the crude enamine was taken up in 200 ml. of N,N-dimethylformamide. Twenty-three grams (0.23 mole) of ethyl acrylate was added dropwise to the enamine solution at reflux and the reaction mixture was refluxed for 40 hr. The solvent was removed *in vacuo* on a steam bath and the enamine was hydrolyzed by refluxing for 2 hr. with 150 ml. of water and 8 ml. of glacial acetic acid. After cooling, the mixture was extracted thoroughly with ether and the ether extract was washed with dilute acid, base, and water, and finally dried over sodium sulfate. The ether was removed and the residue was distilled to afford 18.6 g., b.p. 160–162° at 1 mm. Allowing for recovered starting material the yield was 63%.

Anal. Calcd. for $C_{14}H_{21}NO_3$: C, 66.9; H, 8.4; N, 5.6. Found C, 66.9; H, 8.5; N, 5.6.

3-Oxohexahydrojulolidine (II).—Twenty grams (0.80 mole) of I was hydrogenated in 100 ml. of absolute ethanol at 1800 p.s.i. and 125° using 7 g. of W-7 Raney nickel as catalyst. The catalyst was removed by filtration, the solvent was removed *in vacuo*, and the residue was distilled, giving 8.3 g. (54%) of II, b.p. 144–150° at 0.1 mm.

Anal. Calcd. for $C_{12}H_{19}NO$: C, 74.5; H, 9.9; N, 7.2. Found: C, 74.2; H, 9.9; N, 7.1.

Reduction of II to Hexahydrojulolidine.—To a solution of 1.2 g. of powdered lithium aluminum hydride in 40 ml. of dry tetrahydrofuran was added 6.1 g. of II in 20 ml. of tetrahydrofuran. The reaction was refluxed 4 hr. and then treated first with ethyl acetate and finally with water to destroy the unused hydride. The mixture was filtered, the gelatinous precipitate was washed well with tetrahydrofuran, and the filtrate and washings were combined and dried over sodium sulfate. Removal of solvent and distillation gave 3.6 g. (72%) of hexahydrojulolidine, b.p. 110–120° at 5 mm.

Three grams of this product was chromatographed following the procedure of Bohlmann[7] to give 1.5 g. of III, picrate m.p. 225–226°, and 1.0 g. of IV, picrate m.p. 186–187°.

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(7) F. Bohlmann and C. Arndt, *Chem. Ber.*, **91**, 2167 (1958).

Preparation of Quinol Ethers

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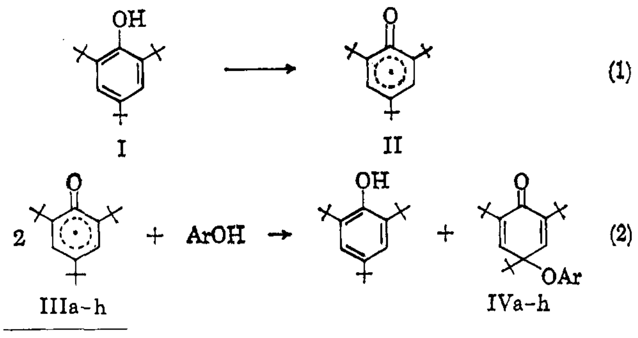
Chemical reactions of radicals obtained by oxidation of sterically hindered phenols such as 2,4,6-tri-*t*-butylphenol (I) have been widely studied during recent years.[1-3] An interesting result was reported by Müller, Ley and Schlechte, who found that 2 moles of 2,4,6-tri-*t*-butylphenoxyl (II) react with 1 mole of a phenol (III) to form 1 mole of 2,4,6-tri-*t*-butylphenol (I) and 1 mole of a 4-quinol ether (IV)[4] (reactions 1 and 2). For preparative use this reaction has the disadvantage that the quinol ether is often difficult to separate from the simultaneously formed I. Reoxidation of I to II with potassium ferricyanide in this reaction has been practiced, but this procedure is very tedious.[4,5]



I II (1)

IIIa-h IVa-h (2)

Another method of preparing quinol ethers of this type is the reaction of 4-bromo-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one with alkali phenolates.[4] The reaction can be carried out in an organic solvent; however, separate preparation of the starting materials from the phenols is required.

