

The Anodic Oxidation of Organic Compounds. IV. Mechanism of Electrochemical Methoxylation of N,N-Dimethylbenzylamine

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Received June 12, 1968

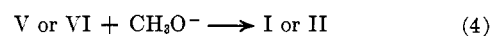
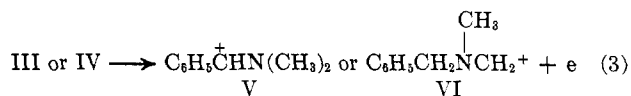
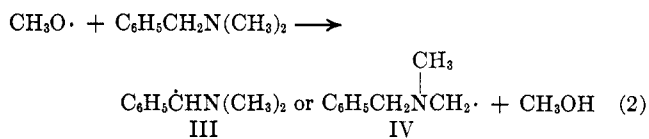
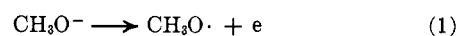
Evidence is presented that the anodic methoxylation of N,N-dimethylbenzylamine (DMB) in alkaline methanolic solution occurs by direct charge transfer of adsorbed DMB at the anode followed by the reaction of the resultant cation radical with solvent. A recent alternative proposal suggesting that electrochemically generated methoxy radicals attack DMB to give the cation radical is considered to be less tenable.

On the basis of the nature of the products formed, we proposed in a recent paper¹ that anodic methoxylation of amines probably occurs *via* discharge of adsorbed amine, followed by reaction of the resultant cation radical with solvent. The major products derived from the methoxylation of N,N-dimethylbenzylamine (DMB) at constant current in a one-compartment cell were α -methoxy-N,N-dimethylbenzylamine (I) and N-methoxymethyl-N-methylbenzylamine (II), obtained in a ratio of 1:4, respectively. The unexpected preponderance of N-methyl over N-benzyl substitution was attributed in part to the effect of adsorption of DMB on the anode prior to charge transfer. Subsequently we demonstrated² that the methoxylation and dimerization of the related amine, N,N-dimethylaniline, in methanolic KOH and NH₄NO₃ solution, respectively, occurred *via* a one-electron oxidation of the adsorbed amine. The subject of anodic oxidation of amines has been reviewed recently.³



Smith and Mann⁴ have reexamined the anodic methoxylation of DMB using both KOH and KOCH₃ electrolytes. Carrying out the reaction potentiostatically in two-compartment cells (anode and cathode compartments were separated by a fritted-glass diaphragm), they found that a 5–10% yield of methoxylation product was formed with KOCH₃ as electrolyte. In their hands, no methoxylated product was obtained with KOH electrolyte, but only N-methylbenzylamine and DMB, despite the use of 3–5 faradays/mol.⁵ Studying current-voltage curves they found that addition of amine to a 1 M KOCH₃–CH₃OH solution failed to produce an increase in current. On the basis of these and other observations the following conclusions were made: (i) methoxide ion is necessary for methoxylation of DMB; (ii) since the limiting current for methoxide ion discharge had apparently not been exceeded the current efficiency for the amine reaction would accordingly be very low; (iii) the initial step in anodic methoxylation of aliphatic amines involves, not anodic oxidation of amine, but discharge of

methoxide to methoxy radical according to eq 1–4 below.



Believing that the mechanism of methoxylation of DMB could be similar to that established for N,N-dimethylaniline,² we have again examined the electro-oxidation of DMB both potentiostatically and galvanostatically in both one- and two-compartment electrolysis cells.

Results and Discussion

Tafel plots (log current density against potential) for anodic oxidation of DMB in 0.5 M KOH–CH₃OH are shown in Figure 1. In the linear region (slope, 255 mV/decade) an increase in the concentration of DMB lowers the current density markedly from that of background (slope, 300 mV/decade). At more positive potentials the curves merge and become indistinguishable from background. The reaction order plots (log current density against log concentration of amine) shown in Figure 2 suggest that the electrochemical process occurring below 1.1 V is increasingly inhibited, with a limiting current being reached as the DMB concentration is increased.

