those of *m*-nitrobenzaldehyde or *m*-nitroacetophenone (see Table III).[15]

X.—Compound X shows a well-defined maximum at 290 mμ, which we associate with the *p*-methoxybenzophenone or *p*-methoxyacetophenone chromophore. This B-band is displaced bathochromically as would be anticipated on introducing a *p*-methoxy substituent. Further, the band at 290 mμ (ϵ 32,500) has its analog in the spectrum of *p*-methoxybenzophenone which in ethanol shows a doublet band at 283 and 288 mμ (ϵ 16,000),[16] with about half the above extinction coefficient. (*p*-Methoxybenzophenone in ethanol also shows a second B-band at 249 mμ, ϵ 9000,[16] which has previously been referred to in this paper.) This again confirms the hypothesis of the molecule absorbing as two or more chromophoric entities and, as expected, the infrared carbonyl band of X (1664 cm.$^{-1}$) occurs at a lower frequency than that in compounds I (1675 cm.$^{-1}$) and IV (1669 cm.$^{-1}$).

The nitrobenzene B-band would be expected to be hypsochromically displaced and intensified since the $-COC_6H_4OCH_3$-*p* group may be regarded as a better electron-withdrawing substituent than the –COPh group (see general point (ii)). This is borne out by the data, since no nitrobenzene B-band is observed for compound X in the region 230 to 260 mμ, but a band now occurs at 229 mμ which may be associated with nitrobenzene absorption (*cf.* Table III for the nitrobenzene B-band of *m*-nitrobenzophenone).

Acknowledgments.—The authors are indebted to Miss Florence Jackman, Miss V. M. Walsh and to Rev. Bro. D. C. Clancy for the careful determination of the ultraviolet absorption data, and to Dr. Lester P. Kuhn for the infrared data. Thanks are also due to Dr. M. J. Kamlet for valuable discussions.

Financial assistance from the Research Corporation, the U. S. Public Health Service, National Cancer Institute (C-3325 C1), and the National Research Council of Canada is gratefully acknowledged.

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[15] If only one *o*-methyl substituent is present it is possible that the "normal" benzophenone absorption still contributes to the observed absorption band. For example, the inflection near 260 mμ for compound V may partly be associated with such benzophenone absorption. More precisely, in a substituted benzophenone up to four B-bands may contribute to the observed absorption spectrum.[16] Whenever two such B-bands are likely to occur at similar wave length, as for compound V where both the nitrobenzene B-band and the *p*-methylbenzoyl B-band would be expected to absorb near 260 mμ, any band *assignment is clearly tentative. In this connection it should* be noted that our previous assignment[1] which ascribed this band to the 2,4-dimethylbenzoyl moiety was perhaps too definite if only because it is extremely difficult to obtain the precise location of the maximal absorption for compound V. In fact, compound V affords only very indistinct maxima and numerous determinations were necessary before the present data were accepted. These data, incidentally, should now replace the earlier values.[1]

[16] Unpublished information.

[CONTRIBUTION FROM THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

Reaction of 4-Dimethylaminoazobenzene and Related Compounds with 4,4'-Bis-(dimethylamino)-benzhydrol[1]

BY KENICHI FUKUI, YOSHIAKI INAMOTO, HISAO KITANO AND CHIKAYOSHI NAGATA

RECEIVED APRIL 13, 1959

Reaction of 4,4'-bis-(dimethylamino)-benzhydrol (Michler's hydrol) with 4-dimethylaminoazobenzene, 2'-methyl-4-dimethylaminoazobenzene, 3'-methyl-4-dimethylaminoazobenzene and 4-methylaminoazobenzene catalyzed by sulfuric acid affords 4'-alkylated products in each case, *e.g.*, 4'-[4,4'-bis-(dimethylamino)-benzhydryl]-4-dimethylaminoazobenzene. Neither azobenzene nor 4'-methyl-4-dimethylaminoazobenzene is alkylated under similar conditions.

Investigation of chemical reactivities of carcinogenic compounds may contribute to the elucidation of mechanism of carcinogenesis by these compounds, since the first step in carcinogenesis is believed to be a chemical combination of these compounds with proteins.[2] It seems very interesting to study the Friedel–Crafts alkylation[3] of 4-dimethylaminoazobenzene (DAB) and related compounds, some of which are powerful carcinogens,[2] because electrophilic substitution of DAB other than nitration[4] and sulfonation[5] has not been reported.