Our interest in oxidations with active manganese dioxide[6] has now led to a very convenient method for the preparation of quinol ethers. We observed that 2,4,6-tri-*t*-butylphenol (I) in benzene solution in contact with active manganese dioxide instantly forms the blue solution of 2,4,6-tri-*t*-butylphenoxyl (II) in apparently high yield. Successive additions of 1 mole of a phenol (IIIa–h) per mole of 2,4,6-tri-*t*-butylphenol (I) to the MnO_2-containing radical solution leads to irreversible discharge of the blue color. Since the 2,4,6-tri-*t*-butylphenol formed in the reaction is immediately reoxidized by the manganese dioxide present, the isolation of the quinol ether is no longer difficult. Filtration and evaporation of the solvent give the quinol ethers (IVa–h) in excellent yield and high state of purity. We have used this method to prepare quinol ethers previously not reported (see Table I), including the reaction product of 2,4,6-tri-*t*-butylphenoxyl with the unsubstituted phenoxy radical.

Table I

Ar in III and IV	Quinolid bands in IV (cm.$^{-1}$)
a, Phenyl	1645, 1665[a]
b, 2,4,6-Trichlorophenyl	1645, 1666[b]
c, Pentachlorophenyl	1642, 1664[b]
d, 4-Phenylmercaptophenyl	1645, 1665[b]
e, 4-Methoxyphenyl	1636, 1662[b]
f, 4-Benzoyloxyphenyl	1640, 1662[b]
g, 4-Benzyloxyphenyl	1640, 1662[b]
h, 4-Phenoxyphenyl	1645, 1665[a]

[a] Liquid film. [b] In potassium bromide.

The infrared spectra (see Table I) of all quinol ethers prepared exhibit double peaks at about 6 μ, typical for compounds with quinolid structure.[4]

Compared with known procedures for quinol ether formation, this new method appears to be the most convenient, since the starting materials are easily available, the reaction is carried out in an organic solvent, and the procedure does not involve any separation problems.

When we extended the reaction of phenols with active manganese dioxide to the cooxidation of 4-bromo-2,6-di-*t*-butylphenol (V) and pentachlorophenol (reaction 3), we isolated in excellent yield the aromatic quinone ketal VII, 4,4-bis(pentachlorophenoxy)-2,6-di-*t*-butyl-2,5-cyclohexadiene-1-one. Its structure is confirmed by analytical data (see Experimental), its infrared spectrum (bands at 1655 and 1680 cm.$^{-1}$, in KBr), and its conversion into pentachlorophenol and 2,6-di-*t*-butyl-benzoquinone-1,4 by treatment with boiling 96% ethanol.

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(1) E. Müller, A. Riecker, and K. Scheffler, *Ann. Chem.*, **645**, 92 (1961), and previous papers.

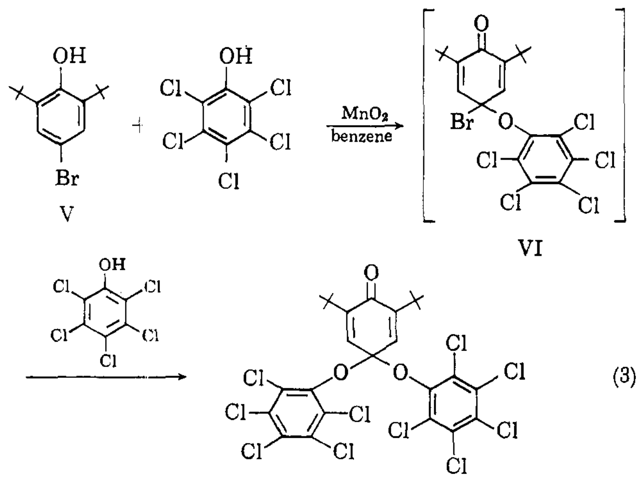
(2) C. D. Cook and N. D. Gilmour, *J. Org. Chem.*, **25**, 1429 (1960), and previous papers.