While the above results provide qualitative information concerning amine adsorption, no conclusions may be drawn about a suitable mechanism of oxidation of DMB. A more direct approach to the mechanism may be taken by examination of the products formed in a series of electrolyses carried out under controlled potential conditions. The method is an extension of the technique applied by Parker and Burgert⁶ to establish a mechanism for anodic cyanation of aromatic compounds.

The results of electrolysis of DMB in 0.5 M KOH–CH₃OH are summarized in Table I. No amine methoxylation products are observed below 1.00 V *vs.* sce (expt 1 and 2). Under the same conditions, but at potentials more anodic than 1.10 V (expt 3 and 4), amine-derived products are formed. The same prod-

(1) N. L. Weinberg and E. A. Brown, *J. Org. Chem.*, **31**, 4058 (1966).(2) N. L. Weinberg and T. B. Reddy, *J. Amer. Chem. Soc.*, **90**, 91 (1968).(3) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).(4) P. J. Smith and C. K. Mann, *J. Org. Chem.*, **33**, 316 (1968).

(5) The formation of dealkylation product rather than ethers with KOH is believed to be caused by hydrolysis of I and II, due, at least in part, to inadequate drying of the crude product. Smith and Mann used a 3-A Molecular Sieve, while we have employed anhydrous magnesium sulfate as the desiccant.

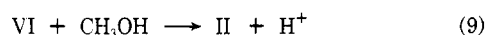
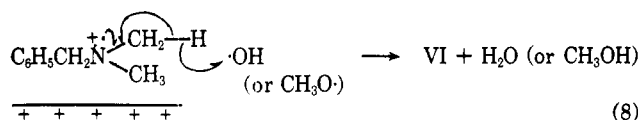
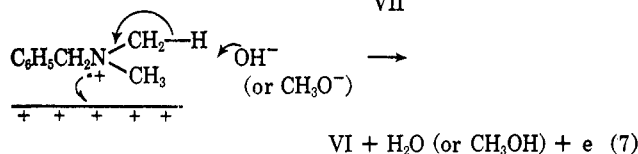
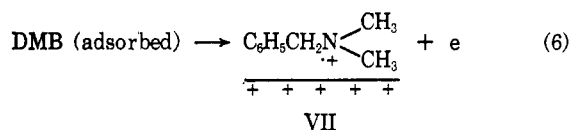
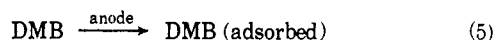
(6) V. D. Parker and B. E. Burgert, *Tetrahedron Lett.*, 4065 (1965).

TABLE I
 PRODUCT DISTRIBUTION IN ELECTROLYSIS OF DMB^a

Expt	DMB concn, mol l. ⁻¹	Anode potential, V vs. sce	Faradays mol ⁻¹ of DMB	Area per cent of components ^e									
				1 ^d	DMB	I	II	5	6	7	8	9	
1 ^b	0.20	0.90	0.516		100								
2 ^b	0.20	1.00	0.516		100								
3 ^b	0.20	1.10	0.516	3.2	78.3	0.3	14.0	0.2	0.2	0.1	0.1	3.7	
4 ^b	0.20	1.20	0.516	2.2	84.0	1.0	9.4	1.0	1.0	0.1	0.1	1.2	
5 ^c	0.20	1.30	0.516		>99			+		+			
6 ^{b,f}	1.00	1.30	1.55		35.8	0.8	41.0	0.7	2.6	2.7	0.6	15.8	
7 ^c	0.10	1.40	2.00	9.7	50.2		26.8	1.1	2.2	0.2	1.0	8.8	
8 ^b	0.50	1.85	2.00	6.5	22.0		42.2	3.4	8.6	1.7	3.1	12.5	
9 ^c	0.50	1.9-2.3 ^g	3.00	4.9	12.1	0.7	48.5	2.3	18.0	1.8	1.2	8.3	
10 ^b	0.40	2.1-2.4 ^h	0.50	1.0	88.7	+	6.3	+	+	+	+	4.0	

