

Oxidation of Lignin Model Compounds with Chlorine Dioxide and Chlorite. Reactions with Stilbenes

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The reaction products from the oxidation of several different types of stilbenes with chlorine dioxide have been isolated and characterised. *trans*-Stilbene was oxidised to α,α' -epoxy-bibenzyl which then underwent rearrangement or was attacked by nucleophiles present in the reaction mixture. 4-Hydroxy-3,3',4'-trimethoxy-*trans*-stilbene was attacked mainly on its phenolic hydroxyl group, resulting in formation of polymers. Some veratraldehyde and veratric acid, as well as vanillin and vanillic acid was also formed by attack at the double bond. *cis*-2,3-Diphenyl-prop-2-en-1-ol gave mainly allylic oxidation products, whereas *cis*-2,3-di-(3,4-dimethoxyphenyl)-prop-2-en-1-ol mainly underwent oxidative cleavage into veratraldehyde and 3,4-dimethoxyphenacyl alcohol. The reaction paths are discussed.

Most of the model studies¹⁻⁴ of the reaction between lignin and chlorine dioxide have been performed with lignin model compounds which contain free phenolic groups, e.g. vanillin and guaiacol. Such studies are informative for the reactions of chlorine dioxide when used in the first bleaching stage of sulfate pulp. However, for the final stages of bleaching, where the main part of the chlorine dioxide reacts, these model compounds are of less relevance, since most of the phenolic groups in lignin evidently are oxidised during the earlier stages.

Final bleaching with chlorine dioxide gives pulps with high brightness. Chlorine dioxide thus reacts with the colour-giving elements of lignin. The chlorine dioxide oxidation of model compounds of such elements are therefore of greater interest than the reaction of phenols for the understanding of how the lignin residues

react during the final bleaching. They may also be of interest for understanding the reactions of a first bleaching stage with chlorine dioxide.

The structure of these colour-giving elements are, however, unknown. They may include conjugated systems composed of carbonyl groups, double bonds, or aromatic as well as quinoid structures.

On this basis we have studied how chlorine dioxide reacts with models containing one type of these elements, viz. double bonds conjugated with benzene nuclei. Four different stilbene derivatives were chosen as models.

The action of chlorine dioxide on organic compounds is generally a complex process as the chlorine dioxide is primarily reduced to chlorine and chlorite^{5,6} which may both react with the starting material, the intermediates, or the reaction products. Complicated reaction products are therefore expected from the chlorine dioxide oxidation of stilbenes.

RESULTS AND DISCUSSION

The stilbene derivatives chosen were *trans*-stilbene, *cis*-2,3-diphenyl-prop-2-en-1-ol, *cis*-2,3-di-(3,4-dimethoxyphenyl)-prop-2-en-1-ol, and 4-hydroxy-3,3',4'-trimethoxy-*trans*-stilbene.

Treatments with chlorine dioxide were carried out in aqueous *t*-butanol or dioxane solutions and in non-aqueous solutions (chloroform or carbon tetrachloride).

In a typical experiment chlorine dioxide solution was added in darkness at room temperature to the stilbene solution. The reaction products obtained were first separated into two fractions containing acidic and neutral compounds, respectively. The neutral part was fractionated

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further by column chromatography. If a sub-fraction contained two or more compounds, their respective yields were determined from the peak areas of the gas chromatograms ("GLC:s") or of the NMR spectra. The acid fractions were analysed by spectral methods and by GLC/MS after methylation.

trans-Stilbene. The chlorine dioxide treatment of *trans*-stilbene in carbon tetrachloride solution yielded the following main products: α -chloro-benzyl phenyl ketone (yield 43 %), *trans*- α,α' -epoxy-bibenzyl (yield 36 %), and α,α' -dichloro-bibenzyl (yield 7 %). The presence of small amounts of benzil in the reaction mixture was also observed. The yields were estimated from the peak areas of the NMR spectrum and were substantiated by the isolation of the chloro ketone and the dichloro compound in amounts corresponding to those mentioned above. The isolated dichloro compound consisted mainly of the *racem.* form like the product obtained after chlorination of *trans*-stilbene.⁷ The epoxide had mostly decomposed during the working-up procedure.

