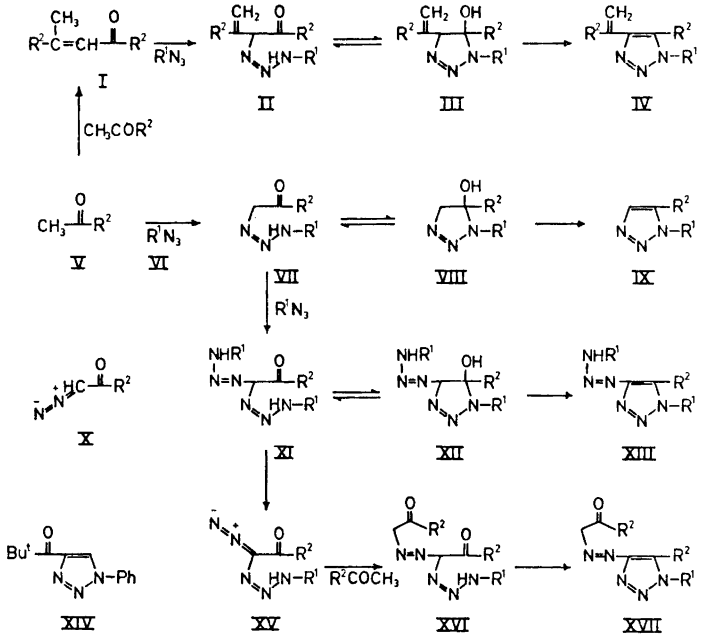
Under the influence of potassium *tert*-butoxide (PTB) organic azides, *e.g.* benzyl and phenyl azide, react with methyl ketones, *e.g.* acetone, pinacolone, and acetophenone, to give 5-hydroxy-Δ^2-1,2,3-triazolines, which under these reaction conditions normally react further, either by eliminating water under the formation of 1,2,3-triazoles (IX) or, after ring-opening, by reacting with one further molecule of azide to give bis-triazeno ketones (XI). XI may ring-close and eliminate water under formation of a triazenotriazole (XIII) or eliminate an amine under formation of an aliphatic diazo compound (XV), which is in a position to couple with an additional molecule of methyl ketone to give ketoazo compounds (XVII). In solution XVII is shown to be present in the NH tautomeric form (ketohydrazone) with the possibility of either a *cis* (chelated) or a *trans* configuration about the C=N bond. The position of the equilibrium between these two forms depends on substituents and solvent.

As reported previously [1,2] organic azides react with various ketones under the influence of potassium *tert*-butoxide (PTB) to give 5-hydroxy-Δ^2-1,2,3-triazolines. The reason that the reactions of methyl ketones have been singled out is that the triazolines formed here (those formed from methyl ethyl ketone being exceptions [1,2]) normally react further to give more complex compounds. The reactions of three methyl ketones with benzyl azide and phenyl azide have been investigated. They are summarized in Scheme 1 and may be rationalized in terms of reactivity of the azide and position of the always existing [1,2] equilibrium between the initially formed triazene VII and its ring-chain tautomer, the hydroxytriazoline VIII.

* Present address.

REACTIONS OF METHYL KETONES WITH BENZYL AZIDE (R^1 = benzyl)

The reaction (Scheme 1) of benzyl azide with acetone (R^2 = methyl) in the presence of PTB produced 1-benzyl-5-methyl-1,2,3-triazole (IXa), formed by dehydration of VIIIa, and 1-benzyl-4-isopropenyl-5-methyl-1,2,3-triazole



Yields

	R^1	R^2	IV	VIII	IX	XII	XIII	XVII
a	$PhCH_2$	Me	40		37			
b	$PhCH_2$	But			34	24		
c	$PhCH_2$	Ph		24	31			
d	Ph	Me	1.3		0.9		1.6	74
e	Ph	But						31
f	Ph	Ph		13				11

Scheme 1.

(IVa), identified by comparison with the corresponding 1-phenyl compound (IVd, *vide infra*). IVa is presumably formed from the triazene IIa by ring-closure and dehydration (IIa→IIIa→IVa). IIa might be produced either by reaction of preformed mesityl oxide (Ia) with benzyl azide or by reaction of VIIa (which is in equilibrium with VIIIa) with a second molecule of acetone. The latter possibility could be excluded, however, since treatment of VIIIa

(prepared in a 7 % yield from acetone and benzyl azide, using short reaction time) with acetone in the presence of PTB gave IXa and not IVa. Although the self-condensation of acetone in basic media often stops at the stage of the β-hydroxyketone,[3] dehydration to mesityl oxide may well take place in the presence of the very strong base PTB. In support of this interpretation NMR analysis of the mixture resulting from the PTB-catalyzed reaction of mesityl oxide with benzyl azide demonstrated a high yield of IVa.

The reaction of benzyl azide with pinacolone ($R^2 = Bu^t$) gave a mixture of 1-benzyl-5-*tert*-butyl-1,2,3-triazole (IXb) and the benzyltriazeno hydroxytriazoline XIIb. As expected, no IVb was formed, the self-condensation V→I being highly retarded by the bulky *tert*-butyl groups. XIIb, a tautomer of the bis-triazene XIb, must be formed from VIIb by reaction with an additional molecule of azide. This is quite conceivable, since a *tert*-butyl group at the 5-position of a 5-hydroxy-Δ^2-1,2,3-triazoline is known to retard the dehydration to triazole,[4] thus giving the benzyl azide a better chance to attack VIIb. No VIIIb is, however, accumulated in the reaction mixture, as demonstrated by NMR spectra of samples taken at intervals. The reactions VIIIb→IXb and VIIb→XIb must therefore proceed with comparable rates and much faster than the initial step, V + VI→VII (the equilibration VII⇌VIII is considered to be relatively fast). The compounds IXb and XIIb were formed in almost exactly the same ratio when a threefold excess of pinacolone was used in place of an equimolecular amount.

The reaction of benzyl azide with acetophenone ($R^2 = Ph$) yielded a mixture of 1-benzyl-5-phenyl-5-hydroxy-Δ^2-1,2,3-triazoline (VIIIc) and its dehydration product, 1-benzyl-5-phenyl-1,2,3-triazole (IXc); but the NMR spectrum of the product mixture showed no signs of XIIc, significant signals within the range 5.6 – 6.8 ppm being absent (the H-4 proton of XIIb lies at 5.54 ppm). Obviously the dehydration of VIIIc is relatively slow, and it is surprising that VIIc does not react with more azide to form XI (or its tautomer XII), as was the case with VIIb. However, it may be explained by the general reluctance of 5-phenyl-5-hydroxy-Δ^2-1,2,3-triazolines toward ring-opening [1,2] in combination with a relatively high reactivity of acetophenone, resulting in a rather short reaction time (2.5 h as compared with 5 days for pinacolone). As reported elsewhere [4] bulky groups at the 5-position seem to retard the dehydration of 5-hydroxy triazolines, and this may be the reason why VIIIc is not fully converted into IXc.

