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On the Formation and Beckmann Rearrangement of *N*-Cyanatoimines. Crystal Structure of 2-Phenyl-4(3*H*)-quinazolinone

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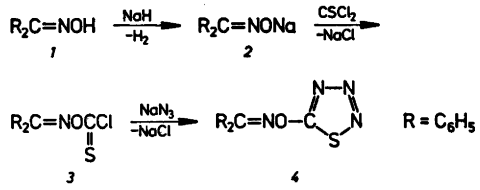
Dedicated to Professor K. A. Jensen on his 70th birthday

N-Cyanato(diphenylmethanimine) (*5*) has been generated in carbon tetrachloride solution from the corresponding thiatriazole (*4*). It is thermally unstable isomerizing rapidly in a Beckmann type rearrangement to *N*-phenylbenzimidoyl isocyanate (*6*). This is also thermally unstable but was characterized by infrared spectroscopy and the reaction with ethanol. *N*-Phenylbenzimidoyl isocyanate undergoes intramolecular electrophilic substitution in carbon tetrachloride with formation of *7*. A three-dimensional single-crystal X-ray structure determination at 85 K has proved *7* to be 2-phenyl-4(3*H*)-quinazolinone, thus settling the discussion on the exact structure of this compound. The crystals are monoclinic, space group $C2/c$ with cell dimensions at 85 K: $a = 30.095(13)$ Å, $b = 4.964(2)$ Å, $c = 16.630(4)$ Å, $\beta = 121.50°(3)$, with eight molecules per unit cell. The positional parameters and isotropic temperature factors for all atoms have been refined to a conventional *R* index of 9.7 % for 1322 reflections.

In continuation of studies on the chemistry of thiatriazoles and cyanates we have investigated the thermal decomposition of the hitherto unknown 5-(diphenylmethaniminoxy)-1,2,3,4-thiatriazole (*4*) with the intention of obtaining an *N*-cyanatoimine (*5*). This type of compound has barely been studied although Grigat and Pütter assumed that the product obtained by treating *p*-quinonedioxime with cyanogen chloride in the presence of base was the corresponding quinone di(*N*-cyanatoimine).[1] However, the product was not characterized or investigated because of its highly explosive nature.

Compound *3* was prepared *in situ* according to the method of Cross *et al.*[2] Upon reaction with sodium azide compound *4* was obtained (39 %) (Scheme 1). It is a thermally unstable



Scheme 1.

compound, melting and decomposing almost explosively around 130 °C. The infrared spectrum is devoid of an azide band in the 2100—2200 cm^{-1} region [3] which unambiguously proves it to be a thiatriazole and not a thioacyl azide.[3,4] Thermal degradation in boiling CCl_4 results in precipitation of a white solid which is identified as 2-phenyl-4(3*H*)-quinazolinone (*7*) (Scheme 2).

Although 2-substituted 4-quinazolinones have been known for a long time, considerable doubt has existed as to which of the three possible tautomers is actually the dominant. Recently, these structures have been formulated as 2-substituted 4-hydroxyquinazoles,[5] 2-substituted 4(1H)-quinazolinones [6] and 2-substituted 4(3*H*)-

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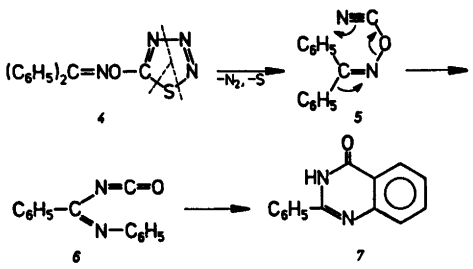

Scheme 2.

quinazolinones.[7,8] The assignment of the latter structure to the phenyl derivative (*7*) is based on energetic considerations, since 1-methyl-2-phenyl-4(1*H*)-quinazolinone was shown to undergo intramolecular rearrangement to 3-methyl-2-phenyl-4(3*H*)-quinazolinone at 260–305 °C.[7] This assignment was supported by IR, UV and ^{1}H NMR studies of *7*. As such studies, however convincing, can rarely be considered proof, we have undertaken a three-dimensional single-crystal X-ray structure determination at 85 K to settle the question once and for all (*vide infra*).