Sulfuric acid was chosen as catalyst for these alkylation studies because it seemed a milder reagent than aluminum chloride which causes rearrangements[3] and fission of the azo linkage.[6] In addition, sulfuric acid serves as a solvent for the reaction. 4,4'-Bis-(dimethylamino)-benzhydrol (Michler's hydrol) was adopted as the alkylating agent for DAB because it was considered one of the highly reactive alcohols owing to the fact that nuclear alkylation of *p*-nitrosodimethylaniline can be effected by Michler's hydrol, while not by benzyl alcohol and benzhydrol[7] which are relatively active alkylating agents.[3]

Although Michler's hydrol has been utilized for the alkylation of various aromatic compounds, *e.g.*, amines,[8–10] phenols,[11] *m*-xylene,[12] aryl hal-

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[1] This work is supported financially by a grant-in-aid from the Ministry of Education, Japan.

[2] J. A. Miller and E. C. Miller, "Advances in Cancer Research," Academic Press, Inc., New York, N. Y., 1953, Vol. 1, p. 339.

[3] C. C. Price, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1946, Vol. 3, p. 1.

[4] E. Noelting, *Ber.*, **20**, 2992 (1887).

[5] R. Möhlau, *ibid.*, **17**, 1490 (1884).

[6] C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 660.

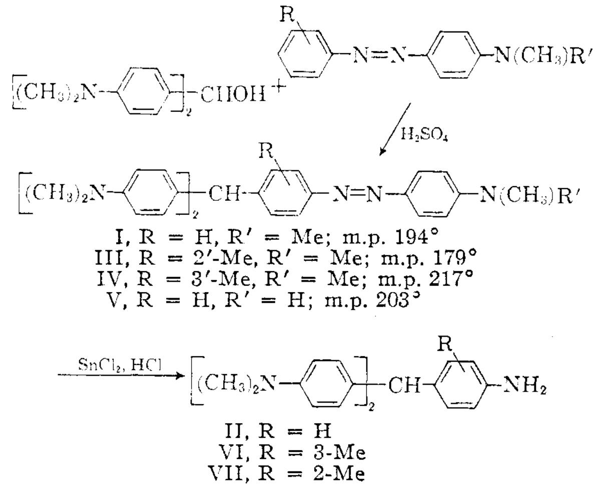
[7] R. Möhlau and V. Klopfer, *Ber.*, **32**, 2146 (1899).

[8] K. Venkataraman, "The Chemistry of Synthetic Dyes," Academic Press, Inc., New York, N. Y., 1952, Vol. 2, p. 718; E. Noelting, *Ber.*, **24**, 3126 (1891); F. Seel and L. Suchanek, *ibid.*, **83**, 438 (1950); E. F. Pratt and L. Q. Green, THIS JOURNAL, **75**, 275 (1953).

[9] F. Reitzenstein and O. Runge, *J. prakt. Chem.*, [2] **71**, 67 (1905).

ides,[13] quinones,[7] sulfonic acids,[14] etc., nuclear alkylation of azo compounds has been unsuccessful. Reaction of Michler's hydrol with aminoazobenzene and aminophenylazonaphthalene in ethanol resulted in formation of N-substituted leucoauramines[15] but not of nuclear-alkylated products. Although with *p*-hydroxyazobenzene and 1-phenylazo-4-hydroxynaphthalene nuclear substitutions by Michler's hydrol do occur in ethanol, this reaction is not an example of alkylation of azo compounds since *p*-hydroxyazo compounds undergo alkylation in *p*-quinonehydrazone form.[16]

Reaction of DAB with Michler's hydrol in 98% sulfuric acid at 40° for 10 hr. gives 4'-[4,4'-bis-(dimethylamino)-benzhydryl]-DAB (I). The solution of I in dil. hydrochloric acid is deep scarlet, and in glacial acetic acid I turns bluish-green on the addition of lead dioxide. Reductive fission of the azo linkage in I leads to 4-amino-4',4''-bis-(dimethylamino)-triphenylmethane (II). These observations suggest that in I the alkyl residue of Michler's hydrol is situated in the 4'-position of DAB. The structure of I was confirmed by comparison with an authentic specimen. Success in alkylation of DAB appears to be limited to Michler's hydrol. Other alcohols such as *n*-propyl, isopropyl and *t*-butyl alcohols as well as benzhydrol do not give nuclear-alkylated derivatives, but unchanged DAB is recovered. Benzyl and α-methylbenzyl alcohols cannot be used, because they polymerize vigorously on mixing with sulfuric acid.[17]



