film) 3320 (m), 2960–2790 (s), 1470 (s), 1390 (m–s), 1365 (m), 1310 (w), 1270 (w–m), 1245 (m), 1150 (s), 1110 (s), 1030 (w), 965 (w), 940 (w), 910 (m), 880 (w), 800 (m–s), 850 (s), and 640 cm^{-1} (w); nmr (C_6D_6) δ 0.9 (s, 6 H), 0.95 (s, 2 H), and 2.4 (d, 10 H).

General Procedure for Preparation of the 2-Phenyl-1,3,2-dioxaboracyclohexanes.—The dioxaboracyclohexanes were prepared from the appropriate 1,3-propanediol and phenylboric acid in benzene by azeotropic removal of water.

2-Phenyl-5-methyl-1,3,2-dioxaboracyclohexane (7).—Phenylboric acid (2.6 g, 0.021 mol) and 2-methyl-1,3-propanediol[30] (1.9 g, 0.021 mol) gave 3.5 g (95%) of 7, bp 103–105° (3 mm), mp 30–31°.

Anal. Calcd. for $C_{10}H_{13}BO_2$: C, 68.22; H, 7.45. Found: C, 68.28; H, 7.58.

Compound 7 had the following properties: infrared (thin film) 3060 (w), 2960 (m), 2900 (m), 1600 (m–s), 1480 (s), 1445 (s), 1415 (s), 1380 (w), 1350 (s), 1320 (s), 1300 (s), 1255 (s), 1220 (w), 1170 (s), 1140 (s), 1080 (m), 1030 (m), 950 (w), 880 (w), 765 (m), 730 (m–s), 700 (s), 670 (m), and 650 cm^{-1} (s).

2-Phenyl-4,6-dimethyl-1,3,2-dioxaboracyclohexane (9).—Phenylboric acid (1.2 g, 0.01 mol) and *meso*-2,4-pentanediol[41] (1.0 g, 0.01 mol) in toluene gave 1.5 g (88%) of 8, mp 45°, purified by sublimation at 60° (0.5 mm).

Anal. Calcd for $C_{11}H_{15}BO_2$: C, 69.47; H, 7.89. Found: C, 69.64; H, 7.94.

Compound 9 had the following properties: infrared (KBr) 3050 (w), 2990 (m), 2930 (m–w), 1605 (m), 1450 (s), 1410 (s), 1385 (m), 1370 (m), 1360 (m), 1310 (s), 1270 (m–s), 1180 (m), 1155 (s), 1140 (s), 1070 (w), 1030 (m), 900 (w), 830 (w), 780 (m), 715 (s), 660 (m–w), and 650 cm^{-1} (s).

Registry No.—**3**, 6063-69-0; **4**, 29173-11-3; **5**, 34288-22-7; **6**, 4406-77-3; **7**, 34288-24-9; **8**, 5123-13-7; **9**, 7317-42-2; 1-carboethoxy-4,4-dimethyl-2-pyrazoline, 34288-27-2; *N*,*N*′-2,2-tetramethyl-1,3-propanediamine, 31892-15-6; *N*,*N*′-5,5-tetramethyl-2-phenyl-1,3-diazacyclohexane, 34288-29-4.

Acknowledgment.—The authors wish to thank Dr. Ben A. Schoulders, University of Texas, for running the boron spectra and Cynthia A. Milewski for a sample of *meso*-2,4-pentanediol.

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[41] J. G. Pritchard and R. L. Vollmer, *J. Org. Chem.*, **28**, 1545 (1963).

Azimines. I. Reinvestigation of Some Alleged Azimines

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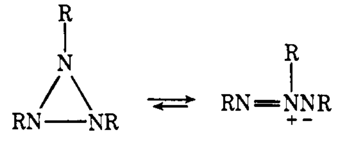
Azimines are the 1,3-dipolar isomers of the unknown triaziridines. Some previously proposed azimine structures are reassigned, based on new spectroscopic evidence. The product formed by bromination and dehydrobromination of *o*-nitrobenzaldehyde phenylhydrazone is assigned structure **5b**; reduction with stannous chloride gives **6b**, *anhydro*-2-(*p*-bromophenyl)-3*H*-benzo-1,2,3-triazinium-4-one hydroxide. Reaction of *o*-aminobenzamide with *N*,*N*-dimethyl-4-nitrosoaniline gives 4,4′-azoxy-*N*,*N*-dimethylaniline, not the previously proposed **6c**. Condensation of indazolinone with *N*,*N*-dimethyl-4-nitrosoaniline does give **6c**, presumably *via* an intermediate triaziridine.