Transients in the formation of *7* from *4* was studied by monitoring the degradation of *4* in CCl_4 by infrared spectroscopy (Scheme 2). On boiling the rise and subsequent disappearance of a strong doublet at 2256 and 2220 cm^{-1} is observed. The first step in the sequence leading to *7* is expected to be loss of nitrogen and sulfur with formation of *5*, the extrusion reaction being common to all hitherto known thiatriazoles.[9] Formation of *5* may be succeeded by isomerization of the cyanate group in analogy with alkyl cyanates which are known to undergo isomerization a reaction which has never been demonstrated for aryl cyanates.[10] Group frequencies for both the cyanate (compound *5*) and the isocyanate group (compound *6*) are reported to be observed in the 2200–2300 cm^{-1} region,[11] thus excluding distinction between compound *5* and *6*. However, significant observations are made in the 700 cm^{-1} region. Generally two very strong single bands appear between 700 and 800 cm^{-1} in the spectra of monosubstituted benzene derivatives.[12]* Accordingly compound *1* as well as *4* exhibit a strong single band at 695 cm^{-1} since the phenyl groups in these compounds are identically attached. During the degradation reaction a doublet of strong intensity is observed at 695 and 690 cm^{-1} indicating the presence of two differently attached phenyl groups. We thus favor structure *6* over structure *5* for the transient since *5* would be expected to exhibit a single band in this region. The separation of *5* cm^{-1} between the two bands compares favorably with published data for related molecules.[13] Obviously the primarily formed cyanate *5* is unstable isomerizing to *6* in a reaction recognized as a Beckmann type rearrangement.[14] Migration of the phenyl group (*5*→*6*) is accompanied by migration and rearrangement of the cyanate group. It is not known whether an electron-deficient moiety (=N$^+$) is intermediate or whether rearrangement of –OCN to –NCO is a cyclic process. On the other hand allylic cyanates isomerise very rapidly to isocyanates by a cyclic mechanism[15] while simple alkyl cyanates are reasonably stable isomerizing *via* an ion-pair mechanism.[16] In fact the rapid isomerization of allylic cyanates prevents their isolation; only rearranged products are obtained on attempted preparation.[15] In a likewise manner a cyclic transition state of relatively low charge separation (*8*) may explain the rapid isomerization of *5* to *6* in boiling non-polar CCl_4.

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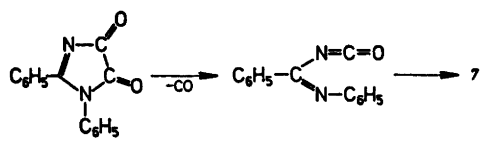
Isocyanate *6* exhibits a remarkable reactivity resulting in an intramolecular electrophilic attack on one of the phenyl groups. The same reaction was observed earlier by Goerdeler and Sappelt in the thermal degradation of imidazolindiones (*9*) strongly supporting the present results (eqn. 1).[17]

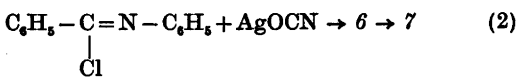


(1)

Compound *6* was not isolated or characterized by the latter investigators.

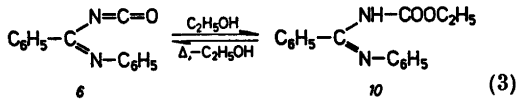
* In the present case only the 700 cm^{-1} band is observed because of the solvent (CCl_4) employed.

Further evidence for the reactivity of *6* is obtained from the reaction between *N*-phenylbenzimidoyl chloride and silver cyanate in acetonitrile. Obviously the first step will be formation of *6* but as expected compound *7* is the end product isolated in 13 % yield (eqn. 2).



$$C_6H_5-C(Cl)=N-C_6H_5 + AgOCN \rightarrow 6 \rightarrow 7 \qquad (2)$$

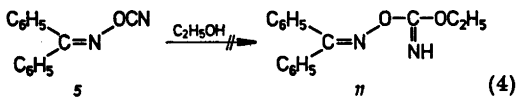
Support for the structure assignments of the intermediates was also obtained from thermal degradation of *4* in ethanol. The product obtained (*10*) is characterized as a reaction product between *6* and ethanol by elemental and mass spectrometric (M^+ 268 *m/e*, calc. 268) analysis (eqn. 3).



$$C_6H_5-C(N=C=O)=N-C_6H_5 \underset{\Delta,-C_2H_5OH}{\overset{C_2H_5OH}{\rightleftharpoons}} C_6H_5-C(NH-COOC_2H_5)=N-C_6H_5 \qquad (3)$$