I, R = H, R' = Me; m.p. 194°
III, R = 2'-Me, R' = Me; m.p. 179°
IV, R = 3'-Me, R' = Me; m.p. 217°
V, R = H, R' = H; m.p. 203°

II, R = H
VI, R = 3-Me
VII, R = 2-Me

2'-, 3'- and 4'-methyl-DAB's, 4-methylaminoazobenzene (MAB) and azobenzene were treated with Michler's hydrol under the same conditions as above. 2'- and 3'-methyl-DAB's and MAB lead to the following compounds, respectively: 2'(III)- and 3'(IV)-methyl-4'-[4,4'-bis-(dimethylamino)-benzhydryl]-DAB's and 4'-[4,4'-bis-(dimethylamino)-benzhydryl]-MAB (V). Alkylation does not proceed with 4'-methyl-DAB and azobenzene, unchanged azo compounds and Michler's hydrol being recovered.

Discussion.—Benzhydrol and its derivatives are ionized in concd. sulfuric acid to stable carbonium ions.[18-21] Although the ionization is promoted by electron-releasing substituents,[21] electron-withdrawing groups do not appreciably suppress the ionization.[19] Reactivities of carbonium ions formed are, on the other hand, enhanced by the presence of electron-withdrawing groups.[20] In view of the possibility that Michler's hydrol may also be ionized to a carbonium ion with ammonium groups, as is suggested by the van't Hoff's *i*-factor of 4,4'-bis-(dimethylamino)-triphenylcarbinol,[19] the higher reactivity of Michler's hydrol over benzhydrol is conceivably due to strong activation by ammonium groups. Indeed Michler's hydrol is so reactive that DAB and its derivatives are readily alkylated in spite of deactivation of the latter compounds owing to salt formation in concd. sulfuric acid.[22]

Experimental[23]

Materials.—Benzhydrol (m.p. 69°), Michler's hydrol (m.p. 96°), azobenzene (m.p. 68°), DAB (m.p. 117°) and MAB (m.p. 88°)[24] were purified by repeated recrystallization. 2'-Methyl-DAB (m.p. 66°), 3'-methyl-DAB (m.p. 120°) and 4'-methyl-DAB (m.p. 171°) were prepared by coupling corresponding diazotized toluidines with dimethylaniline and recrystallization from benzene–ethanol.[24] Several authentic samples were also prepared. 3-Methyl-4-nitrobenzaldehyde (m.p. 64°) and 2-methyl-4-nitrobenzaldehyde (b.p. 158–160° (11 mm.), $n^{20}\text{D}$ 1.5468), utilized to synthesize 3-methyl-4-amino-4',4''-bis-(dimethylamino)-triphenylmethane (VI) and 2-methyl-4-amino-4',4''-bis-(dimethylamino)-triphenylmethane (VII), respectively, were prepared by Beech's method,[25] hydrolysis with hydrochloric acid of corresponding nitrotolualdoximes. The procedures, yields and properties of these authentic specimens are as follows:

4-Amino-4',4''-bis-(dimethylamino)-triphenylmethane (II).—A mixture of 7.5 g. (0.05 mole) of *p*-nitrobenzaldehyde, 18 g. (0.15 mole) of dimethylaniline and 6.8 g. (0.05 mole) of zinc chloride was heated with stirring on a water-bath for 4 hr. Boiling water was poured into the reaction mixture with stirring to dissolve the reaction mass, and the mixture was cooled. The precipitate was filtered off, washed with water and then with cold methanol until brown coloration in filtrate disappeared, and dried to yield 19 g. (almost quantitative) of crude 4-nitro-4',4''-bis-(dimethylamino)-triphenylmethane. After two recrystallizations from benzene–ethanol, yellow needles melted at 177° (lit.[26] 176–177°).

To a solution of 19 g. (0.05 mole) of 4-nitro-4',4''-bis-(dimethylamino)-triphenylmethane in 80 ml. of concd. hydrochloric acid (d. 1.18) and 40 ml. of water was added

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(13) Meister Lucius & Brüning, German Patent 111,506 (May 18, 1899).

(14) Meister Lucius & Brüning, German Patents 108,129 (October 8, 1898), 110,086 (October 14, 1898); A. Leonhardt & Co., German Patent 128,086 (January 15, 1901).