^a Electrolyses carried out in 0.5 M KOH-CH₃OH at 12° using Pt (10 cm²) electrodes, except for expt 10, where a pyrolytic carbon button (0.39 cm², geometrical area) replaced the Pt anode. ^b Two-compartment cell. ^c One-compartment cell. ^d Shown by retention time to be benzaldehyde. Components 5, 6, 7, and 8 are unknown. ^e Determined by gas chromatography on 0.2% SE-30 on glass beads; see Experimental Section for further detail; + value implies trace. ^f Five additional components were observed. A small amount (0.4 g) of II added to the cathode compartment was converted almost entirely into DMB. ^g Constant-current electrolysis at 1.0 A. ^h Constant-current electrolysis at 37.5 mA.

ucts are produced at both Pt and C anodes (expt 10) indicating that platinum oxides are not involved in the oxidation of DMB.⁷ These experiments, taken together with the further observation that the half-wave potential of DMB (at a rotating platinum microelectrode in 0.5 M LiClO₄-CH₃CN) is 0.92 V vs. sce, present strong evidence that DMB is oxidized by the discharged amine mechanism (eq 5-7 and 9). Since solvent discharge occurs simultaneously, the possibility of radical abstraction of DMB cation radical (VII) cannot be ignored (eq 8).



Figures 1 and 2 may be rationalized in terms of these results: below 1.1 V specific adsorption of electroinactive DMB, which is highest at less positive potentials, decreases the rate of discharge of solvent (or electrolyte) by blocking electrode sites. As the anode potential is increased the curves converge possibly owing to preferential adsorption of hydroxide ions. The effect of specifically adsorbed, uncharged, electroinactive substances on electrochemical kinetics has been reviewed by Delahay.⁸

The inflection (0.9-1.1 V) in the curves of Figure 1 could be interpreted as suggesting a change in mech-

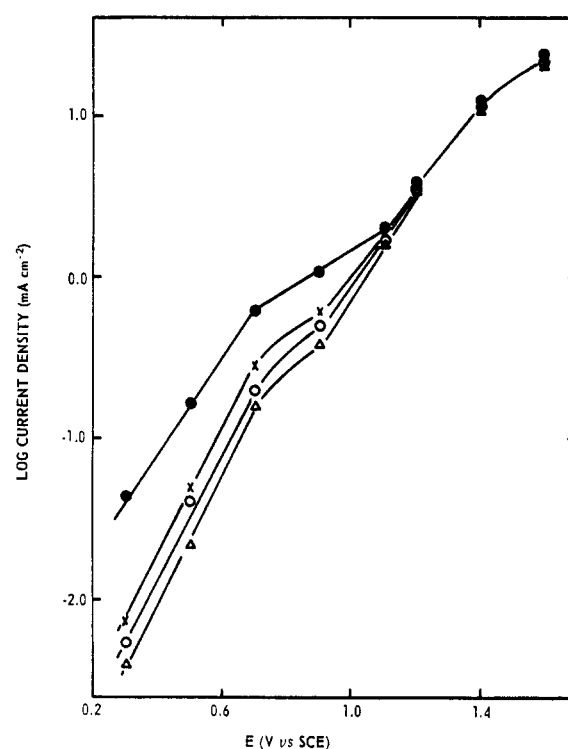


Figure 1.—Tafel plots of oxidation of DMB in 0.5 M KOH-CH₃OH at 12°. Concentration of DMB: ●, 0.00 M; ×, 0.00244 M; ○, 0.00476 M; △, 0.0130 M.

anism for solvent oxidation favoring the radical-abstraction route (eq 1-4). Thus it could be argued that only above the potential of the inflection are methoxy radicals (or hydroxy radicals) formed. However, the inflection begins at about 0.9 V which is well removed from the transition potential for forming amine products. Indeed Bagotzkii and coworkers⁹⁻¹² have studied the adsorption and electrochemical kinetics of methanol oxidation on Pt in aqueous solutions and have found that there is no change of mechanism of solvent oxidation with potential. Their experimental

(9) V. S. Bagotzkii and Y. B. Vasilyev, *Electrochim. Acta*, **12**, 1323 (1967).

(10) O. A. Khazova, Y. B. Vasilyev, and V. S. Bagotzkii, *Elektrokhimiya*, **2**, 267 (1966).

(11) S. S. Beskorovainaya, O. A. Khazova, Y. B. Vasilyev, and V. S. Bagotzkii, *ibid.*, **2**, 932 (1966).