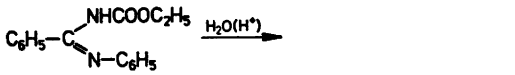
6 *10*

The alternative structure *11* (eqn. 4) is ruled out since the product on hydrolysis in boiling N hydrochloric acid for 1.5 h gives rise to benzoic acid (yield 90 %, eqn. 5). Oxime *11* would afford benzophenone in analogy with benzophenone oxime, which is hydrolyzed quantitatively to benzophenone in aqueous acid.[18]

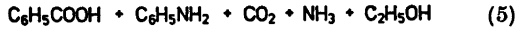


$$(C_6H_5)_2C(OCN)=N \xrightarrow{C_2H_5OH} (C_6H_5)_2C(O-C(=NH)-OC_2H_5)=N \qquad (4)$$

5 *11*



$$C_6H_5-C(NHCOOC_2H_5)=N-C_6H_5 \xrightarrow{H_2O(H^+)}$$



$$C_6H_5COOH + C_6H_5NH_2 + CO_2 + NH_3 + C_2H_5OH \qquad (5)$$

Finally compound *10* splits off ethanol on heating above the m.p. (101 – 102 °C) (eqn. 3) with formation of *7* (see Scheme 2) in agreement with the structure assignment.

Ghadiali and Shah has described compound *10* as an oil obtained from *N*-phenylbenzimidoyl chloride and sodium ethylcarbamate.[19] We have, however, not been able to reproduce their results.

CRYSTALLOGRAPHIC SECTION

Experimental and structure determination. Film diagrams indicated monoclinic symmetry, and the cell volume implied eight molecules in the unit cell. The systematic absences are those of space groups $C2/c$ and Cc. The later structure determination and refinement showed the space group to be the centrosymmetric $C2/c$.

An automatic Picker four-circle diffractometer with graphite-monochromatized Cu$K\alpha$ radiation, equipped with a modified Enraf-Nonius low-temperature device, (liquid N_2) was utilized for preliminary experiments and for the recording of intensity data. The temperature was kept constant within 0.5° at 85 K. A flat, needle-shaped crystal of approximate dimensions 0.3 × 0.05 × 0.02 mm was used for the data collection. The unit cell parameters were determined by a least-squares treatment of the 2θ-values of 17 reflections (2θ from 36 to 103°).

Three-dimensional intensity data were recorded with short (0.083°) ω-scans near the peak positions using a scan speed of 0.25° min^{-1}. Backgrounds were estimated on the basis of a series of background measurements for varying 2θ values. This method of data collection was chosen in order to improve the counting statistics. The intensities of two standard reflections which were remeasured after every 200 reflections showed no significant variation.

Estimated standard deviations for the intensities were obtained from the expression $\sigma(I) = [I + (0.02\ I)^2]^{\frac{1}{2}}$. Of the 1693 unique reflections measured ($2\theta_{max} = 130°$) 1322 had intensities greater than $2\sigma(I)$. These were regarded as observed reflections and the remaining were excluded from further calculations. The intensities were corrected for Lorentz and polarization effects.

The atomic scattering factors used were those of Doyle and Turner [20] for carbon, nitrogen and oxygen, and of Stewart *et al.*[21] for hydrogen.

The phase problem was solved by direct methods utilizing the MULTAN program assembly.[22] When the structure model had been refined to R-factor = 0.12 the hydrogen atoms were placed in calculated positions and included in the refinement. Fullmatrix least squares refinement of all positional parameters and isotropic temperature factors for all atoms resulted in a conventional R of 0.097 and a weighted R_w of 0.084. The function minimized was $S = (\Delta F)^2/\sigma^2(F_o)$.

A difference electron density map showed only spurious peaks of maximum height 0.6 e Å^{-3}. Atomic parameters are given in Table 1. A listing of calculated and observed reflections is available from Department of Chemistry, University of Oslo, Oslo 3, Norway. (Also available from the authors upon request.)

Table 1. Fractional atom coordinates and thermal parameters with estimated standard deviations.