REACTIONS OF METHYL KETONES WITH PHENYL AZIDE (R^1 = phenyl)

The reaction of phenyl azide with acetone yielded four products: 1-phenyl-5-methyl-1,2,3-triazole (IXd) (0.9 %), 1-phenyl-4-isopropenyl-5-methyl-1,2,3-triazole (IVd) (1.3 %), 1-phenyl-4-phenyltriazeno-5-methyl-1,2,3-triazole (XIIId) (1.6 %), and the main product XVIId (74 %), the structure of which shall be discussed later. The presumed intermediate VIIId (in equilibrium with VIId) could not be isolated, but its presence was demonstrated by NMR analysis of the product mixture resulting from the reaction, when it was carried out in dilute solution (ether) and interrupted after one minute. The protons

at the 4-position showed up as a characteristic AB pattern centered at 4.3 ppm ($J_{AB} = 18$ cps).

The structure of IVd was established by NMR spectroscopy and by oxidation with potassium permanganate to give 1-phenyl-4-acetyl-5-methyl-1,2,3-triazole, identical with a sample prepared from ethyl 1-phenyl-5-methyl-1,2,3-triazole-4-carboxylate by aldol condensation with ethyl acetate and subsequent hydrolysis. Furthermore, IVd was produced in a high yield (91 %) from mesityl oxide and phenyl azide.

The structure of XIIId, determined by IR and NMR spectroscopy, was confirmed by an independent synthesis. Curtius transformation of the azide of 1-phenyl-5-methyl-1,2,3-triazole-4-carboxylic acid gave 1-phenyl-4-amino-5-methyl-1,2,3-triazole, which by coupling with benzenediazonium chloride yielded XIIId.

The low yield of IVd shows that the reaction V + VI → VII goes much faster than the self-condensation of acetone (V + V → I). IXd is probably formed in small amounts for two reasons. First, the equilibrium VII ⇌ VIII is shifted considerably more to the left side for R^1 = phenyl than for R^1 = benzyl [1,2] thus making more VII available for reaction with phenyl azide. Second, the reaction VII + VI → XI proceeds much faster for R^1 = phenyl than for R^1 = benzyl. XIIId must be formed *via* XId and XIId, and the low yield shows that the elimination reaction XId → XVd (*vide infra*) is relatively fast.

Phenyl azide and pinacolone reacted to give a 31 % yield of XVIIe along with a compound $C_{13}H_{15}N_3O$, which is possibly 1-phenyl-4-pivaloyl-1,2,3-triazole (XIVe). The formation of XIVe is rather obscure; it must presumably be ascribed to an impurity in the pinacolone, although none such was detectable by NMR.

With acetophenone phenyl azide reacted to give XVIIf (11 %) and the triazoline VIIIf (13 %). As in case c the accumulation of VIII may be explained by a shift to the right of the equilibrium VII ⇌ VIII and by a retarded dehydration of VIII caused by the phenyl group (R^2), and also by a short reaction time.

The formation of XVIIf in a base-catalyzed reaction of phenyl azide with acetophenone has been observed previously by Dimroth *et al.*[5] Using sodium ethoxide as the base they obtained XVIIf in a 20 % yield. The structure was firmly established by independent synthesis and by reductive cleavage into 1,5-diphenyl-4-amino-1,2,3-triazole by zink powder in ethanolic ammonia. Similarly we have converted XVIId into 1-phenyl-4-amino-5-methyl-1,2,3-triazole in a yield of 71 % by catalytic hydrogenation (*cf.* Ref. 6).

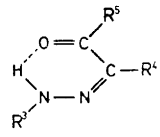
The route V → VII → XI → XVII for formation of XVII was proposed by the above authors,[5] but on somewhat weak evidence.[7] Undoubtedly the bis-triazene XI is an intermediate. The existence of such bis-triazeno ketones, respectively their ring-chain tautomers (XII), has just been demonstrated for R^1 = benzyl (XIIb), and evidence for the occurrence of XId in the reaction mixture of phenyl azide and acetone was provided by the isolation of the dehydration product of XIId, the 4-phenyltriazeno triazole XIIId (1,5-diphenyl-1,2,3-triazole (IXf) did not react with phenyl azide to give XIIIf in the presence of PTB). In addition the potential intermediacy of X (VII → X → XV → XVI → XVII) is rendered improbable by the fact that only a trace,

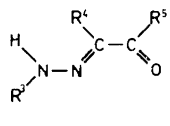
perhaps nothing at all, of pyruvaldehyde 1,5-diphenyl-4-1,2,3-triazolyl hydrazone (an analogue to XVII, *vide infra*) was obtained on successive treatment of diazoacetophenone (X, R^2 = phenyl) with phenyl azide and acetone in the presence of PTB. The compound XVIId was the main product.

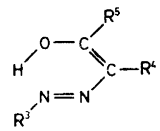
Having established the intermediacy of XI, three routes for the conversion of it into XVII lend themselves to discussion. The route XI→XII→XIII→XVII may be excluded by the fact that XIIId failed to react with acetone in the presence of PTB. Then there remain the two pathways XI→XVI→XVII and XI→XV→XVI→XVII. The presence of a strong diazo band at 2130 cm^{-1} in the IR spectrum of the product mixture from phenyl azide and acetophenone is possibly caused by diazoacetophenone, since a weak signal at 5.90 ppm was present in the NMR spectrum. This suggests that diazo group transfer from phenyl azide, analogous to that from tosyl azide,[8] is well possible, even to singly activated $-CH_2-$ groups as the one in acetone. However, diazo group transfer to VII (VII→XI→XV) should be even more feasible, the methylene group of VII being flanked by both a keto group and an azo group. Actually, VII must be just as activated as malonic ester, to which the possibility of diazo group transfer from phenyl azide has been suggested by others.[9] This in conjunction with the fact that the central nitrogen atom of a triazene chain is an unlikely site for the attack of a carbanion, particularly when the reaction should be intermolecular (V + XI→XVI), suggests that XV is an intermediate between XI and XVI. It is well known that carbanions attack diazo compounds at the extreme nitrogen atom (XV→XVI).[10] The reason that no XVII is formed when R^1 is an alkyl group is now easy to understand: the leaving ability of an aliphatic amine is too poor for the step XI→XV to take place.