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(21) B. S. Stewart and H. A. Smith, *ibid.*, **79**, 5457 (1957).

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(23) All melting points are uncorrected.

(24) J. A. Miller and E. C. Miller, *J. Exptl. Med.*, **87**, 139 (1948); K. Fukui, Y. Inamoto, H. Kitano and C. Nagata, *J. Chem. Soc. Japan, Pure Chem. Section*, **79**, 1215 (1958).

(25) W. F. Beech, *J. Chem. Soc.*, 1297 (1954).

(26) O. Fischer, *Ber.*, **14**, 2520 (1881).

gradually 20 g. (0.31 mole) of zinc dust, and, after reaction had subsided, the mixture was refluxed for 1 hr. The reaction mixture was made alkaline by adding 10% sodium hydroxide solution, and the resulting precipitate was filtered, washed with water and dried. The material was dissolved in hot benzene, and the solution was filtered. After removal of the solvent from the filtrate, 14 g. (81%) of crude 4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (II) was obtained. Crude product was recrystallized from benzene–ethanol to yield colorless plates, m.p. 152° (lit.[26] 151–152°).

3-Methyl-4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (VI). A.—A mixture of 5.4 g. (0.02 mole) of Michler's hydrol, 2.5 g. (0.023 mole) of *o*-toluidine, 5 ml. of concd. hydrochloric acid and 25 ml. of water was refluxed for 4 hr. The reaction mixture was made alkaline by adding 10% sodium hydroxide solution. The resulting precipitate was collected by filtration, washed with water and dried. Crude 3-methyl-4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (VI) weighed 5.7 g. (79%). Recrystallization from benzene–ethanol yielded colorless plates, m.p. 184° (lit.[10,27] 184°).

Anal. Calcd. for $C_{24}H_{29}N_3$: C, 80.18; H, 8.13; N, 11.69. Found: C, 80.39; H, 8.14; N, 11.75.

B.—A mixture of 8.3 g. (0.05 mole) of 3-methyl-4-nitrobenzaldehyde, 18 g. (0.15 mole) of dimethylaniline and 6.8 g. (0.05 mole) of zinc chloride was treated analogously as in the case of the preparation of 4-nitro-4′,4′′-bis-(dimethylamino)-triphenylmethane to yield 12.5 g. (64%) of 3-methyl-4-nitro-4′,4′′-bis-(dimethylamino)-triphenylmethane (m.p. 172°). Reduction of this compound gave 3-methyl-4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (VI) (m.p. 184°) in 69% yield, which was identical with the sample prepared by the method A.

2-Methyl-4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (VII). A.—A mixture of 5.4 g. (0.02 mole) of Michler's hydrol, 2.4 g. (0.022 mole) of *m*-toluidine, 4 ml. of concd. hydrochloric acid and 25 ml. of water was treated similarly as above. Crude 2-methyl-4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (VII) weighed 5.5 g. (77%). Recrystallization from benzene–ethanol yielded colorless plates, m.p. 154° (lit. [27,28] 153–154°).

Anal. Calcd. for $C_{24}H_{29}N_3$: C, 80.18; H, 8.13; N, 11.69. Found: C, 80.26; H, 8.18; N, 11.60.

B.—By the same procedures as above, 8.3 g. (0.05 mole) of 2-methyl-4-nitrobenzaldehyde yielded 10.7 g. (55%) of 2-methyl-4-nitro-4′,4′′-bis-(dimethylamino)-triphenylmethane (m.p. 213°). Reduction of this compound gave 2-methyl-4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (VII) (m.p. 154°) in 73% yield, which was identical with the sample prepared by the method A.

4′-[4,4′-Bis-(dimethylamino)-benzhydryl]-DAB (I).—A mixture of 3.5 g. (0.01 mole) of 4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (II), 5 ml. of concd. hydrochloric acid and 40 ml. of ice-water was diazotized with 0.8 g. (0.011 mole) of sodium nitrite in 10 ml. of water. Resulting diazonium salt solution was treated with 1.2 g. (0.01 mole) of dimethylaniline and sodium acetate solution. The precipitate was filtered off, washed with water and dried to yield 4.1 g. (85%) of crude 4′-[4,4′-bis-(dimethylamino)-benzhydryl]-DAB (I). After recrystallization from benzene and benzene–ethanol, orange-yellow needles melting at 194° were obtained.

