TABLE II

G-VALUES FOR GASES FROM COPOLYMERS[a] OF STYRENE-d_1-METHYL METHACRYLATE AND STYRENE-d_1-METHYL ACRYLATE[b]; DOSE 1.0 × 10^7 RAD

	G(Gas) From Nondeuterated Copolymer[c]	G(d_0-Gas/d_1-Gas)[c] α-d_1-Copolymer	β-d_1-Copolymer	p-d_1-Copolymer	Isotope Effect[d]
H_2 HD	0.072	18 (19)	36 (34)	33 (35)	7.0
CH_4 CH_3D	0.137	23 (23)	36 (36)	69 (62)	7.0
$HCOOCH_3$ $DCOOCH_3$	0.125	17 (12)	34 (30)	52 (93)	5.0
CH_3OH CH_3OD	0.068	[e] (12)	[e] (36)	41 [e]	5.1

[a] Containing 0.5 mole fraction styrene. [b] Figures in parentheses. [c] Corrected for the contribution of hydrogen and HD by the styrene units in the copolymer. [d] Calculated only for the methyl methacrylate copolymer. [e] Not determined.

d_1-styrene, and deuterium or molecules such as ethane, dimethyl ether, or methyl acetate, possibly only from bimolecular radical coupling processes, were not detected.[8]

It is apparent that the bond in the styrene moiety of the copolymer most sensitive to abstraction by ·H, ·CH_3, ·OCH_3, and ·$COOCH_3$ is the α-CH; the β- and p-CH bonds are somewhat more stable to such attack.

The reactions of the initially derived free radicals occur to about the same extent and specificity in the styrene–methyl acrylate copolymer (Table II). The latter is a crosslinking system,[2] in which protection against crosslinking is afforded by the styrene groups present. While the gas yields of this copolymer depend not only on its composition, but on the degree of crosslinking (the unirradiated copolymer is more radiation sensitive than the crosslinked product) the ratio G(d_0-gas/d_1-gas) clearly indicates the significance of abstraction reactions in the radiation chemistry of the copolymer.

The implication of these conclusions is that radiation initiated damage noted in organic polymers is not a simple function of the radiation stability of a particular bond in the molecule.

Acknowledgment. The authors thank Mr. D. Green for preparing some of the deuterated polymers.

DEPARTMENTS OF CHEMISTRY AND ANALYTICAL SERVICES
SCIENTIFIC LABORATORY
FORD MOTOR CO.
DEARBORN, MICH

---

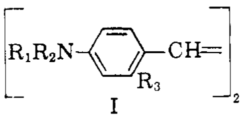
[8] γ-Irradiation of a mixture of polystyrene-d_1 and polymethyl methacrylate, obtained by coprecipitation from a solution of these substances, afforded HD (from polystyrene-d_1) as the only deuterated species.

Some 4,4'-Bisdialkylaminostilbenes

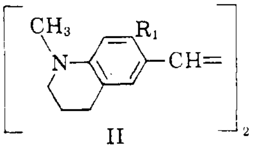
F. H. C. STEWART

Received February 24, 1961

The compound obtained by the action of tin and hydrochloric acid on p-dimethylaminobenzaldehyde was described as 2,6-bisdimethylaminoanthracene by Albano,[1] but was later found to be 4,4'-bisdimethylaminostilbene.[2] This reaction had been extended to various other p-dialkylaminobenzaldehydes and the products erroneously considered to be anthracene derivatives.[3,4] Consequently, in view of the interest which attaches to certain aminostilbenes as carcinogenic agents,[5] it seemed desirable to collect these compounds, with relevant data, under their correct designation as 4,4'-bisdialkylaminostilbenes (I). The compounds are arranged in Table I, which also includes two heterocyclic dialkylaminostilbenes of structure (II). With one exception these stilbene derivatives have not been mentioned in the literature.



I



II

EXPERIMENTAL

The p-dialkylaminobenzaldehydes were prepared from the corresponding tertiary amines by the N,N-dimethylformamide–phosphorus oxychloride procedure of Campaigne and Archer,[7] and the reduction of the aldehydes by tin and hydrochloric acid effected by the standard procedure previously described.[3]

The following intermediates and derivatives have not been reported hitherto.

---

(1) J. D. Albano, *Anal. Assoc. Quim. Argentina*, **34**, 18 (1946).

(2) F. H. C. Stewart, *Chem. & Ind. (London)*, 761 (1957).

(3) F. H. C. Stewart, *J. Chem. Soc.*, 1026 (1957).

(4) F. H. C. Stewart and J. W. Rasburn, *J. Chem. Soc.*, 2237 (1957).

(5) A. Haddow, R. J. C. Harris, G. A. R. Kon, and E. M. F. Roe, *Phil. Trans.*, **241A**, 147 (1948).

(6) E. Campaigne and W. M. Budde, *Proc. Indiana Acad. Sci.*, **58**, 111 (1949).

(7) E. Campaigne and W. L. Archer, *J. Am. Chem. Soc.*, **75**, 989 (1953).

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	$R_1R_2 = \left\|\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}\right\rangle$		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.

CHEMICAL RESEARCH LABORATORIES
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION
MELBOURNE, AUSTRALIA

---

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

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

PAUL M. MADER

Received February 28, 1961

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

---

(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).