Atom	*x*	*y*	*z*	*B*
N(1)	.1524(2)	.1598(9)	.1765(3)	2.47(9)
C(2)	.1240(2)	.3291(12)	.1123(4)	2.80(11)
N(3)	.0706(1)	.3556(9)	.0701(3)	1.89(8)
C(4)	.0422(2)	.2034(12)	.0957(4)	2.97(11)
C(5)	.0718(2)	−.0021(12)	.1678(4)	2.66(11)
C(6)	.1248(2)	−.0138(11)	.2054(4)	2.69(11)
C(7)	.1538(2)	−.2068(11)	.2743(4)	2.47(10)
C(8)	.1304(2)	−.3775(11)	.3059(4)	2.46(10)
C(9)	.0764(2)	−.3642(12)	.2687(4)	2.81(11)
C(10)	.0468(2)	−.1722(12)	.1995(4)	2.83(11)
C(11)	−.0063(1)	.2418(8)	.0585(3)	3.10(8)
C(12)	.1503(2)	.5232(11)	.0814(3)	2.38(10)
C(13)	.2052(2)	.5456(12)	.1363(4)	2.61(11)
C(14)	.2297(2)	.7317(11)	.1088(4)	2.40(10)
C(15)	.2004(2)	.8871(12)	.0295(4)	2.74(11)
C(16)	.1471(2)	.8642(12)	−.0242(4)	3.03(12)
C(17)	.1223(2)	.6817(11)	.0018(4)	2.74(11)
H(3)	.0574(18)	.532(10)	.0095(32)	3.3(12)
H(7)	.1899(19)	−.210(11)	.2976(34)	3.9(13)
H(8)	.1539(18)	−.494(11)	.3580(33)	3.2(12)
H(9)	.0623(21)	−.465(12)	.2935(39)	4.9(15)
H(10)	.0129(24)	−.180(13)	.1710(43)	7.1(19)
H(13)	.2278(17)	.4531(100)	.1975(32)	2.8(11)
H(14)	.2687(19)	.751(10)	.1524(34)	3.5(12)
H(15)	.2171(20)	.993(12)	.0117(35)	4.6(15)
H(16)	.1244(21)	.958(12)	−.0871(40)	6.2(17)
H(17)	.0788(22)	.669(12)	−.0479(40)	6.0(16)

Crystal data

2-Phenyl-4(3*H*)-quinazolinone $C_{14}H_{10}N_2O$, monoclinic, space group: $C2/c$. Cell dimensions at 85 K: $a=30.095(13)$ Å, $b=4.964(2)$ Å, $c=16.630(4)$ Å, $\beta=121.50°(3)$, $V=2118.3$ Å^3. $M=222.2$, $Z=8$, $D_{calc}=1.394$ g cm^{-3}, $F(000)=928$. Systematically absent reflections: hkl for $h+k$ odd, $h0l$ for l odd.

Description of the structure. A view of the molecule is given in Fig. 1, where the atomic numbering also is indicated. Bond lengths and bond angles are listed in Table 2. The bond lengths and angles do not deviate significantly from those found for similar compounds.[23]

The heterodicycle is planar (see Table 3) with the plane of the phenyl ring (C(12)–C(17)) tilted 14.4° relative to this plane. The dihedral angles N(1)–C(2)–C(12) C(13) and N(3)–C(2)–C(12)–C(13) are −12.1 and 165.9°, respectively.

The intermolecular N(3)–O(11) hydrogen bond of 2.827(12) Å is of the type and length usually found for this type of molecules.[24]

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer instrument Model 21 calibrated against CO_2. Elemental analyses were found in agreement with calculated values for all stable compounds.

Preparation of 5-(diphenylmethaniminoxy)-1,2,3,4-thiatriazole (4). A solution of *3*[2] was prepared by adding the sodium salt of benzophenone oxime (0.12 mol prepared from the oxime and sodium hydride) to a stirred solution of thiophosgene (0.12 mol) in tetrahydrofuran (250 ml) initially cooled to 0 °C at such a rate that the temperature did not exceed 10 °C. After stirring at 10 °C for an additional 15 min, a solution of sodium azide (18 g) in ice-water (250 ml) was added at a rate which kept the temperature below 10 °C. Following this addition the stirring was continued for 30 min at 10–15 °C and water (150 ml) and ether (150 ml) were added. After washing with ice-water (3 × 50 ml) the ether layer was dried over $MgSO_4$ at 0 °C and evaporated *in vacuo* to give a semisolid material. A crystalline material (13.1 g, 39 % based on *2*) was obtained after digestion with hexane:ether (2:1, 50 ml) followed by hexane:ether (4:1, 50 ml). Further purification was achieved by digestion with