(3) For a recent review, see H. Musso, *Angew. Chem.*, **75**, 965 (1963).

(4) E. Müller, K. Ley, and G. Schlechte, *Chem. Ber.*, **90**, 2660 (1957).

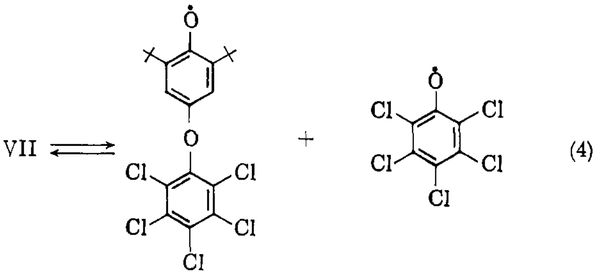
(5) T. Matsuura and H. J. Cahnmann, *J. Am. Chem. Soc.*, **82**, 2055 (1960).

(6) E. Adler and H.-D. Becker, *Acta Chem. Scand.*, **15**, 849 (1961); H.-D. Becker, *ibid.*, **15**, 683 (1961); **16**, 78 (1962).



V VI VII (3)

Upon addition of 2,4,6-tri-*t*-butylphenol to a freshly prepared, colorless solution of VII in benzene, the blue color characteristic of 2,4,6-tri-*t*-butylphenoxyl is formed after a few seconds. This indicates that the aromatic quinone ketal dissociates into phenoxy radicals (reaction 4) that can oxidize 2,4,6-tri-*t*-butylphenol.



(4)

Oxidation of V alone with MnO_2 gives 3,5,3′,5′-tetra-*t*-butyl-diphenoquinone, while oxidation of pentachlorophenol with MnO_2 affords the previously described 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadiene-1-one.[7] We presume that the formation of VII involves the quinol ether VI which could undergo either a nucleophilic[8] or radical displacement reaction to yield VII.

The formation of a mixed aliphatic–aromatic quinone ketal by oxidation of substituted hydroquinone monoalkyl ethers has previously been reported.[9] Aside from one example of a "dimer polyhalogen aroxyl"[10] obtained by oxidation of 4-pentachlorophenoxy-2,3,5,6-tetrachlorophenol, no aromatic quinone ketals have been reported previously.

Experimental[11]

"Active manganese dioxide" was prepared according to Attenburrow,[12] *et al.* Benzene was dried over sodium. All experiments were carried out in screw-cap bottles which were flushed with nitrogen whenever opened. Depending on the quality of the MnO_2, phenols can be strongly adsorbed, thus preventing their reaction with the tri-*t*-butylphenoxyl. In these cases a slightly higher ratio than 1:1 of the phenol (III) to tri-*t*-butylphenol is required for complete disappearance of the blue radical. Recrystallization of the quinol ethers did not cause any major losses of the materials.

4-Phenoxy-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene-1-one (IVa).—2,4,6-Tri-*t*-butylphenol (2.62 g., 10 mmoles) was added to a suspension of 12 g. of active MnO_2 in 100 ml. of benzene and the mixture was shaken under N_2 for 1 min. One gram of phenol (10.6 mmoles) was then added in five portions over a period of 30 min. Between each addition the mixture was shaken for a few minutes. After the last addition of phenol, the blue color of the solution disappeared. The manganese dioxide was removed by filtration using a fine sintered-glass funnel, and the yellow filtrate was evaporated at room temperature under vacuum, yielding 2.75 g. of IVa as a yellow oil, yield 73%.

Anal.[13] Calcd. for $C_{24}H_{34}O_2$: C, 82.49; H, 9.05; mol. wt., 378.53. Found: C, 82.41; H, 9.42; mol. wt., 336 (thermoelectric measurement in dioxane).