The first step in the oxidation of *trans*-stilbene in carbon tetrachloride is most likely an addition of chlorine dioxide to the aliphatic double bond, but subsequent steps are less obvious. The chloro ketone was evidently not formed *via* the epoxide since no chloro ketone was found after treatment of the epoxide with chlorine dioxide, chlorine, or a mixture of them.

When *trans*-stilbene was treated with chlorine dioxide in aqueous dioxane solution the formation of α -chloro- α' -hydroxybibenzyl (yield 44 %), diphenylacetic acid (15 %), α,α' -dihydroxybibenzyl (12 %, the *erythro* and *threo* isomers in about equal amounts), benzoic acid (5 %), benzoin (3 %), benzil (3 %), α,α' -dichloro-bibenzyl (3 %), and α -chloro-benzyl phenyl ketone (2 %) was detected.

The presence of *trans*- α,α' -epoxy-bibenzyl was not observed. However, this does not exclude the possibility that it was formed as an intermediate since it was found to be unstable in the reaction mixture. The α -chloro- α' -hydroxy-bibenzyl and α,α' -dihydroxybibenzyl may have been formed partly *via* the epoxide. Parts of the epoxide may also have rearranged into the diphenyl acetaldehyde which was then oxidised (probably by chlorite¹⁰) to the diphenylacetic acid.

cis-2,3-Diphenyl-prop-2-en-1-ol. When this stilbenol was treated with chlorine dioxide in carbon tetrachloride solution the main products were two allylic oxidation products *viz.* *cis*-2,3-diphenyl acrolein (yield 25 %) and *cis*-2,3-diphenyl-acrylic acid (yield 19 %). The other products found were benzaldehyde (11 %), 2,3-diphenyl-2-chloro-propan-1-ol-3-one (5 %), α -chloro-benzyl phenyl ketone (4 %), and *trans*-stilbene (0.5 %). *cis*-2,3-Diphenyl-acrylic acid might well have been formed by chlorite oxidation¹⁰ of *cis*-2,3-diphenyl-acrolein. An addition of formaldehyde, which reacts rapidly with chlorite, but only slowly with chlorine dioxide⁶ would then suppress the formation of the acid in favour of the aldehyde. We therefore investigated the possibility that chlorine dioxide in the presence of formaldehyde could be used for oxidation of allylic carbinol groups to aldehyde groups. In agreement with the assumption above, the yield of *cis*-2,3-diphenyl acrolein increased to 38 % in the presence of formaldehyde if the oxidation was carried out as described above in carbon tetrachloride solution. If the oxidation was performed in aqueous solution its yield was 27 % in the presence of formaldehyde and only 8 % in the absence of formaldehyde. Chlorine dioxide plus formaldehyde may then in special cases be a cheap reagent for oxidation of allyl alcohols to acroleins.

Chlorine dioxide oxidised *cis*-2,3-di-(3,4-dimethoxyphenyl)-prop-2-en-1-ol in aqueous *t*-butanol solution to 3,4-dimethoxy-phenacyl alcohol (yield 42 %), veratraldehyde (24 %), veratric acid (25 %), and 2,3-dichloro-2,3-di-(3,4-dimethoxyphenyl)-propan-1-ol (20 %). The same products were predominant when the oxidation was carried out in chloroform solution.

Thus, this oxidation involved mainly a cleavage of the aliphatic double bond. No evidence for an allylic oxidation was observed, which clearly distinguished the oxidation of this stilbene derivative from the oxidation of that containing no methoxyl group, *viz.* *cis*-2,3-diphenyl-prop-2-en-1-ol. The methoxylated model compound reacted faster with chlorine dioxide than the one without methoxyl groups. The methoxyl groups evidently promote chlorine dioxide addition to the double bond, rather than oxidation in the allylic position.