Anal. Calcd. for $C_{31}H_{35}N_5$: C, 77.95; H, 7.39; H, 14.66. Found: C, 78.10; H, 7.39; N, 14.54.

2′-Methyl- and 3′-Methyl-4′-[4,4′-bis-(dimethylamino)-benzhydryl]-DAB (III and IV).—3-Methyl- and 2-methyl-4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (VI and VII) (3.6 g., 0.01 mole) were diazotized and coupled with dimethylaniline, respectively. Crude 2′-methyl-4′-[4,4′-bis-(dimethylamino)-benzhydryl]-DAB (III) weighed 3.6 g. (73%). After recrystallization from benzene–ethanol, red needles melted at 179°.

Anal. Calcd. for $C_{32}H_{37}N_5$: C, 78.17; H, 7.59; N, 14.25. Found: C, 78.67; H, 7.55; N, 14.15.

Crude 3′-methyl-4′-[4,4′-bis-(dimethylamino)-benzhydryl]-DAB (IV) weighed 4.3 g. (87%). After recrystallization from benzene–ethanol, brownish-yellow needles melted at 217°.

Anal. Calcd. for $C_{32}H_{37}N_5$: C, 78.17; H, 7.59; N, 14.25. Found: C, 78.54; H, 7.62; N, 14.33.

4′-[4,4′-Bis-(dimethylamino)-benzhydryl]-MAB (V).—A mixture of 6.9 g. (0.02 mole) of 4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (II), 10 ml. of concd. hydrochloric acid and 60 ml. of ice-water was treated with 1.5 g. (0.022 mole) of sodium nitrite in 15 ml. of water. The resulting diazonium salt solution was admixed with 2.1 g. (0.02 mole) of N-methylaniline and sodium acetate solution. The precipitate was filtered off, washed with water and dried. The dried powder was mixed with 4.2 g. (0.03 mole) of N-methylaniline hydrochloride and 21 g. (0.2 mole) of N-methylaniline, and heated at 40° for 2 hr. and then at 60° for 3 hr. with stirring. The reaction mixture was made alkaline by adding 10% sodium hydroxide solution, and distilled with steam. The residual solid was collected by filtration and dried. Crude 4′-[4,4′-bis-(dimethylamino)-benzhydryl]-MAB (V) weighed 6.0 g. (65%). After recrystallization from benzene–ethanol, orange needles melted at 203°.

Anal. Calcd. for $C_{30}H_{33}N_5$: C, 77.72; H, 7.18; N, 15.11. Found: C, 77.58; H, 7.08; N, 15.21.

Reaction of DAB with Michler's Hydrol.—A solution of 4.5 g. (0.02 mole) of DAB and 5.4 g. (0.02 mole) of Michler's hydrol in 100 ml. of 98% sulfuric acid was stirred at 40° for 10 hr. The reaction mixture was poured onto cracked ice with stirring, and made alkaline with cold 10% sodium hydroxide solution, during which the temperature of the mixture was maintained below 10°. After standing in an ice-bath for 1 hr., the precipitate was collected by filtration, washed with water and dried. The crude product was recrystallized once from benzene and then twice from benzene–ethanol to give 6.4 g. (67%) of 4′-[4,4′-bis-(dimethylamino)-benzhydryl]-DAB (I), orange yellow needles, m.p. 194°, undepressed by admixture with the authentic specimen prepared above.

Anal. Calcd. for $C_{31}H_{35}N_5$: C, 77.95; H, 7.39; N, 14.66. Found: C, 78.05; H, 7.28; N, 14.71.

Reductive Fission of 4′-[4,4′-Bis-(dimethylamino)-benzhydryl]-DAB(I).—To a solution of 10 g. (0.044 mole) of stannous chloride ($SnCl_2 \cdot 2H_2O$) in 50 ml. of concd. hydrochloric acid was added 4.8 g. (0.01 mole) of 4′-[4,4′-bis-(dimethylamino)-benzhydryl]-DAB (I) in small portions. The mixture was heated on a water-bath for 0.5 hr. The resulting solution was made strongly alkaline by adding 10% sodium hydroxide solution, and then distilled with steam. The residual solid was collected by filtration, dried and dissolved in hot benzene, and the benzene solution was filtered. After removal of benzene from the filtrate, 3.3 g. (95%) of crude 4-amino-4′,4′′-bis-(dimethylamino)-triphenylmethane (II) was obtained. Three recrystallizations from benzene–ethanol yielded colorless plates, m.p. and mixed m.p. 152°.