4-(2,4,6-Trichlorophenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene-1-one (IVb).—2,4,6-Tri-*t*-butylphenol (524 mg., 2 mmoles was added to a suspension of 5.2 g. of active MnO_2 in 100 ml. of benzene. After shaking for 1 min., 400 mg. of 2,4,6-trichlorophenol (2.04 mmoles) was added in four portions (shaking for 1 min. between each addition). After the last addition, the solution still showed a slightly greenish color. Further addition of 20 mg. of 2,4,6-trichlorophenol gave a yellowish solution. The mixture was filtered as described under IVa; the very slightly greenish filtrate was evaporated at room temperature *in vacuo*, yielding 850 mg. of a slightly yellowish green crystalline residue (93%), m.p. 122–123°. It was recrystallized from hot ethanol; m.p. 127–129°.

Anal. Calcd. for $C_{24}H_{31}Cl_3O_2$ (457.86): C, 62.96; H, 6.82; Cl, 23.23. Found: C, 62.94; H, 6.95; Cl, 23.40.

4-(Pentachlorophenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene-1-one (IVc).—This compound was prepared similarly to IVb from pentachlorophenol; yield 90%, m.p. 157–158° (recrystallized from a hot mixture of ether–ethanol, 8:2), greenish-yellow crystals.

Anal. Calcd. for $C_{24}H_{29}Cl_5O_2$ (526.74): C, 54.73; H, 5.55; Cl, 33.65. Found: C, 54.51; H, 5.57; Cl, 33.44.

4-(4-Phenylmercaptophenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene-1-one (IVd).—This compound was prepared in the same manner as IVb from 2,4,6-tri-*t*-butylphenol and *p*-hydroxydiphenyl thioether. The light greenish-colored oil obtained after evaporation of the filtrate crystallized after treatment with a little ethanol; yield 86%, m.p. 112–113°, yellowish crystals.

Anal. Calcd. for $C_{30}H_{38}O_2S$ (462.60): C, 77.89; H, 8.28; S, 6.91. Found: C, 77.85; H, 8.57; S, 7.10.

4-(4-Methoxy-phenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene-1-one (IVe).—This was prepared in the same manner as IVb from 2,4,6-tri-*t*-butylphenol and 4-methoxyphenol. The green-colored filtrate yielded a green oil (91%) which formed yellow crystals upon treatment with a little ethanol; m.p. 74–75°. It was recrystallized by dissolving in a little ether and addition of a little ethanol; m.p. 77–78° (slightly yellow crystals).

Anal. Calcd. for $C_{25}H_{36}O_3$ (384.54): C, 78.08; H, 9.44. Found: C, 78.31; H, 9.67.

4-(4-Benzyloxy-phenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene-1-one (IVf).—This substance was prepared as described above from 2,4,6-tri-*t*-butylphenol and hydroquinone monobenzoate; yield 87%, yellow needles, m.p. 132–133°. It was recrystallized by addition of ethanol to a warm ether solution.

Anal. Calcd. for $C_{31}H_{38}O_4$ (474.61): C, 78.45; H, 8.07. Found: C, 78.25; H, 8.08.

4-(4-Benzyloxy-phenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene-1-one (IVg).—This substance was prepared as described above from 2,4,6-tri-*t*-butylphenol and hydroquinone monobenzyl ether. The slightly greenish filtrate left an oil after evaporation of the solvent at room temperature under vacuum. Addition of a little ethanol caused rapid crystallization; yield 71%, slightly yellowish crystals. It was recrystallized by dissolving in warm ether and adding ethanol; m.p. 104–105°.

Anal. Calcd. for $C_{31}H_{40}O_3$ (460.63): C, 80.83; H, 8.75. Found: C, 80.89; H, 8.96.

4-(4-Phenoxy-phenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene-1-one. (IVh).—2,4,6-Tri-*t*-butylphenol (1.31 g., 5 mmoles) was added to a suspension of 13 g. of active manganese dioxide in 125

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[7] R. Reed, Jr., *J. Am. Chem. Soc.*, **80**, 219 (1958).

[8] The active manganese dioxide is slightly alkaline.

[9] C. Martius and H. Eilingsfeld, *Ann. Chem.*, **607**, 159 (1957).

[10] E. Müller, A. Rieker, and W. Beckert, *Zeit Naturforsch.*, **17b**, 567 (1962).

[11] Melting points were taken on a Fisher-Johns apparatus and are not corrected.