4-Hydroxy-3,3',4'-trimethoxy-trans-stilbene.

The chlorine dioxide oxidation of this stilbene in chloroform solution gave only a low yield of identifiable products. These products were vanillic and veratric acid (total acid yield 10 %), veratraldehyde, monochlorinated veratraldehyde, and vanillin (each aldehyde in a yield less than 1 %). The main part of the reaction product consisted of a dark, probably polymeric material. The possibility that chlorine dioxide induced vinylic polymerization involving free radicals was excluded since only one mol of stilbene was consumed per mol chlorine dioxide (determined by UV-absorption spectrometry). This polymerisation was probably caused by oxidation of the phenolic hydroxyl group (cf. the polymerisation caused by chlorine dioxide oxidation of other phenols).¹⁻⁵

No general pattern was found in the reactions of the four stilbenes with chlorine dioxide. Epoxidation, allylic oxidation, splitting of the aliphatic double bond, α -chloro ketone formation *etc.* were observed. The phenolic stilbene seemed to be attacked mainly at the free phenolic group.

The products from the oxidation of the methoxylated stilbenes with chlorine dioxide, however, suggest that the conjugated double bonds which possibly are present in the residual lignin, may be cleaved by the dioxide, forming carbonyl groups.

EXPERIMENTAL

General. Unless otherwise stated, the following methods were used. The chlorine dioxide treatment of the stilbenes were carried out at room temperature in darkness. NMR-spectra (in deuterio chloroform) were obtained on a Perkin-Elmer R12 (60 MHz); IR-spectra (in chloroform) on a Perkin-Elmer 237; and UV-spectra, on a Beckman DK-2; GLC on a Perkin-Elmer 800, 900 or F 30; and GLC/MS on a Perkin-Elmer 270. TLC:s were run on silica gel plates with chloroform, chloroform/methanol or toluene as solvents.

trans-Stilbene and chlorine dioxide

Oxidation by chlorine dioxide in carbon tetrachloride. Chlorine dioxide (9 mmol) in carbon tetrachloride (158 ml) was added to *trans*-stilbene (5 mmol, 900 mg) in carbon tetrachloride (10 ml). After 20 h, the reaction mixture gave

the following NMR signals (in carbon tetrachloride solution) (their assignments are given in brackets): δ 3.83 s (*trans*- α,α' -epoxy-bibenzyl) relative peak area 10; δ 5.21 s (α,α' -dichloro-bibenzyl) area 2; δ 6.28 s (α -chloro-benzyl phenyl ketone) area 6; δ 7.0–7.6 m (aromatic protons of the products and of unreacted stilbene) area 125; δ 7.8–8.0 m (α -chloro-benzyl phenyl ketone) area 14. Calculations from the peak areas showed that the mixture consisted of about 46 mol % α -chloro-benzyl phenyl ketone, 36 % *trans*- α,α' -epoxy-bibenzyl and 7 % α,α' -dichloro-bibenzyl.

The mixture was chromatographed on a silica gel column with toluene as eluent. (The reaction mixture was found to contain only negligible amounts of acids). Five fractions were collected.

The following NMR signals of fraction 1 (evaporation residue 109 mg) were observed: δ 5.20 s (assigned to both the *racem.* and the *meso* form of α,α' -dichloro-bibenzyl) relative peak height 3; δ 6.88 s (unassigned) height 0.7; δ 7.14 s (assigned to the *racem.* form of α,α' -dichloro-bibenzyl) height 12.4; δ 7.20–7.45 m (assigned to *trans*-stilbene); δ 7.35 s (assigned to the *meso* form of α,α' -dichloro-bibenzyl), height 4; and δ 7.7 s (assigned to *trans*-stilbene) height 3. TLC of the fraction showed two spots which were indistinguishable from those of *trans*-stilbene and α,α' -dichloro-bibenzyl (the D.L. and the *meso* forms of the latter were not separated).