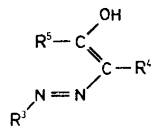
COMMENTS ON THE STRUCTURE OF COMPOUNDS XVIId–f

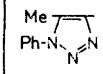
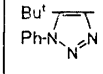
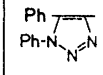
For clarity the compounds XVIId–f were formulated as ketoazo compounds in Scheme 1. Actually this is a misrepresentation of facts, since the NMR spectra do not exhibit signals from $-CH_2-$ groups. This indicates that XVII, at least in solution, adopt other tautomeric forms. Two others are possible: an NH (ketohydrazone) and an OH (enolazo) form (*cf.* Scheme 2). The NH form may exist as two geometrical isomers with respect to the C=N double bond, the NH_{cis} and NH_{trans} forms. Leaving out the possibility of a, presumably unstable,[11] *cis* geometry about the N=N double bond, the OH form may analogously exist as two geometrical isomers with respect to the C=C double bond, the OH_{cis} and OH_{trans} forms. Seemingly the NH_{cis} and OH_{cis} forms both have the possibility of forming intramolecular hydrogen bonds, as illustrated in Scheme 2; but it seems to be an established fact that an NH···O=C grouping is much more stable than an N···HO grouping,[12–16] at least if the oxygen atom is not attached to a potential aromatic system [15,17,18] (the postulated enolazo structure of some cyclohexane derivatives [19] does not seem to be well founded). In particular an N=N···HO grouping is relatively very unstable.[20] Therefore it can probably be assumed that an eventual OH_{cis} form would not form an intramolecular hydrogen bond, as opposed to the NH_{cis} form.









	R^3	R^4	R^5
XVIId		H	Me
XVIIe		H	Bu
XVIIf		H	Ph
XVIII	Ph	H	Me
XIX	Ph	H	Ph
XX	Ph	Me	Me

Scheme 2.

The problem of differentiating between the four structures in question is a very subtle one, even after the advent of NMR spectroscopy. IR spectra are certainly considered in the following, but since they are difficult to interpret, the emphasis has been placed on the proton NMR spectra. With the purpose of enlarging the experimental basis, the compounds XVIII – XX (*cf.* Scheme 2) have been included in the discussion. The spectra (IR and NMR) of XVIII and XIX were recorded by us, while those of XX and its *N*-methylated derivative are described in the literature.[14] All available NMR data are collected in Table 1. Some compounds (XVIId and XVIII in $CDCl_3$ and XVIIe in DMSO) appear two times for the same solvent. This is because an equilibration, which may easily be followed by NMR spectroscopy, takes place between two of the structures shown in Scheme 2 when these substances are dissolved. On basis of the position of the exchangeable NH or OH proton, the so-called acidic proton, the species present in chloroform solution could be classified in two groups. One group has the acidic proton at very low field (13.7 – 14.4 ppm), the position being insensitive to variations in the concentration. This is just what is to be expected for an intramolecularly hydrogen bonded (chelated) proton,[14] and the group is therefore assumed to represent the NH_{cis} form. The other group has its acidic proton at higher field (8.0 – 10.1 ppm), the position this time being somewhat dependent on the concentration. All members of this group have R^5 = methyl, and the constant chemical shift of this methyl group (2.46 – 2.51 ppm) suggests that the group contains only one of the forms shown in Scheme 2. Based solely on the position of the acidic proton this form could be either one of the OH forms, or it could be the NH_{trans} form. However, the fact that the position of the NMR signal of neither R^4 nor R^5 differs much between XX and its *N*-methylated derivative makes it plausible that their structures are very much alike. The OH forms may therefore be excluded as possible structures, and since an unchelated NH_{cis} form is hard to imagine, the group must be identified with the NH_{trans} form. This conclusion is supported by the appearance of a characteristic [14] conjugated carbonyl

Table 1. NMR data (magnet temperature) of the compounds shown in Scheme 2. δ-Values of the acidic protons are in parenthesis when dependent on concentration. The position of $R^4=H$ (situated in the aromatic region) in XVIId–f in $CDCl_3$ was confirmed by running the spectra at both 60 and 100 Mc.

	Compound	3 % w/v in $CDCl_3$ (XX 0.8 M) R^3	R^4	R^5	NH	Other signals
NH_{trans}	XVIId	2.38(s,5-Me) 7.55("s", 1-Ph)	7.35(d, 1H)	2.51(s, 3H)	(10.1)	
	XVIII	6.8–7.6(m)		2.46(s, 3H)	(8.5)	
	XX[14]		1.98(3H)	2.49(3H)	(8.0)	
	XX(N-Me)[14]		2.04(3H)	2.48(3H)		4.49(3H,N-Me)
NH_{cis}	XVIId	2.43(s, 5-Me)	7.04(s, 1H)	2.29(s, 3H)	(13.7)	
	XVIII	6.8–7.6(m)		2.28(s, 3H)	13.9	
	XVIIe	1.29(s, 9H, 5-Bu) 7.2–7.7(m, 5H)	7.39(s, 1H)	1.29(s, 9H)	13.7	
	XVIIf	7.1–8.1(m)	7.83(s, 1H)	7.1–8.1(m)	14.4	
	XIX	6.8–8.2(m)	7.74(s, 1H)	6.8–8.2(m)	14.4	
		6 % w/v in DMSO-d_6				
NH_{trans}	XVIId	2.28(s, 3H, 5-Me) 7.64(s, 5H)	7.35(s, 1H)	2.42(s, 3H)	11.3	
	XVIII	6.7–7.6(m, 5H)		2.34(s, 3H)	11.2	
unknown	XVIIe	1.18 or 1.26(s, 9H) 7.62(s, 5H)	7.34(s, 1H)	1.26 or 1.18 (s, 9H)	10.15	
	XVIIf	7.0–7.8(m)	7.76(s)	7.0–7.8(m)	11.3	
	XIX	6.7–8.2(m)	7.80(s)	6.7–8.2(m)	11.6	
NH_{cis}	XVIIe	1.24 or 1.20(s)	7.49?	1.20 or 1.24 (s)	13.4	

band at 1665 cm^{-1} in the IR spectra of XVIId and XVIII in freshly prepared chloroform solutions as well as in KBr. Yagi[21] also arrived at the NH_{trans} configuration for compound XVIII in CCl_4 solution and in the crystalline phase, and so did Elguero *et al.* for XX in chloroform solution.[14]

According to the above authors,[14] the carbonyl band of those compounds which in chloroform solution are present in the NH_{cis} form occurs at an unexpected low frequency (1628 cm^{-1} for XVIIe and below 1630 cm^{-1} for XVIIf and XIX in $CHCl_3$ as well as in KBr). Thus the chelate hydrogen bond must be stronger than usual,[14] as is also indicated by the very high δ-value of the acidic proton, there being a linear relationship between the C=O stretching frequency and the chemical shift of the proton in the grouping NH···O=C in closely related compounds.[22]

In dimethyl sulfoxide XVIId and XVIII are in the NH_{trans} form, showing carbonyl bands at 1650 cm^{-1}. XVIIe is present in two forms at equilibrium, one with the acidic proton at 13.4 ppm, presumably the chelated NH_{cis} form,

and another form with the acidic proton at 10.15 ppm. We are unable to identify this latter form with certainty, but the NH_{trans} form may possibly be excluded, since an eventual C=O absorption must occur below 1630 cm^{-1}, which is very low for an unchelated C=O group. XVIIf and XIX cannot be in the NH_{cis} form, since the acidic proton is unchelated as judged from its position in the NMR spectrum; but we are not in a position to tell which of the remaining three forms is the correct one. No C=O absorption occurred above 1620 cm^{-1} and 1625 cm^{-1}, respectively.