[12] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. N. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

[13] Analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

ml. of benzene, and 930 mg. of *p*-phenoxyphenol (5 mmoles) was added in four portions as described above. Filtration and evaporation of the yellow solution gave IVh as a yellow oil, yield 1.85 g. (82%).

Anal. Calcd. for $C_{30}H_{38}O_3$ C, 80.68; H, 8.59; mol. wt., 446.60. Found: C, 80.50; H, 8.71; mol. wt., 436 (thermoelectric measurement in dioxane).

4,4-Bis(pentachlorophenoxy)-2,6-di-*t*-butyl-2,5-cyclohexadiene-1-one (VII).—Active manganese dioxide (26 g.) was added to a solution of 2.66 g. of pentachlorophenol (10 mmoles) and 1.43 g. of 4-bromo-2,6-di-*t*-butylphenol in 300 ml. of benzene. The suspension was shaken under N_2 for 30 min. The MnO_2 was removed by filtration through a fine sintered-glass funnel and washed with 200 ml. of benzene. Evaporation of the light yellow filtrate gave a light yellow, crystalline residue which was washed with 150 ml. of absolute ethanol; yield 3.05 g. (83%), m.p. 155°. The substance was recrystallized by dissolving in cold chloroform. Addition of absolute ethanol gave fine, colorless needles of VII, m.p. 166–167° dec.

Anal. Calcd. for $C_{26}H_{20}Cl_{10}O_3$: C, 42.49; H, 2.72; Cl, 48.25; mol. wt., 734.80. Found: C, 42.24; H, 2.82; Cl, 48.38; mol. wt., 698 (thermoelectric measurement in chloroform).

Hydrolysis of VII.—A suspension of VII (500 mg.) in 25 ml. of 96% ethanol was refluxed for 45 min. The clear, yellow solution formed was evaporated *in vacuo*, yielding a semisolid yellow residue. Treatment with 5 ml. of cold petroleum ether (b.p. 30–60°) and filtration gave 305 mg. (84%) of pentachlorophenol, m.p. 189–190°. Mixture melting point with authentic material gave no depression. Evaporation of the filtrate gave a yellow oil that formed yellow crystals of 2,6-di-*t*-butylbenzoquinone; yield 110 mg. (73%), m.p. 67–68° (lit.[14] m.p. 67–68°). The infrared spectrum was identical with that of authentic material.

Oxidation of 4-bromo-2,6-di-*t*-butylphenol.—A solution of 2.85 g. of 4-bromo-2,6-di-*t*-butylphenol (10 mmoles) in 175 ml. of benzene was shaken with 20 g. of active manganese dioxide for 35 min. The manganese dioxide was removed by filtration and washed with 50 ml. of benzene. Evaporation of the dark brown filtrate gave a solid, brown residue that was treated with 20 ml. of methanol, filtered, and dried at 105°. The yield of 3,3′,5,5′-tetra-*t*-butyldiphenoquinone was 1.9 g. (92%). The substance formed red-brown crystals upon heating; m.p. 245–246° (lit.[15] m.p. 245–247°). Mixture melting point with authentic material gave no depression.

Oxidation of Pentachlorophenol.—A solution of 2.66 g. of pentachlorophenol (10 mmoles) in 175 ml. of benzene was shaken with 20 g. of active manganese dioxide for 35 min. The yellow filtrate obtained after removal of the manganese dioxide was evaporated at room temperature *in vacuo*, yielding a solid yellow residue that was washed with 20 ml. of ethanol. Filtration gave 1.5 g. of yellow crystals having m.p. 165–167°. The substance was dissolved in a little benzene, cold methanol was added, and the mixture was kept at −20° a few minutes. Then most of the solvent was rapidly removed *in vacuo*, yielding 1.2 g. (45%) of 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadiene-1-one, m.p. 177–178° (lit.[7] m.p. 177–178°). Its infrared spectrum was completely identical with that of authentic material.

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[14] E. Müller and K. Ley, *Chem. Ber.*, **88**, 601 (1955).

[15] H. Hart and F. A. Cassis, Jr., *J. Am. Chem. Soc.*, **73**, 3179 (1951).

