TABLE I

4,4′-BISDIALKYLAMINOSTILBENES

Compound	R_1	R_2	R_3	Yield, %	M.P.	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
I	CH_3	CH_3	H	33	253–254[a]	$C_{18}H_{22}N_2$	—	—	—	—	—	—
I	C_2H_5	C_2H_5	H	55	133.5–134.5[b]	$C_{22}H_{30}N_2$	81.9	9.4	8.7	82.3	9.0	9.0
I	CH_3	C_2H_5	H	25	167–168[c]	$C_{20}H_{26}N_2$	81.6	8.9	9.5	81.9	8.7	9.4
I	CH_3	CH_3	CH_3	39	175–176[c]	$C_{20}H_{26}N_2$	81.6	8.9	9.5	81.4	8.7	9.4
I	CH_3	CH_3	Cl	48	205.5–206.5[d]	$C_{18}H_{20}N_2Cl_2$	64.5	6.0	—	64.8	5.7	—
I	CH_3	CH_3	OCH_3	55	206–207[c]	$C_{20}H_{26}N_2O_2$	73.6	8.0	8.6	73.8	6.9	8.7
I	CH_3	CH_3	C_6H_5	37	173.5–174.5[c]	$C_{30}H_{30}N_2$	86.5	7.0	6.5	86.4	6.8	6.6
I	$R_1R_2 = \left.\begin{matrix}CH_2\text{—}CH_2\\ \vert\\ CH_2\text{—}CH_2\end{matrix}\right\rangle$		H	57	315–318[d]	$C_{22}H_{26}N_2$	82.7	8.2	8.8	83.1	8.0	9.0
II	H	—	—	54[e]	151–152.5[c]	$C_{22}H_{26}N_2$	82.7	8.2	8.8	83.2	8.5	8.8
II	CH_3	—	—	33[e]	168.5–169.5[c]	$C_{24}H_{30}N_2$	83.2	8.7	8.1	83.4	8.7	7.9
1,2-Di-8′-julolidylethylene				70–75	221–223[c]	$C_{26}H_{30}N_2$	84.2	8.2	7.6	84.6	8.1	7.7

[a] Literature m.p. 250° (ref. 1); 253–254°.[6] [b] From ethanol. [c] From benzene-ethanol (1:2). [d] From benzene. [e] Yellow needles.

1,7-Dimethyl-1,2,3,4-tetrahydroquinoline was obtained in 59% yield by reduction of the corresponding quinoline methiodide with tin and hydrochloric acid,[8] and was a colorless liquid with marked blue fluorescence, b.p. 127–130°/14 mm.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.9; H, 9.4; N, 8.7. Found: C, 82.2; H, 9.0; N, 8.2.

The methiodide formed colorless needles from methanol-ether mixture, m.p. 159–160°. The crystals turned brown rapidly in air.

Anal. Calcd. for $C_{12}H_{18}NI$: C, 47.5; H, 6.0; N, 4.6. Found: C, 47.7; H, 5.7; N, 4.6.

The methopicrate gave yellow crystals from aqueous ethanol, m.p. 108–109°.

Anal. Calcd. for $C_{18}H_{20}N_4O_7$: C, 53.5; H, 5.0; N, 13.8. Found: C, 53.5; H, 5.5; N, 13.9.

The picrate was prepared in benzene, and recrystallized from ethanol, m.p. 148.5–149.5°.

Anal. Calcd. for $C_{17}H_{18}N_4O_7$: C, 52.3; H, 4.7; N, 14.4. Found: C, 52.4; H, 5.1; N, 14.3.

1,7-Dimethyl-6-formyl-1,2,3,4-tetrahydroquinoline was obtained in 76% yield. Oily liquid, b.p. 208–216°/14 mm.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.2; H, 8.0. Found: C, 76.0; H, 8.0.

Th oxime formed colorless plates from aqueous ethanol, m.p. 131–133°.

Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.6; H, 7.9; N, 13.7. Found: C, 70.6; H, 8.1; N, 13.3.

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(8) J. Meisenheimer, *Ann.*, **385**, 138 (1911).