As expected, coupling was not observed between R^4=H and R^5=Me (compounds XVIId and XVIII), but this fact alone would certainly not have been sufficient evidence for excluding the OH forms, since an allylic coupling may sometimes vanish.[23] In chelated β-thioketothiolesters [24] the corresponding coupling is 1.1 cps. In the NH_{trans} form of XVIId (in $CDCl_3$) the protons R^4=H and NH surprisingly couple with a coupling constant of 1 cps. The doublet at 7.35 ppm collapses to a singlet on treatment of the $CDCl_3$ solution with deuterium oxide or on irradiation of the proton at 10.1 ppm with a strong secondary field. The coupling is missing in the chelated NH_{cis} form, but whether this is owing to an unfavorable conformation or to a reduced bond order of the N–H bond is not known. The coupling is also absent in DMSO solution.

Table 2. Equilibrium content (%) of the NH_{cis} form in solution.

Solvent	XVIId	XVIII	XVIIe	XVIIf	XIX
$CDCl_3$	20 [a]	42 [b]	100	100	100
DMSO-d_6	0	0	15	0	0

[a] Equilibration time: approx. 10 min. [b] Equilibration time: a few hours.

The equilibrium content of the NH_{cis} form in solution is given in Table 2. Obviously it is lower in DMSO solution than in chloroform solution. This is quite conceivable in view of the capability of DMSO to act as a proton acceptor, those structures that are in a position to form intermolecular hydrogen bonds being stabilized relative to the NH_{cis} form. The effect is, however, surprisingly dramatic in that it results in complete reversal of the equilibrium position for two compounds, namely XVIIf and XIX. The difference between XVIId and XVIII on one hand and XVIIe, XVIIf, and XIX on the other is also striking. In chloroform solution the last three compounds are entirely in the NH_{cis} form, whereas the first two are only present partly in this form (20 % and 42 %, respectively). The explanation must probably be sought in the R^5 substituent, and since XVIIe (R^5 aliphatic) falls in the same group as XVIIf and XIX (R^5 aromatic), it is probably for steric rather than for electronic reasons that this group prefers the chelated NH_{cis} form. This is in line with the enhanced chelation in β-diketones containing bulky substituents, and the reason is possibly that steric repulsion between R^4 and R^5 results in a

reduction of the distance between the NH and C=O groups, thus making the hydrogen bond stronger.[25,26]

The ketoazo tautomer cannot be an intermediate in the equilibration $NH_{trans} \rightleftharpoons NH_{cis}$, since $R^4 = H$ is not exchanged with deuterium on treatment of the chloroform solutions of XVIId–f with deuterium oxide (*cf.* Refs. 15 and 27). However, this does not necessarily imply the OH tautomers as intermediates, since phenylhydrazones are able to equilibrate spontaneously between *cis* and *trans* forms.[27,28]

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded on a Varian A-60 or HA-100 instrument. Unless otherwise stated the solvent was $CDCl_3$ with TMS as an internal standard. Chemical shifts are given as δ-values. Analyses of NMR spectra were done on a first order basis, except for AB systems which were treated on a second order basis. IR spectra were recorded on a Perkin-Elmer model 421 instrument, using NaCl cells for measuring in chloroform solution and BaF_2 cells for dimethyl sulfoxide. Preparative thin-layer chromatography (TLC) was carried out using Merck Kieselgel PF_{254}.

A stock solution of PTB in *tert*-butyl alcohol was prepared by dissolving 19.6 g of potassium in 400 ml of *tert*-butyl alcohol (Fluka, *puriss.* grade) at reflux temperature. When needed an appropriate amount of this solution was pipetted off. The stock solution kept for months.

Pyruvaldehyde monophenylhydrazone (XVIII) and phenylglyoxal monophenylhydrazone (XIX) were prepared by coupling phenyl diazonium chloride with acetoacetic acid and benzoylacetic acid, respectively.[29]

Reaction of benzyl azide with acetone. Benzyl azide (1.24 ml, 0.01 mol) and acetone (2.2 ml, 0.03 mol) were added to 20 ml of PTB solution. The color immediately turned yellow and gradually shifted to reddish brown. A slight evolution of heat was observed after approx. 10 min, and cooling was necessary to keep the temperature below 30°C. No evolution of nitrogen occurred. TLC did not show the presence of any azide after 2 h of reaction, and after 3.5 h the mixture was poured into 200 ml of ice-water. Extraction with ether, drying over Na_2SO_4, and removal of the solvent gave 2.37 g of an orange oil. Preparative TLC of 383 mg of this oil, using ethyl acetate-pentane (1:3) as eluent, gave two main fractions. *Fraction 1* (fastest running) consisted of 136 mg (40 %) of 1-benzyl-4-isopropenyl-5-methyl-1,2,3-triazole (IVa) as a yellow syrup. Low-temperature crystallization from ether-pentane gave an almost colorless product with m.p. 35–36°C. (Found: C 73.04; H 7.21; N 19.85. Calc. for $C_{13}H_{15}N_3$: C 73.20; H 7.09; N 19.70), NMR data: 2.26 (s,3H), 2.26 (t, $J = 1.2$ cps, 3H), 5.18 (q, $J = 1.2$ cps, 2H) (this signal collapsed to a singlet on irradiation at 2.26 ppm), 5.51 (s,2H), and 7.0–7.5 ppm (m,5H). *Fraction 2* contained 104 mg (37 %) of 1-benzyl-5-methyl-1,2,3-triazole (IXa) as a yellow syrup. Several recrystallizations from ethyl acetate-pentane gave a white, crystalline product with m.p. 80–81°C (reported [30] 84°C). NMR data: 2.19 (*d*, $J = 0.8$ cps, 3H), 7.48 (broad s, 1H), 5.51 (broad s, 2H), and 7.0–7.5 ppm (m, 5H). The ratio IXa:IVa = 37:40 = 0.92 was also found by integration of the NMR spectrum of the crude product mixture.