Self-Condensation of Phthalide

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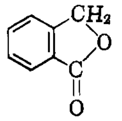
Phthalide (I) is known to react with aldehydes or esters in the presence of base to yield aldol condensation products or phthalidyl ketones.[1–3] It has now been observed that phthalide also can undergo a base-catalyzed self-condensation. The base-catalyzed self-condensation of the two isomers of phthalide, coumaranone (II) and isocoumaranone (III), had been reported earlier.[4,5]



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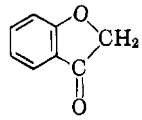
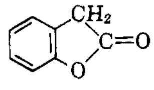
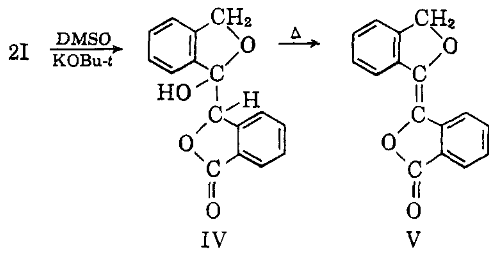


II



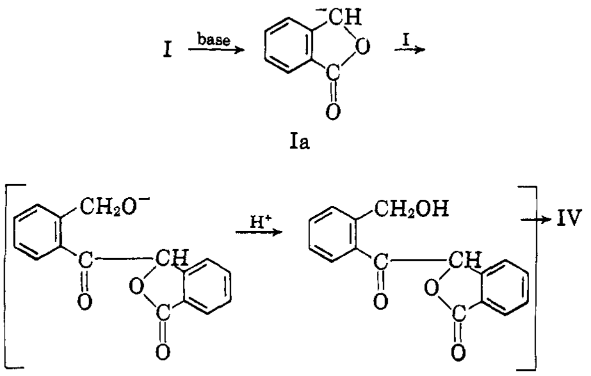
III

Treatment of phthalide in dimethyl sulfoxide with potassium *t*-butoxide at room temperature leads to a dimer (IV) that can be isolated in 75% yield. Upon being heating above its melting point, IV readily eliminates water to yield the stilbene V (phthalanylidenephthalide). This product is formed directly if the self-condensation of phthalide is carried out at 65°. On the



basis of its ultraviolet spectroscopical comparison with the known biphthalide the *trans* structure can be assigned to V (Fig. 1).

The mechanism of the formation of IV probably involves the phthalidyl carbanion (Ia) that undergoes an ester condensation which is followed by intramolecular acetalization.



When the base-catalyzed reaction of phthalide was extended to 3-alkoxy-substituted phthalides (phthalaldehydic acid pseudo esters) in dimethyl sulfoxide or dimethylformamide, the only crystalline product was a colorless substance that analyzed for $C_{16}H_8O_4$ (formed in 15% yield). The color produced by H_2SO_4–HNO_3, the solubility properties, and the melting point (335°)[6] were all in agreement with biphthalide (VI). However, biphthalide has been reported to form yellow crystals.[7] It has been assigned the *trans* structure when its syn-

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[1] R. L. Horton and K. C. Murdock, *J. Org. Chem.*, **25**, 938 (1960).

[2] H. Zimmer and R. D. Barry, *ibid.*, **27**, 1602 (1962).

[3] W. Wislicenus, *Ber.*, **20**, 2061 (1887).

[4] K. Fries and W. Pfaffendorf, *ibid.*, **44**, 114 (1911); see also W. Baker and R. Banks, *J. Chem. Soc.*, 279 (1939).

[5] J. N. Chatterjee, *J. Indian Chem. Soc.*, **33**, 175 (1956).

[6] See F. K. Beilstein, "Handbuch der organischen Chemie," 4th Ed., Vol. 19, p. 176; Suppl. I, p. 688; Suppl. II, p. 192.

[7] E. Ador, *Ann.*, **164**, 229 (1872); P. Karrer, *et al.*, *Helv. Chim. Acta*, **11**, 233 (1928); M. Pailer, H. Woerther, and A. Meller, *Monatsh.*, **92**, 1037 (1961).