1,3 dipoles have been of substantial interest, originally as intermediates in the synthesis of five-membered heterocycles,[1] and more recently as valence isomers of three-membered heterocycles.[2,3] The three-nitrogen valence isomer pair comprising the cyclic triaziridines and the open dipolar azimines remains, however, almost unexplored. The literature reveals no extant reports of triaziridines,[4] and only scattered examples of azimines (see below). Expecting the latter to be more stable, we here report the establishment of structure of some cyclic azimines. An accompanying paper[5] reports on the reactions of nitrenes with azo compounds, a potential synthetic route to azimines.[6] Other synthetic routes are also being investigated, and will be reported subsequently.[7]



Products from *o*-Nitrobenzaldehyde Phenylhydrazone.—In a series of papers in 1925–1931, Chattaway[8-11] reported that halogenation of *o*-nitrobenzaldehyde phenylhydrazone, followed by treatment with base, gave a series of compounds A, to which he assigned structure **1**[9] (Scheme I). Reduction of compounds A with stannous chloride gave a series of compounds B, assigned triaziridine structures **2**. This work was subsequently reinvestigated by Gibson,[12] who proposed the new structures **3a** and **4a** for materials A and B (Ar = 2,4-dibromophenyl), respectively. The anthranil *N*-oxide structure **3a** was apparently based on mechanistic considerations and ultraviolet and infrared spectra, especially bands at 1248 and 1570 cm^{-1} in the latter, assigned as $\overset{+\,-}{\geqslant \mathrm{NO}}$ and -N=N- stretching frequencies, respectively. Compound B was assigned the azimine structure **4a**, since the possibility of B being the straightforward reduction product of **3a**, the

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[1] R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963). Most recent paper: R. Knorr, R. Huisgen, and G. K. Staudinger, *Chem. Ber.*, **103**, 2639 (1970).

[2] Oxaziridine–nitrone pair: J. S. Splitter and M. Calvin, *J. Org. Chem.*, **23**, 651 (1958); E. Schmitz, "Dreiringe mit Zwei Heteroatomen," Springer-Verlag, West Berlin, 1967, pp 14–15, 19–20, 35–36.

[3] General discussion, especially oxadiaziridine–azoxy compound pair: (a) F. D. Greene and S. S. Hecht, *J. Org. Chem.*, **35**, 2482 (1970); (b) H. Mauser, G. Gauglitz, and F. Stier, *Justus Liebigs Ann. Chem.*, **739**, 84 (1970).

[4] One uncorroborated report: M. Colonna and A. Risaliti, *Gazz. Chim. Ital.*, **91**, 204 (1961).

[5] R. C. Kerber and P. J. Heffron, *J. Org. Chem.*, **37**, 1592 (1972).

[6] A recent example of this reaction: K.-H. Koch and E. Fahr, *Angew. Chem., Int. Ed. Engl.*, **9**, 634 (1970).

[7] Unpublished work by S.-M. Liu, L. Colen, and R. Liotta in these laboratories.

[8] F. D. Chattaway and A. J. Walker, *J. Chem. Soc.*, 2407 (1925), 323 (1927).

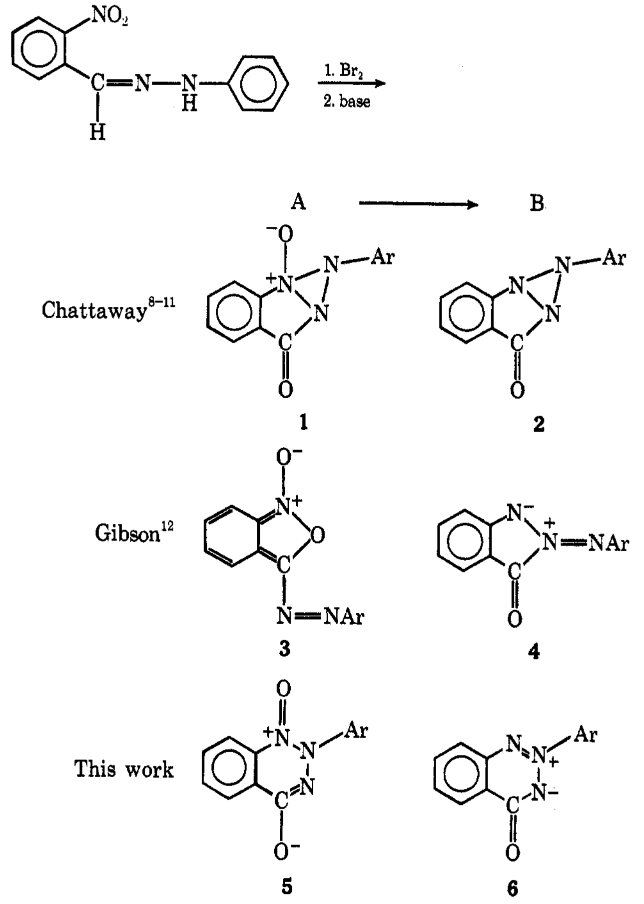
[9] F. D. Chattaway and A. J. Walker, *ibid.*, 323 (1927).

[10] (a) F. D. Chattaway and A. B. Adamson, *ibid.*, 157 (1930); (b) *ibid.*, 2787, 2792 (1931).

[11] For a review, see J. G. Erickson in "The Chemistry of Heterocyclic Compounds," Vol. 10, A. Weissberger, Ed., Interscience, New York, N. Y., 1956, p 27.

[12] M. S. Gibson, *Tetrahedron*, **18**, 1377 (1962); *Nature (London)*, **193**, 474 (1962).