(12) V. S. Bagotzkii and Y. B. Vasilyev, *Electrochim. Acta*, **11**, 1439 (1966).

(7) There is considerable evidence which implicates platinum oxides (formed electrochemically on the anode surface) in certain oxidations.²

(8) P. Delahay, "Double Layer and Electrode Kinetics," Interscience Publishers, New York, N. Y., 1965, pp 228-233.

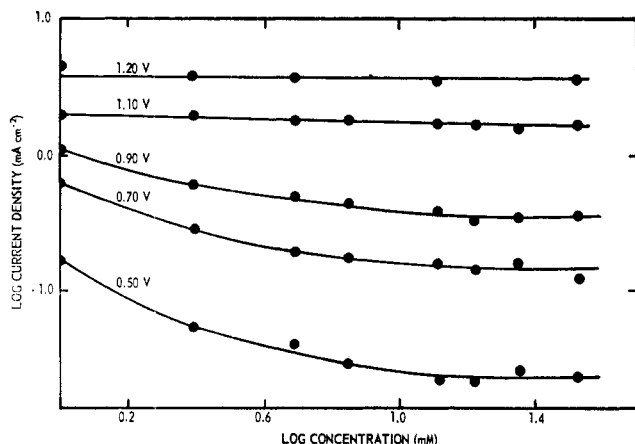
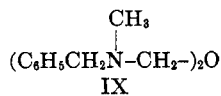
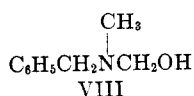


Figure 2.—Log-log plots of current density against concentration of DMB at constant potentials from 0.50 to 1.20 V vs. sce, in 0.5 M KOH-CH₃OH at 12°.

results have been explained by considering that dissociatively chemisorbed alcohol residues are chemically oxidized by adsorbed hydroxy radicals (formed as the result of discharge of hydroxide ions in alkaline solutions) in the slow step of the process.

Again in favor of the radical-abstraction route, it could be argued that the above results may be explained in terms of current density. (For example, the Kolbe reaction is known to require high current densities for successful coupling of alkyl radicals).¹³ Thus at low current density (low anode potential) methoxy (or hydroxy) radicals would preferentially react with solvent rather than DMB, while at high current density (more positive anode potential) DMB would be attacked. Adsorbed amine, however, would be expected to be attacked by electrochemically generated radicals in the low current density region where coverage by DMB is greatest. A current density argument is thus in disagreement with the experimental results of Figures 1 and 2 and Table I.

The major products found in the electrolysis of DMB (Table I, in order of increasing retention time) are benzaldehyde, the ethers I and II, and an unisolated compound, peak 9, believed to be N-hydroxymethyl-N-methylbenzylamine (VIII) or the ether IX. Gas chromatographic analysis of a mixture of formaldehyde (excess) and N-methylbenzylamine showed only one high-boiling component with a retention time corresponding to peak 9. Only II could be isolated by distillation. Contrary to the observations of Smith and Mann, the yield and current efficiency for formation of amine-derived product using KOH as electrolyte is quite good. The current efficiencies for formation of the major compounds in expt 3 are estimated as follows: benzaldehyde, 15.5%; I and II, 45.7%; VIII, 12.4%.



Significantly at 1.30 V in a one-compartment cell only traces of amine-derived product are formed (expt 5). It is believed that cathodic reduction of the

products I, II, and VIII (or IX) to DMB occurs almost as rapidly as these are formed. Support for this conclusion was derived from expt 6 carried out at 1.30 V using a two-compartment cell. Addition of compound II to the cathode solution provided almost pure DMB after work-up. On forcing the reaction to occur by passage of larger amounts of current (expt 7 and 9; see also ref 1) at higher potentials, amine-derived products may be formed in a one-compartment cell in good yield.