Attempted Alkylation of DAB with Some Alcohols.—A solution of 0.5 g. (0.002 mole) of DAB and 0.002 mole of an alcohol in 10 ml. of 98% sulfuric acid was maintained at 40° for 10 hr. The reaction mixture was treated by the same procedure as that described for the reaction with Michler's hydrol. On the reactions with *n*-propyl alcohol, isopropyl alcohol, *t*-butyl alcohol and benzhydrol, yellow material was obtained in each case, which, after recrystallization from benzene, gave unchanged DAB. Recovery of purified DAB was: 0.40 g. (80%) for the reaction with *n*-propyl alcohol; 0.45 g. (90%) with isopropyl alcohol; 0.40 g. (80%) with *t*-butyl alcohol; 0.40 g. (80%) with benzhydrol.

Reaction of 2′-Methyl-DAB, 3′-Methyl-DAB and MAB with Michler's Hydrol.—A mixture of 0.02 mole of an azo compound, 5.4 g. (0.02 mole) of Michler's hydrol and 100 ml. of 98% sulfuric acid was treated in the same way as in the case of DAB. The procedure of reductive fission was also the same.

2′-Methyl-DAB yielded 7.4 g. (75%) of 2′-methyl-4′-[4,4′-bis-(dimethylamino)-benzhydryl]-DAB (III), red needles, m.p. 179°, undepressed by admixture with the authentic specimen.

Anal. Calcd. for $C_{32}H_{37}N_5$: C, 78.17; H, 7.59; N, 14.25. Found: C, 78.56; H, 7.50; N, 14.18.

Reductive fission of III gave 3.3 g. (92%) of 3-methyl-4-amino-4′,4″-bis-(dimethylamino)-triphenylmethane (VI),

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(27) Reitzenstein and Runge[9] reported melting points 141–143° for VI and 224–225° for VII. Their substances with these melting points, however, cannot be VI and VII, respectively.

(28) Beilstein's "Handbuch der organischen Chemie," Vol. 13, 1930, p. 319.

colorless plates, m.p. 184°, identified by a mixed melting point.

3-Methyl-DAB yielded 7.2 g. (71%) of 3′-methyl-4′-[4,4′-bis-(dimethylamino)-benzhydryl]-DAB (IV), brownish-yellow needles, m.p. and mixed m.p. 217°.

Anal. Calcd. for $C_{32}H_{37}N_5$: C, 78.17; H, 7.59; N, 14.25. Found: C, 78.20; H, 7.61; N, 14.30.

Reductive fission of IV gave 3.2 g. (89%) of 2-methyl-4-amino-4′,4″-bis-(dimethylamino)-triphenylmethane (VII) colorless plates, m.p. 154°, identified by a mixed melting point.

MAB yielded 6.5 g. (70%) of 4′-[4,4′-bis-(dimethylamino)-benzhydryl]-MAB (V), orange needles, m.p. 203°, undepressed by admixture with the authentic specimen.

Anal. Calcd. for $C_{30}H_{33}N_5$: C, 77.72; H, 7.18; N, 15.11. Found: C, 77.78; H, 7.19; N, 15.21.

Reductive fission of V gave 3.2 g. (93%) of 4-amino-4′,4″-bis-(dimethylamino)-triphenylmethane (II), colorless plates, m.p. and mixed m.p. 152°.

Attempted Alkylation of Azobenzene and 4′-Methyl-DAB with Michler's Hydrol.—Reaction was carried out with 0.002 mole of an azo compound, 0.5 g. (0.002 mole) of Michler's hydrol and 10 ml. of 98% sulfuric acid at 40° for 10 hr.

In the case of azobenzene, the mixture was poured onto cracked ice. The yellow solid precipitated immediately. This material was filtered off, washed with water and dried. After three recrystallizations from benzene–light petroleum (b.p. 75–120°), 0.3 g. (75%) of azobenzene was recovered. On the other hand, the aqueous filtrate was neutralized and extracted with ether. By removal of ether from the extract, crude Michler's hydrol was recovered almost quantitatively.

In the case of 4′-methyl-DAB, the mixture was poured onto cracked ice. The resulting deep red mixture was neutralized to give yellow precipitate. This material was filtered off, washed with cold methanol and recrystallized from benzene. Recovered 4′-methyl-DAB weighed 0.4 g. (80%). The methanol washings were evaporated to dryness, and the residue was dissolved in 50% ethanol. The solution was decolorized with Norit S.X. 30 and concentrated under reduced pressure to give crude Michler's hydrol (0.4 g., 80%).