SCHEME I
PROPOSED STRUCTURES FOR PRODUCTS FROM HALOGENATION OF *o*-NITROBENZALDEHYDE PHENYLHYDRAZONE

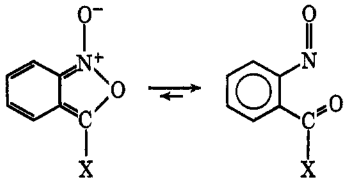


a, Ar = 2,4-Br$_2$C$_6$H$_3$; **b**, Ar = 4-BrC$_6$H$_4$; **c**, Ar = 4-(Me$_2$N)C$_6$H$_4$

3-(arylazo)anthranil, was excluded by the chemical and spectral properties of **4a**, especially by the presence of a carbonyl stretching band in the infrared at 1655 cm^{-1}.

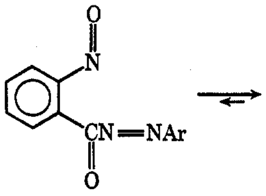
However, this reported >C=O stretching frequency appeared also to be inconsistent with the proposed five-membered ring azimine structure **4a** for material B, inasmuch as the carbonyl stretching frequency for indazolone falls at 1792 cm^{-1},[13] and the positive charge on the 2 nitrogen might be expected to raise the frequency even higher. Consequently, we undertook a reinvestigation of these materials.

Reaction of *o*-nitrobenzaldehyde phenylhydrazone with 2 equiv of bromine in acetic acid containing excess sodium acetate[8] gave directly the material A (Ar = *p*-bromophenyl), assigned the anthranil *N*-oxide structure **3b** by Gibson.[12] Anthranil *N*-oxides are an unknown[14] class of compound thought to be unstable with respect to the isomeric *o*-nitroso carbonyl compounds.[15] Nonetheless, structure **3b** provides an adequate explanation of the principal feature of the infrared spectrum of A (Ar = *p*-bromophenyl), a strong band at 1630 cm^{-1}, which may be assigned to >C=N–, by analogy with benzofuroxans[16] and nitronic esters.[17] In contrast, the isomeric nitroso compound **7** does not fit the spectra; for example, A lacks the carbonyl stretching band found at about 1715 cm^{-1} in (aroylazo)benzenes,[18] the strong nitroso stretching frequency normally found near 1500 cm^{-1},[19] or the n → π* absorption of the nitroso group, found at 765 nm (ε 6060) in *o*-nitrosobenzophenone.[20]

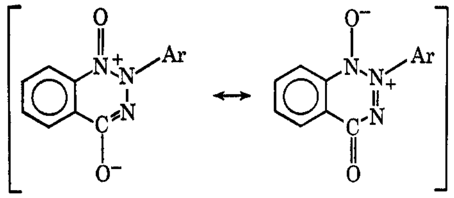


7, X = N=NC$_6$H$_4$Br

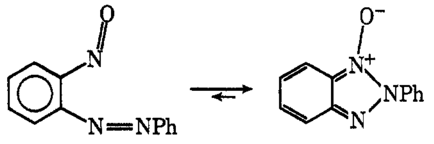
One additional structure which should be considered for A is **5b**, which may be formed by intramolecular cyclization of the azo and nitroso groups of **7**. Such a cyclization evidently occurs spontaneously in the *o*-nitrosoazobenzenes, which exist in the form of 2-arylbenzotriazole 1-oxides.[15,21]



7



5b



The structure **5b** for material A is reconcilable with the spectral data and, assuming a mobile equilibrium between **7** and **5b**, with the chemical reactions reported by Chattaway[9] (formation of ArH on treatment with ethanolic KOH; oxidation to *o*-nitrobenzoic acid with KMnO$_4$; and, especially, reduction to B with stannous chloride).

Material B (Ar = *p*-bromophenyl) was obtained in 57% yield on reduction of A (**5b**) with stannous chloride. The infrared spectrum showed a carbonyl stretching band at 1675 cm^{-1} [*cf.* Gibson's value of

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[13] E. F. Ullman and E. A. Bartkus, *Chem. Ind.* (*London*), 93 (1962).

[14] One reported exception: H. H. Szmant and C. M. Harmuth, *J. Amer. Chem. Soc.*, **81**, 962 (1959).

[15] K. H. Wünsch and A. J. Boulton, *Advan. Heterocycl. Chem.*, **8**, 332 (1967).

[16] A. R. Katritzky, Ed., "Physical Methods in Heterocyclic Chemistry," Vol. II, Academic Press, New York, N. Y., 1963, p 239.

[17] N. Kornblum and R. A. Brown, *J. Amer. Chem. Soc.*, **86**, 2681 (1964).

[18] E. Fahr and H. Lind, *Angew. Chem., Int. Ed. Engl.*, **5**, 372 (1966).

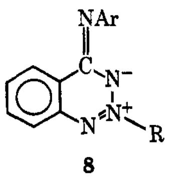
[19] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., London, 1958, p 306.

[20] S. Kim, S. S. Friedrich, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **92**, 5452 (1970).

[21] This may be inferred from the numerous (colorless) benzotriazole *N*-oxides which are reported, and the lack of *o*-nitrosoazo compounds: F. R. Benson and W. L. Savell, *Chem. Rev.*, **46**, 1 (1950). However, no infrared spectra seem to be reported for the supposed benzotriazole *N*-oxides.