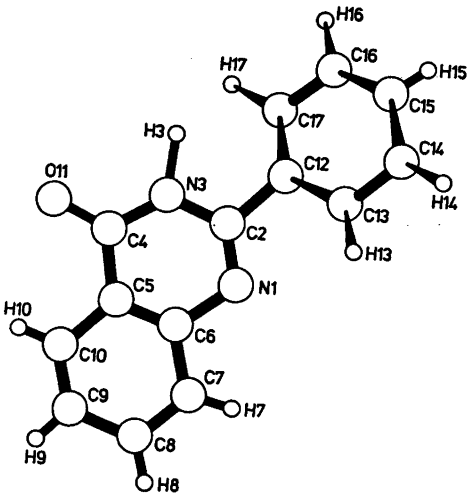


Fig. 1. The molecule projected on the plane of the dicycle, with the atomic numbering indicated.

cold ethanol to give an almost colorless material which was used for the subsequent experiments. An analytically pure sample was obtained by recrystallization from ether at −80 °C. M.p. *ca.* 130 °C (decomp.). IR(CCl_4): 3070 w, 1495 d,w, 1458 vs, 1445 s, 1330 m, 1310 m, 1288 s, 1229 w, 1056 w, 978 m, 930 m, 870 s, 695 s, 632 w, 604 w.

Thermal decomposition of 4 *in boiling* CCl_4. (a) Decomposition monitored by infrared spectroscopy. Thiatriazole *4* (1.0 g) in CCl_4 (10 ml) was kept at reflux temperature and samples (0.5 ml) for infrared analysis were taken at intervals. Nitrogen evolution was immediately observed but had diminished considerably after 10 min and practically stopped after 15 min. The infrared spectra exhibit a weak doublet at 2256 and 2220 cm^{-1} which had developed to a strong band in 10 min. However, the band at 1485 cm^{-1} arising from *4* is still observable. The latter band is absent after 25 min, but the bands at 2256 and 2220 cm^{-1} had decreased slightly and crystalline *7* had begun to separate from the solution. This compound is insoluble in cold CCl_4 as evidenced by lack of the strong $\nu_{C=O}$ band at 1670 cm^{-1} (see below) in the above solution. The spectrum in CCl_4 recorded after 25 min boiling may thus be the spectrum of compound *6* solely: 3070 w, 2256 vs, 2220 s, 1705 s, 1629 s, 1596 s, 1490 m, 1446 m, 1314 w, 1270 m, 1201 m, 1123 w, 1074 w, 1027 w, 1002 w, 982 s, 695 and 690 d, vs, and 670 m. (b) Thiatriazole *4* (1.0 g) in CCl_4 (10 ml) was refluxed for 1 h. After cooling the solid material

Table 2. Bond lengths (Å) and bond angles (°), with estimated standard deviations.

Bond lengths		Bond angles	
N(1)−C(2)	1.273(7)	C(2)−N(1)−C(6)	115.1(5)
C(2)−N(3)	1.385(8)	N(1)−C(2)−N(3)	125.4(6)
N(3)−C(4)	1.364(8)	N(1)−C(2)−C(12)	118.0(6)
C(4)−C(5)	1.468(8)	N(3)−C(2)−C(12)	116.6(5)
C(5)−C(6)	1.377(9)	C(2)−N(3)−C(4)	122.7(5)
N(1)−C(6)	1.442(8)	N(3)−C(4)−C(5)	115.4(6)
C(6)−C(7)	1.396(8)	N(3)−C(4)−O(11)	120.9(5)
C(7)−C(8)	1.372(9)	C(5)−C(4)−O(11)	123.8(6)
C(8)−C(9)	1.405(10)	C(4)−C(5)−C(6)	117.6(6)
C(9)−C(10)	1.398(8)	C(4)−C(5)−C(10)	120.7(6)
C(5)−C(10)	1.402(9)	C(6)−C(5)−C(10)	121.7(5)
C(4)−O(11)	1.267(8)	N(1)−C(6)−C(5)	123.8(5)
C(2)−C(12)	1.497(9)	N(1)−C(6)−C(7)	117.4(6)
C(12)−C(13)	1.414(9)	C(5)−C(6)−C(7)	118.8(6)
C(13)−C(14)	1.398(9)	C(6)−C(7)−C(8)	120.8(6)
C(14)−C(15)	1.377(8)	C(7)−C(8)−C(9)	120.6(5)
C(15)−C(16)	1.374(10)	C(8)−C(9)−C(10)	119.2(6)
C(16)−C(17)	1.380(9)	C(5)−C(10)−C(9)	119.0(6)
C(12)−C(17)	1.384(7)	C(2)−C(12)−C(13)	118.5(5)
Hydrogen bond:		C(2)−C(12)−C(17)	121.8(6)
N(3)−O(11)($-x$,1$-y$,$-z$)	2.827(12)	C(13)−C(12)−C(17)	119.7(6)
		C(12)−C(13)−C(14)	118.5(5)
		C(13)−C(14)−C(15)	120.1(6)
		C(14)−C(15)−C(16)	121.4(6)
		C(15)−C(16)−C(17)	119.4(6)
		C(12)−C(17)−C(16)	120.9(6)