The TLC and the NMR signals of fraction 2 (33 mg) were indistinguishable from those of an authentic sample of *trans*-stilbene epoxide and in accordance with those given by Ceccarelli *et al.*¹¹

Fraction 3 (42 mg) was a mixture of the components in fractions 2 and 4.

Fraction 4 (422 mg) showed NMR and IR spectra indistinguishable from those of an authentic sample of α -chloro-benzyl phenyl ketone, and had a m.p. 65–67.5 °C (lit.¹² 68.5 °C).

Fraction 5 (122 mg) consisted of about two thirds diphenylacetaldehyde as shown by comparing its IR and NMR spectra with those of an authentic sample. The presence of NMR signals at δ 7.7–8.0, together with a GLC analysis of the crude product of another run, indicated the presence of small amounts of benzil.

Oxidation by chlorine dioxide in aqueous dioxane solution. A dioxane (350 ml)/water (265 ml) solution of *trans*-stilbene (10 mmol, 1.80 g) and chlorine dioxide (19 mmol) was kept for 2.5 days and was then partly evaporated to remove chlorine dioxide and most of the dioxane. The resulting solution was divided by extraction with a sodium hydrogen carbonate solution into an acid (0.31 g) and a neutral fraction (1.71 g).

The NMR spectrum of the acid fraction was run both before and after methylation with

diazomethane in absolute methanol. The methylated fraction was also analysed by GLC (3 % OV-17). By comparing the retention times and NMR signals obtained with those from benzoic and diphenyl-acetic acid the fraction was found to consist almost exclusively of these acids. Their yields were estimated from the NMR signals.

1.40 g of the neutral fraction was fractionated on a silica gel column with chloroform as eluent. The following fractions were taken:

Fraction 1 (74 mg) consisted of α, α' -dichloro-bibenzyl (mainly the *D,L* form) as shown by NMR (cf. the experiment in carbon tetrachloride solution).

Fraction 2 (155 mg) was a mixture of α -chloro-benzyl phenyl ketone, benzil and an unidentified compound. Benzil and the chloro ketone were identified from GLC (OV-17, 145 °C, R_T = 23 and 31 min, respectively) and by comparing the NMR and IR spectra of these fractions with those of authentic compounds. The yields of the two compounds were estimated by GLC and their NMR integral signals.

Fraction 3 (772 mg) gave NMR signals at δ 7.20, 7.18, 7.09, 7.05 (four s, 10 H); δ 4.95 (s, 1 H); δ 4.88 (s, 1 H) and δ 3.21 (broad s, 1 H). Its IR spectrum showed strong absorption at 3550 cm^{-1} and 3400 cm^{-1} due to the presence of hydroxyl groups. The spectral and chromatographic properties of this fraction were equal to those of the mixture of the *erythro* and *threo* forms of α -chloro- α' -hydroxy-bibenzyl obtained by chlorination of *trans*-stilbene in a dioxane/water system.

Fraction 4 (60 mg). Its TLC and spectra (NMR and IR) were indistinguishable from those of an authentic sample of benzoin. Its m.p. was 131.4–132.5 °C (lit.¹³ 137 °C).

Fraction 5 (103 mg). Two of its TLC spots were coloured red when sprayed with lead tetraacetate solution followed by Schiff's reagent (suggesting the presence of α -diols). Its IR spectrum showed absorption (3590 cm^{-1}) indicating hydroxyl groups. Its NMR spectrum showed the following main peaks: δ 7.21 (s, 10 H); δ 4.76 (s, 2 H); and 2.7 (broad s, 2 H), which correspond to the reported¹⁴ data for *meso*- α, α' -dihydroxy-bibenzyl. An NMR signal at δ 4.61 was assigned to *D,L*- α, α' -dihydroxy-bibenzyl (see fraction 6).