1655 for B (Ar = 2,4-dibromophenyl)]. Since 3-arylbenzo-1,2,3-triazin-4-ones have carbonyl stretching frequencies at about 1685 cm^{-1},[22] and since 3-(*p*-bromophenyl)benzotriazinone has nearly the same reported melting point (196°)[9] as B (199–200°), an authentic sample of the former was prepared for comparison. The two materials were not identical, as shown by infrared comparison and depressed mixture melting point. However, the spectra showed many similarities, suggesting a six-membered azimine structure **6b** for material B. This was also consistent with the 60-MHz pmr spectrum of B in DMSO at 100°, which showed a two-proton doublet at τ 1.8 ($J \approx 9$ Hz), a four-proton singlet at τ 2.0, and another two-proton doublet at τ 2.2 ($J \approx 9$ Hz); the substantial deshielding of the *p*-bromophenyl ring is consistent with structure **6**, in which the ring is bonded to the positive central nitrogen of the azimine grouping, but not with **4**.

Confirmation that the material B had structure **6b** was obtained from the mass spectrum, which showed, in addition to a substantial (24%) parent peak at *m/e* 301 and 303, important fragments at *m/e* 273 and 275 ($P - N_2$ or CO), 245 and 247 ($P - N_2 - CO$), 183 and 185 (p-$BrC_6H_4N_2^+$), 166 ($P - N_2 - CO - Br$), and 155 and 157 ($BrC_6H_4^+$). The fragmentation pattern observed is analogous to those of the recently reported iminoazimines **8**.[23]



8

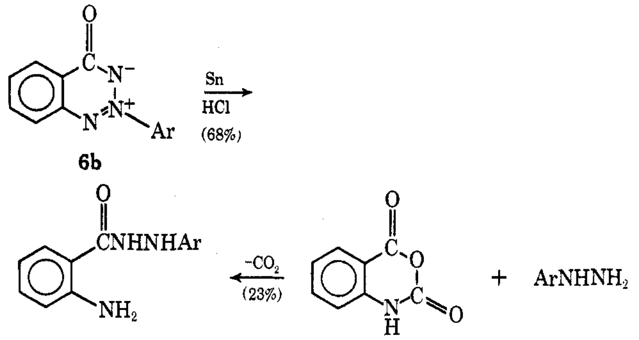
Ar = *o*-CNC_6H_4, *o*-ClC_6H_4, *o*-$O_2NC_6H_4$
R = Me, Et, Pr

Fragments such as $BrC_6H_4N^+$, $C_5H_4Br^+$, $C_7H_4N_2O^+$, and $C_7H_4O^+$, which would be expected from a material of structure **4b**, are absent from the observed mass spectrum of B. These data appear to support structure **6b** for this material. The structure **6b** is also supported by recent reports of alkylation of salts of benzo-1,2,3-triazin-4-one to give, in addition to the expected O- and N(3)-alkylated products, products which appear to be N(2)-alkylated azimines, **6** (Ar = CH_3, CH_3CH_2).[24] The spectroscopic data for these compounds [ν_{CO} 1630 cm^{-1}, λ_{max} *ca.* 340 nm (log ϵ 3.9), deshielded methyl group in the nmr (τ 5.55)] are consistent with those of **6b**, allowing for the differences between a 2-alkyl and a 2-aryl substituent.

Reduction of compound B (**6b**) with tin in hydrochloric acid gave the *p*-bromophenylhydrazide of anthranilic acid, identical with an authentic sample.[9]

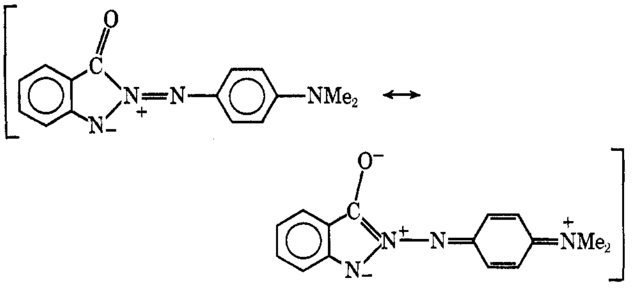
Reaction of **6b** with ethanolic KOH[9] gave a complex mixture from which pure products could not be isolated.

The six-membered ring azimine structure **6b** for B, which is uniquely consistent with the spectroscopic and chemical information, appears also to lend support to the proposed structure **5b** for material A.



Product from Anthranilamide and 4-Nitrosodimethylaniline.—Jennen has reported that condensation of anthranilamide with 4-nitroso-*N*,*N*-dimethylaniline (**9**) gave rise to a material C, mp 249°, assigned the structure **6c**.[25] However, the reported analysis did not fit the formula $C_{15}H_{14}N_4O$, and no other support for the structure **6c** for C was offered. Repetition of this reaction gave a product, mp 243–244°, which was apparently that obtained by Jennen. The infrared spectrum of this material showed neither carbonyl nor ortho-substituted benzene ring absorption. A doublet at 813 and 824 cm^{-1} indicated only para-substituted rings.[26] The 60-MHz pmr spectrum (DMSO-d_6 at 150°) showed a singlet at τ 7.00 (area 6) for the dimethylamino groups, a doublet at τ 3.25 ($J \approx 9$ Hz, area 2), and a pair of overlapping doublets at τ 1.89 and 2.05 ($J \approx 9$ Hz, area 2). These data and a correct analysis for $C_{16}H_{20}N_4O$ showed the material C to be 4,4′-azoxy-*N*,*N*-dimethylaniline (lit.[27] mp 244.5°).