Table 3. Deviations from least-squares planes (Å × 10^3). The deviations for those atoms used to define the plane are given in italicized numbers.

Atom	Plane I	Plane II	Atom	Plane I	Plane II
N(1)	*18*	−178	C(10)	*−2*	333
C(2)	*0*	37	O(11)	*29*	833
N(3)	*−29*	345	C(12)	63	*4*
C(4)	*−4*	491	C(13)	398	*−3*
C(5)	*−17*	225	C(14)	490	*0*
C(6)	*8*	−80	C(15)	248	*1*
C(7)	*0*	−332	C(16)	−86	*0*
C(8)	*3*	−246	C(17)	−180	*−2*
C(9)	*−6*	80			

was isolated by filtration. Recrystallization from benzene (15 ml), followed by washing with cold benzene (2 × 3 ml) and hexane gave *7* (0.3 g, 36 %). M.p. 241 – 242 °C. Lit. 241 °C.[25]

Formation of 7 *from* N-*phenyl benzimidoyl-chloride and silver cyanate.* *N*-Phenylbenzimidoyl chloride (1 g) and silver cyanate (1 g) in dry acetonitrile (10 ml) were heated to reflux for 1 h. The solvent was removed *in vacuo* and the remaining material taken up in a mixture of methylene chloride and an aqueous solution of sodium thiosulfate. The phases were carefully mixed by shaking, the methylene chloride layer dried over $MgSO_4$ and the solvent removed by evaporation *in vacuo*. The impure material obtained was recrystallized from benzene to yield *7*, (0.13 g, 13 % based on *N*-phenyl-benzimidoyl chloride). M.p. 239 °C. Lit. 241 °C.[25] The infrared spectrum (KBr) which exhibits a strong band at 1670 cm^{-1} ($\nu_{C=O}$) and two characteristic strong bands at 768 and 693 cm^{-1} due to phenyl [13] is identical with the infrared spectrum of *7* obtained from *4* (see above).

Thermal decomposition of 4 *in ethanol. Formation of* 10. Thiatriazole *4* (1.0 g) in abs. ethanol (5 ml) and 2 drops of triethylamine was heated to reflux for 30 min. Evaporation of the solvent *in vacuo* gave a mixture of sulfur and an oil which was extracted with ether. Filtration and evaporation of the ether left a slowly crystallizing oil (0.98 g), which was purified by dissolving in ether (10 ml) and extraction of the ether phase with 4 N hydrochloric acid (10 ml). The aqueous phase was extracted several times with ether and finally neutralized with 2 N sodium hydroxide (20 ml) causing separation of *10* which was taken up in ether. The ether phase was washed with water, dried over $MgSO_4$ and evaporated to dryness. The resulting oil (*10*) solidified rapidly, was digested with hexane and recrystallized from hexane/benzene. M.p. 101 – 102 °C.

Hydrolysis of 10. Compound *10* (5 × 10^{-4} mol) was dissolved in N hydrochloric acid (5 ml) and refluxed for 1.5 h. A crystalline material (40 mg), m.p. 120 – 121 °C, was obtained on cooling in ice. This was identified as benzoic acid by comparison with an authentic sample. (IR spectra, mixture m.p.). Ether extraction of the hydrolysis mixture gave an additional 14 mg benzoic acid (m.p. 121 – 122 °C) after recrystallization from water thus giving a combined yield of benzoic acid of 90 % based on *10*.

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