Carrying out the reaction in the following manner the intermediate hydroxytriazoline could be isolated. Acetone (1.5 ml) was added to 2.48 ml of benzyl azide in 20 ml of PTB solution. After 10 min the reaction mixture was poured into 150 ml of ice-water, and the product was extracted with methylene chloride (2 × 100 ml). Drying and evaporation resulted in an orange, thin oil mainly consisting of benzyl azide. This was removed at 0.01 mmHg/40–60°C, and from the residue 278 mg (7 %) of 1-benzyl-5-methyl-5-hydroxy-Δ^2-1,2,3-triazoline (VIIIa) was obtained by low temperature crystallization from ether. Two recrystallizations from ethyl acetate-pentane gave a white product with m.p. 90–91°C. (Found: C 62.80; H 6.87; N 22.17. Calc. for $C_{10}H_{13}N_3O$: C 62.81; H 6.85; N 21.98). NMR data: 1.43 (s, 3H, $C-CH_3$), 7.36 ("s", 5H, aromatic protons), calc. δ-values for the benzylic protons: 4.70 and 4.98 ppm ($J_{AB} = 16$), and calc. δ-values for the protons at the 4-position: 4.26 and 3.78 ppm ($J_{AB} = 17.5$ cps).

Treatment of VIIIa with acetone in the presence of PTB. Acetone (0.11 ml, 1.5 mmol) and VIIIa (86 mg, 0.5 mmol) were added to 5 ml of PTB solution, and the mixture was let stand for 7 h at room temperature. The mixture was then poured into 40 ml of ice-water and extracted with ether. Drying (Na_2SO_4) and removal of the solvent gave an oily crystal mixture, which mainly consisted of 1-benzyl-5-methyl-1,2,3-triazole as apparent from the NMR spectrum. No 1-benzyl-4-isopropenyl-5-methyl-1,2,3-triazole (IVa) was detectable by NMR. Treatment with activated carbon in water followed by recrystallization from the same solvent gave 60 mg (77 %) of 1-benzyl-5-methyl-1,2,3-triazole (IXa) (m.p. 77 – 79°C).

Reaction of benzyl azide with pinacolone. Benzyl azide (1.24 ml, 0.01 mol) and pinacolone (1.25 ml, 0.01 mol) were added to 20 ml of PTB solution. The mixture was allowed to stand at room temperature for 5 days, during which time the color changed from yellow to orange. All azide was consumed (NMR). Only negligible nitrogen evolution occurred. The reaction mixture was poured into 75 ml of ice-water, and the separating oil was extracted with ether. The ether and *tert*-butyl alcohol were removed *in vacuo*, and the residue was dissolved in 20 ml of methylene chloride and dried over Na_2SO_4. Filtration and removal of the solvent gave 2.25 g of an orange oil. This oil (0.428 g) was subjected to preparative TLC using ether-benzene (1:2) as eluent. Two main fractions were obtained. *Fraction 1* (fastest running) consisted of 80 mg (24 %) of 1-benzyl-4-benzyltriazeno-5-*tert*-butyl-5-hydroxy-Δ^2-1,2,3-triazoline (XIIb) as a light yellow syrup. Crystallization from ether-pentane gave a white product with m.p. 106 – 107°C (nitrogen evolution). (Found: C 65.68; H 7.12; N 23.00. Calc. for $C_{20}H_{26}N_6O$: C 65.54; H 7.15; N 22.93). IR data (KBr): 3390 cm^{-1} (sharp and strong, presumably NH), 3220 cm^{-1} (broadened but strong, presumably OH). No C=O band was present neither in $CHCl_3$ solution nor in KBr. NMR data (4 % w/v, $CDCl_3$, 100 Mc): 8.4 (broad, 1H), 4.1 (broad, 1H), 0.90 (s,9H), 5.54 (broad s, 1H, nonexchangeable with deuterium on treatment with D_2O, identified as the proton at the 4-position), and 7.0 – 7.6 ppm (multiplet, 10H, aromatic protons). The CH_2 group of the triazene side chain is a broad singlet at 4.64 ppm, and that attached to the triazoline ring constitutes an AB system with $\delta_A = 4.70$ ppm, $\delta_B = 4.82$ ppm, and $J_{AB} = 16$ cps, indicating that the equilibration XIb⇌XIIb [1] is not fast enough to render the two benzyl groups equivalent. *Fraction 2* consisted of 139 mg (34 %) of 1-benzyl-5-*tert*-butyl-1,2,3-triazole (IXb) as a yellow syrup. Low temperature crystallization from ether gave a light yellow compound with m.p. 38 – 39°C. (Found: C 72.36; H 7.89; N 19.65. Calc. for $C_{13}H_{17}N_3$: C 72.52; H 7.96; N 19.52). NMR data: 1.28 (s,9H), 5,71 (s,2H), 7.50 (s,1H), and 6.8 – 7.6 ppm (m, 5H).

Using a threefold excess of pinacolone almost the same ratio between IXb and XIIb was obtained (2.9 instead of 3.2), as apparent from the NMR spectrum of the crude product mixture.

Reaction of benzyl azide with acetophenone. Benzyl azide (1.24 ml, 0.01 mol) and acetophenone (1.17 ml, 0.01 mol) were added to 20 ml of PTB solution. A yellow color immediately developed, and this had changed to deep reddish brown after 2.5 h, at which time the mixture was poured into 200 ml of ice-water. The product was extracted with ether (100 + 3 × 50 ml), and after removal of the solvent (ultimately using 1 mmHg/40°C) a mixture of oil and crystals remained. The crystals were washed with a few ml of methylene chloride at 0°C and with water. 1-Benzyl-5-phenyl-5-hydroxy-Δ^2-1,2,3-triazoline (VIIIc) (0.61 g, 24 %) with m.p. 119 – 123°C (decomp.) resulted. Recrystallization from ethyl acetate raised the m.p. to 127 – 128°C (N_2-evolution). (Found: C 71.34; H 5.94; N 16.78. Calc. for $C_{15}H_{15}N_3O$: C 71.13; H 5.97; N 16.59). NMR data: 4.63 (s,2H, $-CH_2Ph$) and 7.1 – 7.7 ppm with a sharp peak at 7.26 ppm (aromatic protons). The two protons at the 4-position appeared as an AB system with calculated δ-values of 4.08 and 4.49 ppm ($J_{AB} = 18$ cps).

The methylene chloride phase was dried over Na_2SO_4, and removal of the solvent resulted in a thick, orange oil. Preparative TLC (ethyl acetate:pentane, 1:3) of 285 mg gave several fractions, one of which consisted of 129 mg (31 %) of 1-benzyl-5-phenyl-1,2,3-triazole (IXc) as a thick oil. Repeated recrystallization from ethyl acetate-pentane gave a product with m.p. 69 – 70°C (reported [31] 69 – 70°C).