KYOTO, JAPAN

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, NITRO RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

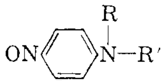
Nitrosoanilines

BY JOHN J. D'AMICO, CHING CHEN TUNG AND LLOYD A. WALKER

RECEIVED MARCH 14, 1959

A variety of N- and *p*-nitroso-anilines were prepared by standard methods. Nitrosation of 3-anilinopropionitrile, β-anilinopropionic acid or ethyl β-anilinopropionate with sodium nitrite and methanolic hydrogen chloride was accompanied by alcoholysis, esterification or transesterification, yielding methyl β-(*p*-nitrosoanilino)-propionate (XLIII). The *para* rearrangement of the nitroso group in esters like XII and XIII catalyzed by hydrochloric acid–acetic acid took place with concurrent hydrolysis of the ester function; the corresponding nitrile XVIII was not hydrolyzed under the rearrangement conditions. Oxidation of the *p*-nitroso group in XLIII with dilute nitric acid occurred with simultaneous nitration to methyl β-(2,4-dinitroanilino)-propionate (XLVIII).

The discovery that Butyl rubber modified with N-methyl-N,4-dinitrosoaniline[1] gives a Butyl vulcanizate with improved low-temperature and resilience properties, increased 300% modulus, decreased hardness, increased electrical resistivity and better processing characteristics,[2] has made it desirable to prepare new structurally related nitroso compounds. Although a number of nitroso compounds have been prepared possessing the general formula where X = hydrogen, R =



alkyl or phenyl and R′ = hydrogen, alkyl or nitroso, a limited number of examples were found containing other substituents. The purpose of this investigation was to vary the R, R′ and X radicals and to determine whether these structural modifications enhanced the properties of the Butyl vulcanizate. The detailed evaluation data for these new compounds will be reported in forthcoming patents.

In the preparation of the nitroso-anilines some of the intermediates were not readily available. This necessitated their synthesis by the following known general methods: Employing the elegant procedure described by Moon,[3] 2,5-dichlorobenzothiazole was prepared by the reaction of 5-chloro-2-mercaptobenzothiazole with excess sulfuryl chloride. The acid hydrolysis of 3-anilinopropionitrile furnished the desired 3-anilinopropionamide. N-(2-Chloroallyl)-aniline (I), N-(3-chloro-2-butenyl)-aniline (II), N-(2-chloroallyl)-N-(2-methoxyethyl)-aniline (III), 1-(2,3,6-trichlorobenzyl)-4-phenylpiperazine (IV) and N,N′-diphenyl-2-butene-1,4-diamine (V) were prepared by the reaction of aniline, N-(2-methoxyethyl)-aniline or 1-phenylpiperazine with either 2,3-dichloro-1-propene, 1,3-dichloro-2-butene, 2,3,6-trichlorobenzyl chloride or 1,4-dichloro-2-butene. The reaction of aniline or N-methylaniline with 2-chlorobenzothiazole or 2,5-dichlorobenzothiazole gave 2-anilino-5-chlorobenzothiazole (VI), 2-(N-methylanilino)-benzothiazole (VII) and 5-chloro-2-(N-methylanilino)-benzothiazole (VIII), respectively. 5-Chloro-2-[2-(diethylamino)-ethylamino]-benzothiazole was obtained in 96% yield by the reaction of 2,5-dichlorobenzothiazole with N,N-diethyl ethylenediamine.

The N-nitroso N-substituted anilines were prepared by the reaction of the appropriate N-substituted aniline hydrochlorides in an aqueous or ethyl alcohol medium with aqueous sodium nitrite.

The reaction of the N,N-disubstituted aniline hydrochlorides with an aqueous sodium nitrite solution at 0–10°, followed by neutralization of the reaction mixture with 10% aqueous sodium hydroxide gave the N,N-disubstituted *p*-nitrosoanilines (XX–XXVIII). It was anticipated that

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(1) Currently available in 33⅓% active mixture with an inert filler under the trade mark Elastopar.

(2) H. M. Leeper, C. L. Gable, J. J. D'Amico and C. C. Tung, *Rubber World*, **135**, 413 (1956).

(3) N. S. Moon, U. S. Patent 2,469,697.