The above procedure should be helpful in establishing the mechanism(s) of oxidation in a number of other cases where voltammetric data is inconclusive, namely, the alkoxylation of olefins,¹⁴⁻¹⁶ of aromatic compounds,¹⁷⁻²¹ and of amides.²²

Experimental Section

The electronic equipment used for controlled potential electrolyses has been described previously.² The constant-current electrolysis (Table I, expt 9) was carried out with a Harrison Laboratories Model 881 A (± 100 V, ± 1.2 A) dc power supply. Two types of glass electrolysis cells were used which allowed positioning of an aqueous saturated calomel reference (sce) close to but isolated from the anode by a small external frit separated compartment. The cells were either one-compartment (anode and cathode in the same compartment) or two-compartment cells, provided with smooth platinum electrodes (each 10 cm²), nitrogen gas bubbler, thermometer, and magnetic stirring bar. Polarization curves and reaction order data were obtained with the one-compartment cell.

Gas chromatographic analyses were conducted with an F & M Model 5750 research gas chromatograph using stainless steel columns (10 ft \times 0.25 in.) packed with 0.2% SE-30 on glass beads (mesh size 60-80). Infrared spectra were determined with a Perkin-Elmer Model 137 spectrophotometer.

Electrolysis of DMB. A.—The following is a typical description of the electrolysis and work-up procedure (Table I, expt 3). Into the anode compartment of a two-compartment cell was introduced 100 ml of 0.5 M KOH in distilled reagent grade methanol. An equal height of the same solution was added to the cathode and reference compartments. Freshly distilled DMB (2.70 g, 0.020 mol) was added to the anode solution and electrolysis was carried out potentiostatically at 1.10 V vs. sce. The cell was externally cooled at 12°. After 0.516 faradays/mol had been passed, the anode solution was concentrated at reduced pressure (10-20 mm) and 30-35° until most of the solvent had been removed. The residue was taken up in 100 ml of water and extracted with three 75-ml portions of diethyl ether; the combined organic extracts were dried over anhydrous magnesium sulfate. Filtration and reconcentration at reduced pressure below 35° provided 2.65 g of an almost colorless oil. The product distribution for this residue is shown in Table I.

B.—The crude product of expt 9, worked up in a similar manner, was distilled, and a heart-cut of a fraction with bp 40-46° (0.3-0.4 mm) was obtained. According to gas chromatographic analysis, the fraction consisted of N-methoxymethyl-N-methylbenzylamine containing about 5% the compound corresponding to peak 9. The infrared spectrum (neat) of II had characteristic bands at 1605 (w), 1595 (w), 1500 (m), 1460 (s), 1390 (m), 1370 (s), 1175 (s), 1115 (m), 1105 (s), 1070 (s), 1015 (s),

(14) T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka, and S. Tsutsumi, *Tetrahedron Lett.*, 1409 (1963).

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(16) T. Inoue, K. Koyama, T. Matsuoka, and S. Tsutsumi, *ibid.*, **40**, 162 (1967).

(17) T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka, and S. Tsutsumi, *Kogyo Kagaku Zasshi*, **66**, 1659 (1963).

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(20) K. Sasaki, H. Urata, K. Uneyama, and S. Nagaura, *Electrochim. Acta*, **12**, 137 (1967).

(21) K. E. Kolb and C. L. Wilson, *Chem. Commun.*, 271 (1966).

(22) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Amer. Chem. Soc.*, **88**, 4657 (1966).

(13) A. K. Vijh and B. E. Conway, *Chem. Rev.*, **67**, 623 (1967).

930 (s), 870 (m), 743 (s), 702 (s) cm^{-1} . The nmr spectrum in CCl_4 was consistent with the structural assignment.²³

Anal. Calcd for $\text{C}_{10}\text{H}_{15}\text{NO}$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.53; H, 9.16; N, 8.51.

(23) The τ values for the ArCH_2 and NCH_2O groups were incorrectly reversed in the earlier work.¹

Registry No.—N,N-Dimethylbenzylamine, 103-83-3; II, 13657-14-2.

Acknowledgments.—The author wishes to thank A. K. Hoffmann and T. B. Reddy for valuable discussion.

Permanganate Oxidation of N-Aryl-2-naphthylamines

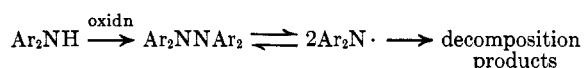
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Received June 17, 1968

The major crystalline products from permanganate oxidation of N-aryl-2-naphthylamines are 1,1'-coupling dimers. Structures were determined by instrumental methods and by degradation to known 7-aryldibenzo[*c,g*]carbazoles. Also formed are significant quantities of carbon-nitrogen coupling products, believed to be the *o*-semidines. 7-Aryldibenzo[*c,g*]carbazoles are formed in minor amounts. No evidence was found for stable symmetrical tetraarylhydrazines.