Reaction of phenyl azide with acetone. In the course of 10 min 4.4 ml (0.06 mol) of acetone was added with stirring to a solution of 5.5 ml (0.05 mol) of phenyl azide in 100 ml of PTB solution. Frequent cooling was necessary to keep the temperature within the range 20 – 30°C. Stirring was continued for half an hour at room temperature, and the

brown mixture was poured into 50 ml of ice. Ether (200 ml) was added, and after shaking and separation, the ether phase was treated with approx. 10 ml of diluted KOH. The solvent was removed from the ether phase on a rotary evaporator (using 1 mmHg/40°C in the last stage). The remaining syrup was treated with 50 ml of 10 % KOH and 200 ml of ether, and the two phases were separated. A voluminous precipitate (XVIId) was formed on acidification of the combined aqueous phases (three in total) with 4 N HCl while cooling in ice-water. Washing with water and drying gave 4.50 g (74 %) of a light brown compound with m.p. 170 – 177°C (gas evolution). Recrystallizations from methanol and ethyl acetate raised the m.p. to 186 – 187°C. (Found: C 59.40; H 5.47; N 28.97. Calc. for $C_{12}H_{13}N_5O$: C 59.24; H 5.38; N 28.78).

The solvent was removed from the ether phase, and the bulk of aniline (1.12 g) was distilled off at 1 mmHg at 25 – 40°C. The components of the residue were separated by TLC using ethyl acetate-benzene (1:2) as eluent. Several spots showed up, but only three main fractions were isolated. *Fraction 1* (fastest running) contained a compound that was shown by IR, NMR, and TLC to be identical with otherwise prepared 1-phenyl-4-isopropenyl-5-methyl-1,2,3-triazole (IVd). Yield 1.3 %. NMR data: 7.52 ("s", 5H, aromatic protons), 2.40 (s,3H,Me at the 5-position), 2.33 (dd ($J_1 = 1.0$ cps, $J_2 = 1.6$ cps), 3H, Me of the isopropenyl group), and 5.2 – 5.4 ppm (two poorly resolved quartets, 2H, $=CH_2$). *Fraction 2* consisted of 1-phenyl-4-phenyltriazeno-5-methyl-1,2,3-triazole (XIIId) as red crystals with m.p. 152 – 155°C (gas evolution). Recrystallization from ethyl acetate raised the m.p. to 162 – 163°C (gas evolution). Yield 1.6 %. IR showed the identity with an otherwise prepared sample. (Found: C 64.80; H 5.16; N 30.33. Calc. for $C_{15}H_{14}N_6$: C 64.73; H 5.07; N 30.20). NMR: data: 2.54 (s,3H), 7.62 (s, 5H, presumably ring-phenyl), 7.2 – 7.6 (m, 5H), and 9.9 ppm (broad s, 1H). *Fraction 3* was shown by IR and NMR to contain 1-phenyl-5-methyl-1,2,3-triazole [32] (IXd), but one further TLC separation (ethyl acetate) was necessary to obtain a pure product. Yield 0.9 %.

XVIId was acetylated by boiling 371 mg of the crude product for 13 h with 10 ml of acetic anhydride. Excess solvent was removed, leaving a brown crystallizing syrup. Recrystallization from methanol gave 228 mg (53 %) of a brown product with m.p. 156 – 157°C, and recrystallization from ethyl acetate-ether gave a white product with m.p. 157 – 158°C. (Found: C 59.06; H 5.41; N 24.77. Calc. for $C_{14}H_{15}N_5O_2$: C 58.94; H 5.30; N 24.55). NMR data: 2.20 (s, 3H), 2.49 (s,3H), 2.66 (s, 3H), 6.94 (s, 1H), and 7.58 ppm (s, 5H). IR data: the following absorptions were present within the range 1500 – 2000 cm^{-1}: 1715, 1690, and 1580 cm^{-1}, all strong bands.

XVIId was hydrogenated in the following way. Crude XVIId (481 mg) and 5 mg of PtO_2 catalyst were dispersed in a mixture of 1 ml of conc. HCl and 15 ml of methanol. Hydrogenation was continued for 18 h at a hydrogen pressure of 1 atm., whereby 95 ml of hydrogen was absorbed. Platinum and solvent were removed, and 5 ml of water was added. After neutralization with saturated $NaHCO_3$, the product was extracted with methylene chloride. Drying and evaporation gave a brownish syrup, which was purified by treatment with activated carbon in water. Extraction of the aqueous phase with methylene chloride yielded 246 mg (71 %) of weakly miscolored crystals of m.p. 93 – 95°C. Recrystallization from ethyl acetate-cyclohexane raised the m.p. to 102 – 103°C. IR, NMR, and mixed m.p. showed the identity with otherwise prepared 1-phenyl-4-amino-5-methyl-1,2,3-triazole.

Reaction of phenyl azide with mesityl oxide. In the course of 5 min a total of 5.7 ml (0.05 mol) of mesityl oxide was added with stirring to a solution of 5.5 ml (0.05 mol) of phenyl azide in 50 ml of PTB solution. The mixture was cooled continuously in an ice-water bath. The reddish brown reaction mixture stayed in the cooling bath for 10 min, and it was then allowed to stand at room temperature for 30 min before being poured into 300 ml of ice-water. Extraction with ether and evaporation (1 mmHg/40°C in the last stage) left 9.05 g (91 %) of a brown crystal cake. Recrystallization from pentane gave a product (IVd) with m.p. 65 – 66°C, identical with the product obtained from phenyl azide and acetone. (Found: C 72.41; H 6.71; N 21.31. Calc. for $C_{12}H_{13}N_3$: C 72.35; H 6.57; N 21.10).

IVd was converted into 1-phenyl-4-acetyl-5-methyl-1,2,3-triazole in the following manner. To 0.524 g of the above IVd, dissolved in 20 ml of 50 % acetic acid, was added, while stirring, 5 g of $KMnO_4$ at such a rate that the temperature remained in the range 35 – 40°C. Stirring was continued for half an hour, and a mixture of 50 ml of water and 10 ml of conc. hydrochloric acid was then added. While cooling in ice-water, Na_2SO_3

(approx. 10 g) was added slowly until all MnO_2 had dissolved, and the mixture was then neutralized with solid $NaHCO_3$. Extraction with methylene chloride, drying over $MgSO_4$, and evaporation gave 0.304 g (58 %) of a crystallizing oil. After recrystallization from pentane the m.p. was 99 – 100°C as reported.[33] Mixed m.p., IR, and NMR showed the identity with the 1-phenyl-4-acetyl-5-methyl-1,2,3-triazole prepared from 1-phenyl-5-methyl-4-1,2,3-triazole-carboxylic acid (see below).