Product from Indazolinone and Nitrosodimethylaniline.—Jennen also reported the synthesis of another azimine, by condensation of indazolinone and **9**. The product, material D, was assigned the structure **10** (analogous to Gibson's **4**), and was described initially as a blue dye[28] and later as a red-purple compound, mp 198°.[25]



10

Condensation of indazolinone with **9**, using methanolic KOH, gave a very dark solution from which a purple, crystalline product, mp *ca.* 186°, was obtained after recrystallization from chloroform, and then from DMSO. Chromatography of the residue from the recrystallizations led to isolation of several by-products, including *N*,*N*-dimethyl-*p*-phenylenediamine, 4,4′-azo-*N*,*N*-dimethylaniline, and *N*-benzoyl-*N*′,*N*′-dimethyl-*p*-phenylenediamine.

Evaporation of a saturated solution of the purple material D in methanol containing 5% carbon tetra-

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[22] M. S. Gibson, *J. Chem. Soc.*, 3539 (1963).

[23] R. A. W. Johnstone, *et al.*, *J. Chem. Soc. C*, 1238 (1970); H. N. E. Stevens and M. F. G. Stevens, *ibid.*, 2289 (1970).

[24] G. Wagner and H. Gentzsch, *Pharmazie*, **23**, 629 (1968). The authors do not firmly decide between the 1- and 2-alkylated structures for these materials, but the bulk of the evidence favors the latter.

[25] J. J. Jennen, *Meded. Vlaam. Chem. Ver.*, **18**, 43 (1956).

[26] J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 33.

[27] E. Bornstein, *Ber.*, **29**, 1479 (1896).

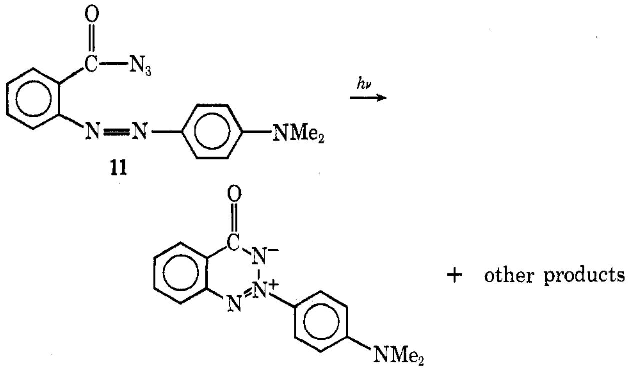
[28] J. J. Jennen, *Ind. Chim. Belge*, **16**, 472 (1951). D has been shown to be different from 2[4′-(dimethylamino)phenylazo]benzamide: L. Moelants and R. Janssen, *Bull. Soc. Chim. Belg.*, **66**, 209 (1957).

chloride gave shiny blue-black needles, mp 199–200°, which showed the same infrared spectrum as the less pure purple materials. This spectrum showed a carbonyl stretching band at 1655 cm^{-1}, and bands at 817 and 781 cm^{-1} for the para- and ortho-substituted rings. The nmr spectrum (in DMSO-d_6 at 150°) of D was similar to that of B (**6b**), showing a sharp singlet at τ 6.84 for the dimethylamino protons, a doublet (2H, $J \approx 10$ Hz) at τ 3.08, a multiplet (4H) at τ 2.3, and another doublet (2H, $J \approx 10$ Hz) at τ 1.56. These data suggested the analogous structure **6c** for D.

The color of D is due to an intense long-wavelength absorption which appears at 548 nm in ethanol, 530 nm in chloroform, and 522 nm in dioxane. The absence of such a band in B in contrast to D and the solvent dependence of its wavelength suggest that this is a charge transfer absorption analogous to the long-wavelength band (λ_{max} 390 nm in ethanol, 380 nm in dioxane, 352 nm in hexane) found in *p*-nitro-*N*,*N*-dimethylaniline.[29] Its appearance in D (**6c**) appears to support the notion that the aryl group is bonded to the electron-deficient 2 nitrogen in **6c** rather than a terminal nitrogen of the azimine group, as in **10**.

The structural analogy between B (**6b**) and D (**6c**) was confirmed by their very similar mass spectra. Thus, both feature large parent peaks, small fragments corresponding to loss of 28 and 56 amu, and large fragments at masses corresponding to $C_6H_4NAr^+$, Ar^+, $C_6H_4N^+$, and $C_5H_3^+$.