Fraction 6 (104 mg). Its IR spectrum showed absorption at 3590 cm^{-1} and its TLC spots showed positive reaction with lead tetraacetate followed by Schiff's reagent. Its NMR spectrum showed signals at δ 7.20–7.05 (4 s, 10 H); 4.62 (s, 2 H) and 3.0 (broad s, 2 H) and was assigned to *D,L*- α, α' -dihydroxy-bibenzyl.

cis-2,3-Diphenyl-2-propen-1-ol and chlorine dioxide

A carbon tetrachloride solution of *cis*-2,3-diphenyl-2-propen-1-ol (6.2 mmol) and chlorine

dioxide (6.6 mmol) was reacted for 18 h and was then washed with ice water and evaporated to dryness. The residue (1.6 g) was separated into neutral and acid components as usual by partition between sodium hydrogen carbonate solution and ether.

The acidic part consisted of *cis*-2,3-diphenyl-acrylic acid (yield 19 %, m.p. 174–175 °C, lit.¹⁵ 172–173 °C, NMR indistinguishable from that of an authentic sample) contaminated with small amounts of benzoic acid which was observed by GLC/MS analyses of the fraction after diazomethane methylation.

An aliquot (90 %, i.e. 1.2 g) of the neutral fraction was eluted with chloroform from a silica gel column; five fractions (together 1.03 g) were collected.

Fraction 1 (400 mg) was rechromatographed on a silica gel column with hexane/toluene 1:1 as eluent. The separation was still incomplete, but *trans*-stilbene (0.5 %), α -chloro-benzyl phenyl ketone (4 %) and benzaldehyde (11 %) and small amounts of *cis*-2,3-diphenyl-acrolein were identified by NMR signals and TLC. The yields were estimated from the NMR integrals.

Fraction 2 (309 g) consisted of *cis*-2,3-diphenyl-acrolein (yield 25 %) m.p. 93.5–94.5 °C, lit.¹⁶ 95 °C. NMR: δ 9.67 (s, 1 H); δ 7.4–7.1 (m, 11 H). TLC and GLC (OV-17, 3 %, 170 °C) showed that the fraction was practically pure. MS: *m/e* 208 (molecular ion, base peak), 207 (50 % of the base peak height), 192 (20), 179 (70), 178 (75), 165 (30), 152 (20), 105 (30) and 103 (45).

Fraction 3 (89 mg) contained according to NMR and TLC mainly *cis*-2,3-diphenyl-acrolein (see fraction 2) and 2,3-diphenyl-2-chloro-propan-1-ol-3-one (see fraction 4) but also an unidentified compound.

Fraction 4 (88 mg). Its IR absorption (3580 and 3450 cm^{-1} for hydroxyl group and 1675 cm^{-1} for keto group conjugated with double bond) and its NMR spectrum [δ 7.8–7.0 (m, 12 H); δ 4.1 (m, 2 H) and δ 2.95 (broad s, 1 H)] indicated that it consisted of 2,3-diphenyl-2-chloro-propan-1-ol-3-one (5 %).

Fraction 5 (144 mg) was a complicated mixture which contained, besides unidentified material, the chloro ketone from fraction 4 and small amounts of the starting material.

In other runs, *cis*-2,3-diphenyl-prop-2-en-1-ol (5.2 mmol) was reacted with chlorine dioxide (5.2 mmol) in the presence and in the absence of formaldehyde (6 mmol). The reaction was carried out in carbon tetrachloride (as above) and in a mixture of *t*-butanol/water (7:10). The reaction product was analysed by GLC. For results, see text.

cis-2,3-Di-(3,4-dimethoxyphenyl)-prop-2-en-1-ol.¹⁷

Oxidation by chlorine dioxide in aqueous t-butanol solution. Chlorine dioxide (1 mmol) in

water (18.5 ml) was added to *cis*-2,3-di-(3,4-dimethoxyphenyl)-prop-2-en-1-ol (1 mmol) in *t*-butanol (18.5 ml). After one hour the reaction mixture was partly evaporated to remove most of the *t*-butanol, diluted with water and extracted with methylene chloride.