The oxidation of diarylamines to tetraarylhydrazines is well known from the classic work of Wieland and co-workers.⁵ Wieland's views on the reversibility of



diaryl-amino radical formation and on the nature of the decomposition products have been modified by more recent work. Neugebauer and Fischer⁶ have shown that no stable radicals are detected from tetraphenylhydrazine at temperatures as high as 90°. Diarylamino radicals were detected, however, when the benzene rings contained electron-supplying substituents. Contrary to Wieland's original results, the major decomposition product of tetraphenylhydrazine was shown not to be 5,10-diphenyl-5,10-dihydrophenazine.⁷ The hydrazine decomposes irreversibly at 90° with a half-life of about 10 min.⁸ Musso⁹ recently showed the major decomposition product to be an oligomer containing an average of five diphenyl-amino units, formed by nitrogen-carbon coupling.

These several facets of the oxidation of diphenylamine may be considered reasonably well established. In contrast, no aspect of the oxidation of secondary naphthylamines is well understood at this time. N-Arylnaphthylamino radicals have not been identified unambiguously, and there seems to be no agreement on the products of oxidation of secondary naphthylamines.

Wieland and Süsser¹⁰ showed that the permanganate oxidation of di-2-naphthylamine did not yield a hydrazine, and tentatively assigned to the crystalline product an *o*-semidine structure. An analogous structure was

assigned by Rehner and coworkers to a crystalline product of the permanganate oxidation of N-phenyl-2-naphthylamine.¹¹ Somewhat later, Lieber and Somasekhara¹² oxidized a series of dinaphthylamines with potassium permanganate. Completely disregarding the previous work of Wieland¹⁰ and Rehner,¹¹ and without any valid experimental evidence, they assigned symmetrical hydrazine structures to all crystalline products. The hydrazine structure has also been suggested for the oxidation product of N-phenyl-2-naphthylamine.¹³ The oxidation of N-phenyl-1-naphthylamine and di-1-naphthylamine with a variety of oxidizing agents produces *p*-semidine polymers,¹⁴ similar to those formed by decomposing tetraphenylhydrazine.⁹

The present work deals with the products resulting from permanganate oxidation of two N-aryl-2-naphthylamines.

Results and Discussion

The oxidation of N-phenyl-2-naphthylamine or di-2-naphthylamine by neutral potassium permanganate in acetone leads to the dehydrogenated 1,1' dimer as the major crystalline product. Structure proof is shown in Scheme I.

1,1'-Bis(N-phenyl-2-naphthylamine) (**2a**) was found by nmr and infrared spectroscopy to have one amino hydrogen per phenyl-2-naphthylamine residue, *i.e.*, two amino hydrogens per molecule. 1,1'-Bis(di-2-naphthylamine) (**2b**) was too sparingly soluble for accurate nmr integration of the amine hydrogen peak. However, its infrared spectrum indicated the presence of two N-H bonds per molecule. Both dimers gave diacetates (no N-H infrared absorption band and three acetate protons per amine residue). Each oxidative dimer was degraded in excellent yield to the corresponding 7-aryldibenzo[*c,g*]dibenzocarbazole (**3**), which was synthesized by standard methods.

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(5) (a) H. Wieland and S. Gambarjan, *Ber.*, **39**, 1499 (1906); (b) H. Wieland, *Ann.*, **381**, 200 (1911).

(6) F. A. Neugebauer and P. H. H. Fischer, *Chem. Ber.*, **98**, 844 (1965).

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(9) H. Musso, *Chem. Ber.*, **92**, 2881 (1959).

(10) H. Wieland and A. Süsser, *Ann.*, **392**, 169 (1912).

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(12) E. Lieber and S. Somasekhara, *J. Org. Chem.*, **24**, 1775 (1959).

(13) See P. Schneider, *Proc. Rubber Technol. Conf.*, **3rd**, London, 1954, 309 (1954), footnote 29.

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