Reduction of **6c** with tin and hydrochloric acid gave an air-sensitive product which appeared by infrared and vapor phase chromatographic analysis to be a mixture of *N*,*N*-dimethyl-*p*-phenylenediamine and *p*-(*N*,*N*-dimethylamino)phenylhydrazine.[30] An attempt to synthesize authentic **6c** by photolysis of the azide **11** gave only 3% of **6c**, in addition to a number of other products, which will be reported on subsequently.[5]



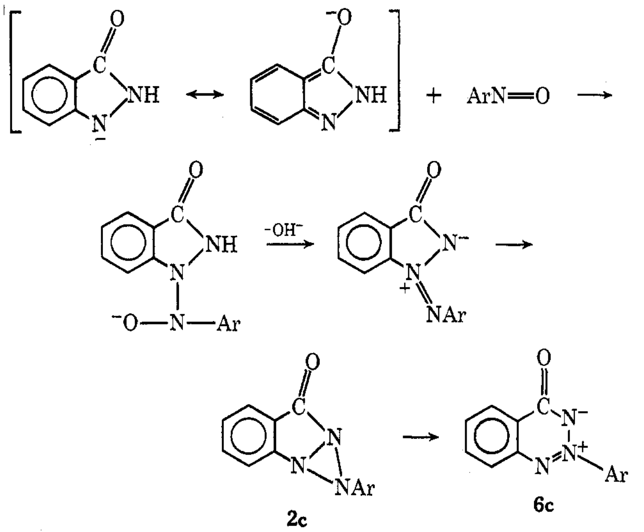
11

6c

Discussion

Our results suggest that materials B and D, both previously assigned five-membered ring azimine structures **4**, in fact have the isomeric six-membered ring azimine structures **6**. The production of **6b** on reduction of material A is to be expected, based on the proposed structure **5b** for A.[31] However, the six-membered ring structure for the product D, from condensation of the five-membered ring starting material, indazolinone, with **9** is more surprising, even though the stability of structures such as **6** relative to **4** may be expected based on lesser ring strain and greater aromatic character of the heterocyclic ring in **6**.

Jennen's proposal of the structure **4c** for the product was evidently based on the idea that reaction of an electrophile such as **9** with the conjugate base of indazolinone would occur most readily at the 2-nitrogen.[25] More recent studies, however, have shown that electrophiles, including acyl chlorides[33] and alkylating agents,[34] react primarily at the 1 nitrogen. It seems probable that reaction of the nitroso compound **9** should begin in the same way. Loss of hydroxide ion from the first intermediate should then give an azimine isomeric with **4** and **6**. Rearrangement to the presumably most stable azimine **6c** may then occur *via* a triaziridine intermediate, **2c**.



2c

6c

In addition to the azimines reported here, a number of others can be found on inspection of the literature.[35–42]

In all of these examples, the azimine grouping is part of an aromatic ring, which no doubt lends stability to the system.[43] However, this structural feature also makes closure of the azimine to a triaziridine more difficult for both electronic and steric reasons.[44] The

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[29] W. D. Kumler, *J. Amer. Chem. Soc.*, **68**, 1184 (1946); H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **46**, 1314 (1963).

[30] R. Stolle and K. T. Gunzert, *J. Prakt. Chem.*, **139**, 141 (1934).

[31] The structure **5b** remains hypothetical pending crystallographic study. It would be formed *via* **3b** and **7**. **3b** could arise by nucleophilic attack of the nitro group[20] on an intermediate nitrilimine.[12,32]

[32] R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962).

[33] R. M. Anderson and J. K. Way, *J. Chem. Soc. C*, 1139 (1967).

[34] J. Schmutz, F. Hunziker, and W. Michaelis, *Helv. Chim. Acta*, **47**, 1986 (1964).

[35] M. P. Schmidt and A. Hagenbocker, *Ber.*, **54**, 2191, 2201 (1921).

[36] For reviews, see M. Ohta and H. Kato in "Nonbenzenoid Aromatics," J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, pp 117–248, and L. C. Behr in "The Chemistry of Heterocyclic Compounds," Vol. 17, A. Weissberger, Ed., Interscience, New York, N. Y., 1962, p 323.

[37] M. J. Perkins, *J. Chem. Soc.*, 3005 (1964).

[38] P. Tavs, H. Sieper, and H. Beecken, *Justus Liebigs Ann. Chem.*, **704**, 150, 161, 166, 172 (1967).

[39] C. W. Rees and R. C. Storr, *J. Chem. Soc. C*, 756 (1969).

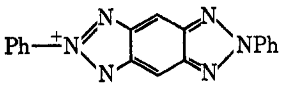
[40] R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *J. Amer. Chem. Soc.*, **89**, 2618, 2626, 2633, 2638 (1967).

[41] R. A. Carboni, U. S. Patent 3,190,886 (1965); *cf. Chem. Abstr.*, **63**, 11749*d* (1965).

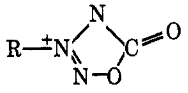
[42] A. W. Murray and K. Vaughan, *Chem. Commun.*, 1282 (1967).

[43] A strong case can also be made that 2*H*-triazoles and 2*H*-benzotriazoles are best represented as cyclic azimines. For evidence, see A. J. Boulton, P. J. Halls, and A. R. Katritzky, *Org. Mag. Resonance*, **1**, 311 (1969), and H. Günther and H.-H. Hinrichs, *Justus Liebigs Ann. Chem.*, **706**, 1 (1967). For reviews, see J. H. Boyer in "Heterocyclic Compounds," Vol. VII, R. C. Elderfield, Ed., Wiley, New York, N. Y., 1961, p 384, and F. R. Benson and W. L. Savell, *Chem. Rev.*, **46**, 1 (1950).