Reaction of the Pseudo Base 1,2-Dihydro-1,2,3-triphenyl-2-quinoxalinol with Alcohols[1a]

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Many of the quaternary ammonium salts in which the quaternary nitrogen is a member of an aromatic ring undergo a reversible reaction with hydroxyl ion to give pseudo bases.[1b] The triphenylmethane dyes behave similarly, giving the analogous carbinol bases. The pseudo and carbinol bases generally react with simple alcohols to give ethers when the alcoholic solutions are heated.[2–10] Considering the scope of the reaction, it is surprising that ether formation has apparently not been observed for the quinoxaline pseudo bases, even though the majority of those reported in the literature were subjected to crystallization from ethyl alcohol.[11–19]

It has now been found that the quinoxaline pseudo base, 1,2-dihydro-1,2,3-triphenyl-2-quinoxalinol (I),[16,17] reacts readily with methyl, ethyl, and *n*-butyl alcohols. The broad band at 3300 cm.$^{-1}$ in the spectrum of I in Nujol mull is absent in the spectra of the reaction products. This loss of absorption in the OH region is consistent with ether formation. The analytical data, too, are in

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(1)(a) Communication No. 2153 from the Kodak Research Laboratories. (b) A. Hantzsch and M. Kalb, *Ber.*, **32**, 3109 (1899).

(2) H. Decker, *J. prakt. Chem.*, **45**, 161 (1892).

(3) H. Decker, *Ber.*, **33**, 1715 (1900).

(4) H. Decker, *Ber.*, **35**, 2588 (1902).

(5) H. Decker, *Ber.*, **35**, 3068 (1902).

(6) H. Decker and A. Kaufmann, *J. prakt. Chem.*, **84**, 425 (1911).

(7) O. Fischer, *Ann.*, **206**, 83 (1881).

(8) O. Fischer, *Ber.*, **33**, 3356 (1900).

(9) O. Fischer and K. Weiss, *Z. Farben. u. Textilchem.*, **1**, 1 (1901); *Chem. Zentr.*, **1902, I**, 471.

(10) J. Herzog and J. Budy, *Ber.*, **44**, 1584 (1911).

(11) O. Fischer and M. Busch, *Ber.*, **24**, 1870 (1891).

(12) E. Täuber, *Ber.*, **25**, 1019 (1892).

(13) P. Jacobson, *Ann.*, **287**, 97 (1895).

(14) P. Jacobson, and H. Strübe, *Ann.*, **303**, 305 (1898).

(15) P. Jacobson, *Ann.*, **427**, 142 (1922).

(16) F. Kehrmann and J. Messinger, *Ber.*, **24**, 1239 (1891).

(17) F. Kehrmann and C. Natcheff, *Ber.*, **31**, 2425 (1898).

(18) F. Kehrmann and E. Falke, *Helv. Chim. Acta*, **7**, 981 (1924).

(19) K. Brand and E. Wild, *Ber.*, **56**, 105 (1923).

accord with the supposition that here, as with other pseudo bases, ethers are formed.

When solutions in methyl alcohol of the ethyl or *n*-butyl ethers of I are heated, the methyl ether is produced. Likewise the methyl ether is converted to the ethyl ether in hot ethyl alcohol. Interconversion of other pseudo base ethers has been reported.[3–5,20]

The ethers are readily cleaved by acid, giving the alcohol and 1,2,3-triphenylquinoxalinium salt. For example, when the *n*-butyl ether is dampened with aqueous ethanol containing hydrochloric acid (*ca.* 4*N*), the odor of *n*-butyl alcohol is noticeable after only fifteen seconds. If the ethyl or *n*-butyl ether is dissolved in aqueous ethanol about 2*N* in hydrochloric acid, the solution, after standing at room temperature for five minutes, yields a precipitate of the pseudo base, I, when diluted with water and made alkaline. The methyl ether is cleaved less rapidly under these conditions, requiring about thirty minutes.

Pseudo base I was first made by Kehrmann and Messinger,[16] who crystallized the crude product twice from boiling ethyl alcohol. The color and melting point reported for the crystallized product suggest that it could have consisted partly of the pseudo base ethyl ether. Indeed, crystallization must be carried out quickly if ether formation is to be avoided. If the ethyl alcohol solution of I is boiled more than three minutes, the product which crystallizes consists of the ether. It is possible that other workers also overlooked an unsuspected reaction of quinoxaline pseudo bases with alcohol. For example, the analytical data given by Jacobson[13–15] for his pseudo bases, all of which were crystallized from ethyl alcohol, do not exclude the possibility that some of his products were actually the ethyl ethers.