Preparation of 1-phenyl-4-acetyl-4-methyl-1,2,3-triazole. Ethyl 1-phenyl-5-methyl-4-1,2,3-triazole-carboxylate [33] (1.15 g), 2 ml of ethyl acetate, and 0.2 g of sodium powder (prepared in xylene) were refluxed in 10 ml of benzene for 8 h. An oil separated when the solution, obtained by evaporation and dissolution in 20 ml of water, was acidified with acetic acid. The oil was extracted with methylene chloride. The NMR spectrum showed that it consisted of ethyl 3-oxo-3-(1-phenyl-5-methyl-4-1,2,3-triazolyl)-propionate rather than the expected 4-acetyl triazole.[33] Column chromatography (ethyl acetate: pentane, 1:3, silica) gave 0.61 g (45 %) of a pure compound, which was crystallized from ether-pentane at −76°C. M.p. 48 – 49°C. (Found: C 61.36; H 5.65; N 15.32. Calc. for $C_{14}H_{15}N_3O_3$: C 61.52; H 5.53; N 15.37). NMR data: 1.32 (t, 3H), 2.63 (s, 3H), 4.27 (s,2H), 4.30 (q, 2H), and 7.3 – 7.9 ppm (m, 5H).

The ethyl ester (0.146 g) was refluxed with 8 ml of 2 % NaOH for one h. 1-Phenyl-4-acetyl-5-methyl-1,2,3-triazole precipitated from the reaction mixture on cooling. The product was filtered off, washed with water, and dried. Yield 71 mg (66 %), m.p. 98°C.

Preparation of 1-phenyl-4-phenyltriazeno-5-methyl-1,2,3-triazole. 1-Phenyl-5-methyl-4-1,2,3-triazole-carboxylic acid [32] (6.8 g, 0.03 mol) was melted together with 6.8 g (0.03 mol) of phosphorus pentachloride. A vigorous reaction took place, and 5 min later the reaction was complete. Phosphorus oxychloride was distilled off *in vacuo* on a water bath, and the residue was dissolved in 80 ml of acetone. Sodium azide (5.8 g), dissolved in 25 ml of water, was added during 5 min, and the mixture was let stand at room temperature for one h. Concentration to half volume and addition of 150 ml of water caused the azide to crystallize. Washing with water and drying gave 6.99 g of a product with m.p. 90 – 91°C (decomp.). Refluxing with 100 ml of abs. ethanol for 24 h resulted in the urethane, m.p. 97 – 100°C, (102 – 103°C after recrystallization of a sample from ethanol-pentane), which on boiling for 4 h with 50 ml of 2 N NaOH gave the wanted 1-phenyl-4-amino-5-methyl-1,2,3-triazole, separating as colorless crystals on cooling. Recrystallization from water gave 4.15 g (79 % based on carboxylic acid), m.p. 99 – 100°C. Repeated recrystallization raised the m.p. to 104 – 105°C. (Found: C 61.94; H 5.98; N 32.30. Calc. for $C_9H_{10}N_4$: C 62.05; H 5.78; N 32.16). The compound has been prepared in a different way by others.[34] NMR data: 2.24 (s, 3H) and 7.54 ppm (s, 5H).

The aminotriazole was converted into 1-phenyl-4-phenyltriazeno-5-methyl-1,2,3-triazole in the following manner. Aniline (0.31 g), dissolved in 10 ml of 4 N HCl, was diazotized with $NaNO_2$, until iodine-starch paper gave a positive reaction (approx. 0.2 g of $NaNO_2$ was required). This solution was added to 0.58 g of 1-phenyl-4-amino-5-methyl-1,2,3-triazole, dissolved in 50 ml of 1 N NaOH. The temperature was kept at *ca.* 20°C by cooling in ice-water. A yellow precipitate formed in a few minutes, and after one h it was filtered off, washed with water, and dried. Yield 0.65 g (70 %) of a light brown product. Recrystallization from ethyl acetate raised the m.p. to 158°C (gas evolution). The IR spectrum proved the identity with XIIId.

Treatment of XIIId with acetone and PTB. XIIId (31 mg, isolated from the reaction mixture of phenyl azide with acetone) was dissolved in 5 ml of PTB solution, and 0.3 ml of acetone was added. After 30 min the mixture was poured into 30 ml of water and 0.5 ml of acetic acid. Extraction (methylene chloride), drying (Na_2SO_4), and evaporation gave an oil, from which 24 mg of crystalline starting material (m.p. 160 – 162°C) was recovered by treatment with 5 ml of ether at 0°C. TLC and NMR showed that no XVIId was present in the mother liquor.

Reaction of phenyl azide with pinacolone. Pinacolone (1.25 ml, 0.01 mol) was added to a solution of 1.1 ml (0.01 mol) of phenyl azide in 20 ml of PTB solution. The reaction mixture rapidly turned reddish brown, and a slight evolution of nitrogen occurred. After 40 min the mixture was poured into 150 ml of ice-water and extracted with ether. Drying over Na_2SO_4 and evaporation of the solvent, using 0.5 mmHg/30°C in the last stage, resulted in 1.47 g of a thick, orange oil. The aniline was distilled off at 0.01 mmHg (heating on a 50°C water bath), and from the residue, which was dissolved in 10 ml of ether, 181 mg of XVIIe crystallized. The compounds in the mother liquor were separated by TLC,

using ether-pentane (1:2) as eluent. Two fractions were isolated. *Fraction 1* (fastest running) consisted of 79 mg (3.5 %) of a yellowish oil, presumably 1-phenyl-4-pivaloyl-1,2,3-triazole (XIVe). Low temperature crystallization from ether gave a white, crystalline product melting at 106°C. (Found: C 68.31; H 6.77; N 18.06. Calc. for $C_{13}H_{15}N_3O$: C 68.09; H 6.59; N 18.33). NMR data: 1.50 (s, 9H), 7.4 – 8.0 (multiplet, 5H), and 8.49 ppm (s, 1H, nonexchangeable on treatment with D_2O). IR data: 1680 cm^{-1} (strong, C=O), 3130 cm^{-1} (strong and sharp). The latter band is characteristic of 1,4-disubstituted 1,2,3-triazoles and excludes the possibility of a 1,5-disubstituted 1,2,3-triazole.[35] Mass spectrum: The molecular ion was present at *m/e* 229. The most conspicuous feature was a large peak at *m/e* 144, representing a cleavage between the pivaloyl group and the triazole nucleus. A metastable peak, which could be accounted for by loss of nitrogen from this ion, was present at *m/e* 93.5. *Fraction 2* consisted of 331 mg of XVIIe as a red syrup, which crystallized on inoculation. Total yield of XVIIe: 0.512 g (31 %). Recrystallization from ethyl acetate-pentane gave yellow crystals, which melted at 130 – 131°C. (Found: C 66.14; H 7.61; N 21.21. Calc. for $C_{18}H_{25}N_5O$: C 66.03; H 7.70; N 21.39).