The acidic part (44 mg, yield 25 % calc. as veratric acid) of the extract was methylated with diazomethane and analysed with GLC/MS (OV-1). It consisted of methyl veratrate contaminated with a small amount of veratraldehyde.

The neutral part (280 mg) was fractionated with chloroform on a silica gel column. The yields were estimated from the NMR integral signal of the raw product and were in agreement with the fraction weights. The following fractions were collected:

Fraction 1 (40 mg). Its NMR, GLC, MS, and TLC properties were indistinguishable from those of an authentic sample of veratraldehyde.

Fraction 2 (23 mg) was a mixture of veratraldehyde, an unknown compound and 3,4-dimethoxy-phenacyl alcohol (see fraction 3).

Fraction 3 (82 mg) consisted according to TLC mainly of one substance which from its NMR and IR spectra appeared to be 3,4-dimethoxy-phenacyl alcohol [NMR: δ_a 7.42 (d, 1 H); δ_b 7.40 (q, 1 H); δ_c 6.85 (d, 1 H); δ_d 4.80 (broad s, 2 H); δ_e 3.90 (s, 6 H); δ_f 3.55 (broad s, 1 H, disappeared upon addition of D_2O). J_{ab} = 1.5 Hz, J_{bc} = 8.5 Hz. IR: a broad absorption at 3450 cm^{-1} , a sharp absorption at 1670 cm^{-1} and doublets at 1590 cm^{-1} and 1510 cm^{-1}]. The NMR and TLC of the acetylated fraction were indistinguishable from those of an authentic sample of 3,4-dimethoxyphenacyl acetate.¹⁸

Fraction 4 (27 mg) consisted of a mixture of 3,4-dimethoxy-phenacyl alcohol and the dichloro-compound from fraction 5 below.

Fraction 5 (30 mg) had the same NMR spectrum [δ 6.75 (m, 3 H); δ 4.95 (s, 1 H); δ 4.35 (s, 2 H) and δ 3.80 (s, 6 H)] as 2,3-dichloro-2,3-di-(3,4-dimethoxyphenyl)-propanol, which was obtained by chlorination of *cis*-2,3-di-(3,4-dimethoxyphenyl)-prop-2-en-1-ol in carbon tetrachloride solution (see below).

Fraction 6 (37 mg) was a mixture of constituents which were not identified, except for a small amount of the dichloro compound of fraction 5.

Oxidation by chlorine dioxide in chloroform solution. An experiment similar to that above was carried out in chloroform. The reaction products were veratric acid (22 %) and a neutral part which did not differ significantly (as shown by TLC and NMR) from the reaction products obtained when the experiment was done in *t*-butanol/water.

Chlorination. *cis*-2,3-Di-(3,4-dimethoxyphenyl)-prop-2-en-1-ol was also reacted with chlorine. When the reaction was performed in carbon tetrachloride, the residue gave after chromatography on silica gel with chloroform, a fraction

(56 %) which was identical with the dichloro compound from fraction 5 above, according to NMR signals and TLC.

When performed in *t*-butanol/water, the chlorination gave the chlorohydrine as the main product.