Although pseudo bases are generally written as carbinols, many of them conceivably could exist in an alternative, open form having a carbonyl group rather than hydroxyl.[21] The absence of a carbonyl band and presence of a hydroxyl band in the infrared spectrum of I rules out the open structure *N*-phenyl-*N'*-α-phenylphenacylidine-*o*-phenylenediamine.

EXPERIMENTAL

Melting points of the pseudo base, I, and its ethers depend on the rate of heating and therefore are of limited use for characterization. The data given first were obtained using the Fisher-Johns apparatus. The sample was heated in 5 min. to within 5° of initial melting. Rate of heating was then 1° per min. until melting started. The rate was then reduced to 0.5° per min. The data in parentheses were obtained using a hot stage with temperature gradient (Kofler-Heizbank, made by Reichert Co., Austria). The sample was dropped on the preheated stage. The approximate minimum temperature at which rapid melting occurred was recorded. Below this temperature, melting was slow and due, presumably, to decomposition. Above this temperature, melting occurred at about the same rate as for pure, stable compounds above their melting points. The temperatures determined in this way should be much closer to the true melting points than those found by slow heating.

1,2-Dihydro-1,2,3-triphenyl-2-quinoxalinol (I) was made as described previously[16] except that the pseudo base was precipitated using potassium hydroxide solution rather than ammonia, and the crude product was crystallized three times from 1:1 cyclohexane-benzene rather than from ethyl alcohol. The brilliant yellow crystals are not fluorescent; m.p. 143–147° (195°).

Anal. Calcd. for $C_{26}H_{20}ON_2$: C, 82.95; H, 5.36; N, 7.44. Found: C, 82.9; H, 5.5; N, 7.2.

1,2-Dihydro-2-methoxy-1,2,3-triphenylquinoxaline. Three grams of I was dissolved in 100 ml. of boiling methyl alcohol. After 4 min., crystals of the product formed. Boiling was continued for another minute. The product (2.88 g.) was separated from the cooled mixture and recrystallized from methyl alcohol. The very pale yellow crystals fluoresce brilliant blue; m.p. 143–147° (175°).

Anal. Calcd. for $C_{27}H_{22}ON_2$: C, 83.05; H, 5.68; N, 7.18. Found: C, 83.4; H, 5.4; N, 7.4.

1,2-Dihydro-2-ethoxy-1,2,3-triphenylquinoxaline. A solution of 3 g. of I in 60 ml. of absolute ethyl alcohol was boiled for 7 min The product (1.38 g.) which crystallized from the cooled solution was recrystallized from ethyl alcohol. The pale yellow crystals fluoresce brilliant blue; m.p. 126–129° (145°).

Anal. Calcd. for $C_{28}H_{24}ON_2$: C, 83.14; H, 5.98; N, 6.93. Found: C, 83.2; H, 5.6; N, 6.9.

2-n-Butoxy-1,2-dihydro-1,2,3-triphenylquinoxaline. A solution of 3 g. of I in 18 ml. of *n*-butyl alcohol was boiled for 10 min. The product (3.15 g.) which crystallized from the cooled solution was recrystallized from *n*-butyl alcohol. The light yellow crystals fluoresce brilliant blue-green; m.p. 118–121° (140°).

Anal. Calcd. for $C_{30}H_{28}ON_2$: C, 83.30; H, 6.52; N, 6.48. Found: C, 83.6; H, 6.6; N, 6.5.

Interconversion of the ethers of I. Solutions of the ethyl and *n*-butyl ethers in methyl alcohol were heated at 70° for 2 and 5 hr., respectively. Crystals of the methyl ether formed during the heating. The product was identified by its infrared spectrum. A solution of the methyl ether in absolute ethyl alcohol was heated 6 hr. at 70°. The cooled solution gave crystals of the ethyl ether, identified by their infrared spectrum.

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(20) A. Werner, *Ber.*, **34**, 3300 (1901).

(21) R. C. Elderfield, *Heterocyclic Compounds*, Vol. 4, R. C. Elderfield, ed., Wiley, New York, 1952, Chap. 1, p. 232.

An Attempted Reductive Rearrangement of Norcamphor

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A recent examination[1] of the stereochemistry of the reduction of 4-*t*-butylcyclohexanone with trimethylamine borane in the presence of boron fluoride led to the conclusion that the reduction proceeds by an initial attack of the boron fluoride on

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(1) W. M. Jones, *J. Am. Chem. Soc.*, **82**, 2528 (1960).