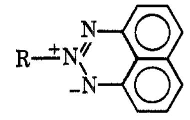
[44] However, see H. Kato, T. Shiba, H. Yoshida, and S. Fujimori, *Chem. Commun.*, 1591 (1970).



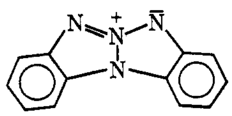
Reference 35



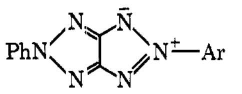
Reference 36



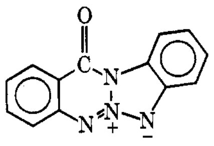
R = alkyl,[37] aryl,[37,38] NH_2[39]



Reference 40



Reference 41



Reference 42

only acyclic azimines reported have been found by Fahr[6] to decompose *in situ*, in contrast to more stable semicyclic ones prepared by an analogous route. Further attempts to obtain acyclic azimines will be reported subsequently.[5,7]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137, ultraviolet–visible spectra on a Beckman DK-2A, and pmr spectra on a Varian A-60. Solvents used for spectra were Spectro Grade, except for DMSO, which was reagent grade, redistilled from calcium hydride at reduced pressure. Reaction and chromatographic solvents were redistilled before use. Drying of wet solutions was by means of magnesium sulfate unless otherwise noted.

***o*-Nitrobenzaldehyde Phenylhydrazone.**—*o*-Nitrobenzaldehyde (20.0 g, 0.132 mol) was dissolved in a mixture of 40 ml of water and 65 ml of ethanol, and added to a solution of 14.3 g (0.132 mol) of phenylhydrazine in 100 ml of water containing 30 ml of acetic acid. After 1 hr, the mixture was cooled in ice and filtered, and the precipitated product was washed with water and then ethanol. Drying over potassium hydroxide left 30.78 g of bright red solid, mp 154–156° (97%) (lit.[45] mp 154°).

Formation of A (5b).—The hydrazone (5.00 g, 20.7 mmol) and anhydrous sodium acetate (12.0 g, 146 mmol) were suspended in 50 ml of glacial acetic acid. A solution of bromine (6.72 g, 42.0 g-atoms) in 20 ml of acetic acid was added dropwise while the solution was stirred. After 1 hr, there remained a brown solution containing a red precipitate, which was poured into 200 ml of water and stirred until the precipitate had become completely yellow. The mixture was then filtered, and the precipitate was washed with water, 5% $NaHCO_3$ solution, water, and ethanol. After drying over KOH, the solid was recrystallized from chloroform, leaving yellow needles, mp 138° dec, yield 3.33 g (46%). The mother liquor yielded an additional 0.93 g, mp 134° dec, on evaporation (lit.[8] mp 144° dec): ir (KBr disc) 3.26 (w, CH), 6.14 (vs, C═N or C═O), 6.36 (m) and 6.76 (m) (Ar), 7.61 (s), 7.94 and 8.03 (d, s), 8.37 (s, $=N^+$-O^-?), 8.67 (m), 9.92 (m), 11.47 (m), 12.17 (m, para-substituted), and 13.18 μ (s, ortho-substituted); uv (95% EtOH) λ_{max} 400 nm (ϵ 5.56×10^3), 286 (1.17×10^4); nmr (CF_3COOH) two multiplets of equal intensity at τ 1.52 and 2.26.

Reduction of A (5b) to B (6b).—Material A (3.13 g, 9.87 mmol) was dissolved in a mixture of 15 ml of acetic acid and 40 ml of concentrated aqueous HCl. The solution was cooled in ice and stirred magnetically while a solution of $SnCl_2 \cdot 2H_2O$ (3.00 g, 13.3 mmol) in 10 ml of concentrated HCl was added dropwise. The mixture was allowed to warm to room temperature and filtered, and the precipitate was washed with 3% HCl (twice) and then with warm (60°) water. The product was recrystallized from methanol-ethanol, yielding 1.69 g (57%) of yellow powder, mp 199–200° (lit.[9] mp 197°). Filtration of the hot alcohol solution during recrystallization gave an orange solid, mp >270°, which showed no carbonyl group in the infrared. Ir of 6b (KBr disc) 3.25–3.35 (w, CH), 5.97 (vs, C═O), 6.38 (w) and 6.79 (m) (Ar), 7.12 (m), 7.50 (m), 7.74 (m), 7.86 (s), 8.82 (m), 9.07 (m), 9.37 and 9.45 (d, m), 9.92 (m), 11.98 (s, para-substituted), and 12.96 μ (s, ortho-substituted); uv (95% EtOH) λ_{max} *ca.* 350 nm (sh, ϵ 13,500), 312 (17,400), 285 (sh, 14,200), and 237 (12,200); nmr (DMSO, 100°) given in text; nmr (CF_3COOH) τ 1.54 (d, $J \approx 9$ Hz, 2 H), 1.42 (s, 4 H), 2.18 (d, $J \approx 9$ Hz, 2 H); mass spectrum (direct inlet at 90°, 50 V ionizing voltage) *m/e* (rel intensity) 303, 301 (24.1,[46] P), 273, 275 (1.4,[46] P − N_2 or CO), 245, 247 (1.2,[46] P − N_2 − CO), 222 (1.3, P − Br), 194 (2.5, P − N_2 or CO − Br), 183, 185 (23.3,[46] $BrC_6H_4N_2^+$), 166 (13.8, P − Br − N_2 − CO), 155, 157 (100.0,[46] $BrC_6H_4^+$), 90 (62, $C_6H_4N^+$), 76 (91, $C_6H_4^+$), 75 (74, $C_6H_3^+$), 64 (25.8, $C_5H_4^+$), 63 (38.8, $C_5H_3^+$), 50 (53.4, $C_4H_2^+$), 39 (34.4, $C_3H_3^+$), 31 (37.9).