Reaction of phenyl azide with acetophenone. Acetophenone (2.33 ml, 0.02 mol) was added, while stirring and cooling (ice-water), to a solution of 2.2 ml (0.02 mol) of phenyl azide in 20 ml of PTB solution. The mixture immediately became dark, and considerable nitrogen evolution occurred. After one min the mixture was poured into 150 ml of ice-water and 10 ml of 4 N HCl. The product was extracted with ether. Drying over Na_2SO_4 and evaporation gave a dark red oil, from whose ethereal solution 0.64 g (13 %) of 1,5-diphenyl-5-hydroxy-Δ^2-1,2,3-triazoline (VIIIf) crystallized on standing. Several recrystallizations from ethyl acetate raised the m.p. (140 – 142°C) to 159 – 160°C (decomp.). (Found: C 70.04; H 5.60; N 17.44. Calc. for $C_{14}H_{13}N_3O$: C 70.26; H 5.47; N 17.56). NMR data: The compound was too sparingly soluble in $CDCl_3$ to allow an NMR spectrum to be recorded in this solvent. In pyridine (4 %) the two hydrogens at the 4-position appeared as an AB system with $\delta_A = 4.57$ ppm, $\delta_B = 5.09$ ppm, and $J_{AB} = 18$ cps.

On washing the Na_2SO_4 used for drying above with water 0.39 g (11 %) of phenylglyoxal 1,5-diphenyl-4-1,2,3-triazolylhydrazone (XVIIf) was left. Mixed m.p., IR, and NMR proved the identity with a sample prepared according to Dimroth *et al.*[5]

Treatment of 1,5-diphenyl-1,2,3-triazole with phenyl azide and PTB. Phenyl azide (1.1 ml, 0.01 mol), 1,5-diphenyl-1,2,3-triazole [36] (1.11 g, 0.01 mol), and tetrahydrofurane (10 ml, distilled over copper(I) chloride and dried over drierite) were added to 15 ml of PTB solution. After 5 months the mixture was poured into 150 ml of water. When the separating oil had crystallized, it was filtered off, washed with water and pentane, leaving 0.97 g of unchanged 1,5-diphenyl-1,2,3-triazole. Considerable amounts of phenyl azide were present in the mother liquor (TLC).

Successive treatment of diazoacetophenone with phenyl azide and acetone in the presence of PTB. Diazoacetophenone [37] (292 mg) was added to a mixture of 0.22 ml of phenyl azide, 5 ml of ether (sodium dried), and 5 ml of ice-cold PTB solution. The mixture immediately became dark, but no nitrogen evolution took place. After two h at 0°C, 0.29 ml of acetone was added, and after an additional period of 0.5 h the mixture was poured into 50 ml of water and 0.5 ml of acetic acid. Extraction (ether), drying (Na_2SO_4), and evaporation gave an oily crystal mixture. The NMR spectrum of this mixture exhibited a weak signal at 2.6 ppm, which could possibly be ascribed to pyruvaldehyde 1,5-diphenyl-4-1,2,3-triazolylhydrazone. However, the signals corresponding to XVIId (Table 1) were approx. ten times stronger.

Acknowledgements. The author thanks Professor C. Pedersen for advice and inspiration. Likewise the constructive criticism by Professor P. Olesen-Larsen is much appreciated.

Microanalyses were performed by Dr. A. Bernhardt.

REFERENCES

1. Olsen, C. E. and Pedersen, C. *Acta Chem. Scand.* **27** (1973). *In press.*
2. Olsen, C. E., Thesis, Technical University of Denmark, DK-2800 Lyngby, Denmark, 1969 (in English).
3. Hine, J. *Physical Organic Chemistry*, McGraw, New York 1962, p. 259.

4. Olsen, C. E. *To be published.*
5. Dimroth, O., Frisoni, E. and Marshall, J. *Ber.* **39** (1906) 3920.
6. Regitz, M. and Stadler, D. *Ann.* **687** (1965) 214.
7. Boyer, J. H. In *Heterocyclic Compounds*, Wiley, New York 1961, Vol. 7, p. 389.
8. Regitz, M. *Angew. Chem.* **79** (1967) 786.
9. Begtrup, M., Larsen, P. S. and Pedersen, C. *Acta Chem. Scand.* **22** (1968) 2476.
10. Regitz, M., Liedhegener, A. and Stadler, D. *Ann.* **713** (1968) 101.
11. Buckingham, J. and Guthrie, R. D. *Chem. Commun.* **1967** 1241.
12. Bose, A. K. and Kugajevsky, I. *Tetrahedron* **23** (1967) 1489.
13. Blanchard, M.-L., Strzelecka, H., Martin, G. J., Simalty, M. and Fugnitto, R. *Bull. Soc. Chim. Fr.* **1967** 2677.
14. Elguero, J., Jacquier, R. and Tarrago, G. *Bull. Soc. Chim. Fr.* **1966** 2981.
15. Brown, N. M. D. and Nonhebel, D. C. *Tetrahedron* **24** (1968) 5655.
16. Jones, R., Ryan, A. J., Sternhell, S. and Wright, S. E. *Tetrahedron* **19** (1963) 1497.
17. Snavely, F. A. and Yoder, C. H. *J. Org. Chem.* **33** (1968) 513.
18. Zollinger, H. *Azo and Diazo Chemistry*, Interscience, New York 1961, Section 13.2.
19. Altiparmakian, R. H. and Braithwaite, R. S. W. *J. Chem. Soc.* **C 1967** 1973.
20. Brealey, G. J. and Kasha, M. *J. Am. Chem. Soc.* **77** (1955) 4462.
21. Yagi, Y. *Bull. Chem. Soc. Jap.* **36** (1963) 487.
22. Dudek, G. O. *J. Org. Chem.* **30** (1965) 548.
23. Newsoroff, G. P. and Sternhell, S. *Tetrahedron Lett.* **1968** 6117.
24. Duus, F., Jacobsen, P. and Lawesson, S.-O. *Tetrahedron* **24** (1968) 5323.
25. Nonhebel, D. C. *Tetrahedron* **24** (1968) 1869.
26. Musso, H. and Bantel, K.-H. *Chem. Ber.* **102** (1969) 686.
27. Bellamy, A. J. and Guthrie, R. D. *J. Chem. Soc.* **C 1968** 2090.
28. Karabatsos, G. J. and Taller, R. A. *J. Am. Chem. Soc.* **85** (1963) 3624.
29. *Organic Syntheses*, Wiley, New York 1952, Vol. 32, p. 84.
30. Wolff, L. and Krüche, R. *Ann.* **394** (1912) 56.
31. Moulin, F. *Helv. Chim. Acta* **35** (1952) 177.
32. Dimroth, O. *Ber.* **35** (1902) 1029.
33. Borsche, W., Hahn, H. and Wagner-Roemmick, M. *Ann.* **554** (1943) 21.
34. Pocar, D., Maiorana, S. and Croce, P. D. *Gazz. Chim. Ital.* **98** (1968) 949.
35. Begtrup, M. *Unpublished results.*
36. Dimroth, O. *Ber.* **35** (1902) 4041.
37. Regitz, M. and Menz, F. *Chem. Ber.* **101** (1968) 2622.

Received January 22, 1973.