4-Hydroxy-3,3',4'-trimethoxy-stilbene¹⁹ and chlorine dioxide

To the stilbene (2 mmol) in chloroform (20 ml) was added chlorine dioxide (2.6 mmol) in chloroform (40 ml). The reaction mixture immediately turned reddish, and subsequently yellow. After 20 min the mixture was evaporated to dryness and a viscous oil (727 mg) was obtained which was analysed by GLC (5 % OV-1, $100 \rightarrow 200^\circ\text{C}$, $+4^\circ\text{C}/\text{min}$) and MS. Veratraldehyde, vanillin, monochlorinated veratraldehyde, and veratric acid were identified. All yields were less than 1 %. The acidic part (34 mg, 9 % if calculated as veratric acid) was methylated with diazomethane and analysed with GLC (5 % OV-1, 180°C) and MS. Methyl veratrate was by far the predominant compound. IR analysis gave the same result. The ester was contaminated with small amounts of veratraldehyde, monochlorinated veratraldehyde, and monochlorinated methyl veratrate (GLC/MS). The neutral fraction consisted of dark polymeric material.

In other experiments, chloroform solutions of the stilbene (10 mM) and chlorine dioxide (5 mM) were mixed in different proportions (10/1, 10/2, 9/4 and 1/1 ml/ml) and were diluted to 25 ml. After 10 min and after 24 h, samples of the solutions were diluted 100 fold and UV-spectra were taken. For results, see text.

α,α' -Epoxy-bibenzyl²⁰ and chlorine dioxide, chlorine, or a mixture of chlorine dioxide and chlorine

A carbon tetrachloride solution (50 ml) of α,α' -epoxy-bibenzyl (1 mmol) and chlorine dioxide (1 mmol) was reacted for 20 h at room temperature in darkness. Two similar experiments were performed with chlorine (1 mmol) and a mixture of chlorine dioxide (1 mmol) and chlorine (0.5 mmol), respectively.

The reaction mixtures were partly evaporated and analysed by NMR.

Only negligible alternations seemed to have occurred, and no α -chloro-benzyl phenyl ketone was detected.

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REFERENCES

1. Husband, R. M., Logan, C. D. and Purves, C. S. *Can. J. Chem.* **33** (1955) 68.
2. Logan, C. D., Husband, R. M. and Purves, C. B. *Can. J. Chem.* **33** (1955) 82.
3. Sarkanen, K. V., Kakeki, K., Murphy, R. A. and White, H. *Tappi* **45** (1962) 24.
4. Dence, C. W., Gupta, M. K. and Sarkanen, K. V. *Tappi* **45** (1962) 29.
5. Lindgren, B. O. *Sv. Papperstidn.* **74** (1971) 57.
6. Lindgren, B. O. and Nilsson, T. *Sv. Papperstidn.* **75** (1972) 161.
7. Buckles, R. E. and Knaack, D. F. *J. Org. Chem.* **25** (1960) 20.
8. Berti, G., Bottari, F., Ferrarini, P. L. and Macchia, B. *J. Org. Chem.* **30** (1965) 4091.
9. House, H. O. *J. Amer. Chem. Soc.* **77** (1955) 3070.
10. Lindgren, B. O. and Nilsson, T. *Acta Chem. Scand.* **27** (1973) 888.
11. Ceccarelli, G., Berti, G., Lippi, G. and Macchia, B. *Org. Magn. Resonance* **2** (1970) 379.
12. Ward, A. M. *Org. Syn. Coll. Vol.* **2** (1943) 159.
13. Adams, R. and Marvel, C. S. *Org. Syn. Coll. Vol.* **1** (1941) 94.
14. Wiemann, J., Dana, G., Sa Le Thi Thuan and Brami, M. *C. R. Acad. Sci. Ser. C* **258** (1964) 3724.
15. Buckles, R. E. and Bremer, K. *Org. Syn. Coll. Vol.* **1** (1941) 94.
16. Benger, M. and Brady, O. L. *J. Chem. Soc.* (1953) 3612.
17. Gierer, J. and Szabo, I. *In press.*
18. Kaufmann, A. and Müller, H. *Ber. Deut. Chem. Ges.* **51** (1918) 123.
19. Gierer, J. and Opara, A. E. *Acta Chem. Scand.* **27** (1973) 2909.
20. Reif, D. J. and House, H. O. *Org. Syn. Coll. Vol.* **4** (1963) 860.

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