3-(*p*-Bromophenyl)benzo-1,2,3-triazin-4-one.—1-(*o*-Carbomethoxyphenyl)-3-(*p*-bromophenyl)triazene was prepared by coupling of diazotized methyl anthranilate (1.4 g, 20 mmol) with *p*-bromoaniline (3.0 g, 18 mmol) according to the method of Chattaway.[9] The crude triazene was refluxed for 2 hr in 60 ml of 67% aqueous ethanol containing 3 ml of triethylamine. Cooling to room temperature gave a precipitate which was washed with ethanol and recrystallized from ethanol, yielding white benzotriazinone, yield 1.80 g (33% overall), mp 204–206° (lit.[9] mp 196°). The infrared spectrum was clearly different from that of 6 (for example, $\nu_{C=O}$ at 1689 cm^{-1} or 5.92 μ). A mixture melting point of 6 and the triazinone was *ca.* 160–175°. Uv (95% EtOH) showed λ_{max} 315 nm (ϵ 10,000), 301 (10,200), and *ca.* 285 (sh, 9300).

Reduction of 6b.[9]—The azimine **6b** (0.201 g, 0.67 mmol) was suspended in a mixture of 5 ml of acetic acid and 4 ml of concentrated HCl, and mossy tin (0.499 g, 4.1 mg-atoms) was added. The mixture was stirred at room temperature for 19 hr, diluted with 10 ml of water, and neutralized with sodium bicarbonate until a precipitate just began to form. The mixture was then extracted with four 25-ml portions of ether, which were washed with water and sodium bicarbonate solution until neutral, and then dried over $MgSO_4$ and evaporated, leaving 0.149 g of light brown solid, mp 162–167° (68% crude yield). Recrystallization from ethanol gave white needles, mp 184.5–185°, of *o*-aminobenzoyl-*p*-bromophenylhydrazide. The ir spectrum (KBr disc) showed important bands at 3.15 (s, NH), 6.14 (s, >C═O), 12.1 (s, para-substituted), and 13.3 (s, ortho-substituted).

***o*-Aminobenzoyl-*p*-bromophenylhydrazide.**—*p*-Bromophenylhydrazine (mp 104–106°, prepared in 60% yield by the method of Michaelis[47]) (0.873 g, 4.67 mmol) and 0.762 g (4.67 mmol) of isatoic anhydride were refluxed for 20 hr in 20 ml of dioxane. The mixture was poured into 50 ml of 5% aqueous HCl, and extracted with three 20-ml portions of ether. The aqueous layer was made alkaline with sodium hydroxide, and extracted again with three 20-ml portions of ether. The latter ether layers were combined, dried over $MgSO_4$, and evaporated, leaving 0.33 g (23%) of crude product. Recrystallization from ethanol gave mp 180–183°, mixture melting point with the previous sample, 180–183°. The infrared spectra of the two samples were identical.

Reaction of Anthranilamide with 9.[25]—Anthranilamide (2.72 g, 20.0 mmol) was suspended in 20 ml of absolute ethanol and added dropwise to a solution of *p*-nitroso-*N*,*N*-dimethylaniline (**9**, 3.00 g, 20.0 mmol) in 20 ml of 50% ethanol-acetic acid. The mixture was refluxed for 10 min, and then allowed to stand in a refrigerator (5–10°) for 19 hr. Filtration gave a small amount of brown solid, mp 231–237°. Addition of ether to the filtrate yielded a larger quantity of precipitate, which was also collected, giving a total of 0.88 g of crude C (36%). Recrystallization from dimethyl sulfoxide (three times) gave red needles (blue reflection), mp 243–244° (lit. mp[27] for *p*,*p*′-bis(dimethylamino)azoxybenzene, 244.5°; reported by Jennen,[25] 249°).

Anal. Calcd for $C_{16}H_{20}N_4O$: C, 67.61; H, 7.04; N, 19.72. Found: C, 67.58; H, 6.97; N, 19.69. Found:[25] C, 67.32; H, 7.05; N, 20.34.

The ir spectrum showed bands at *ca.* 3.4 (w, CH), 6.25 (s), 6.60 (m), 6.95 (w), 7.34 (s, -N═NO), 7.95 (w), 8.14 (w), 8.60

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[45] C. Paal and A. Bodewig, *Ber.*, **25**, 2903 (1892).

[46] Intensity of ^{79}Br peak, relative to base peak at *m/e* 155. The ^{81}Br isotopic peak had an intensity of *ca.* 97% that of the ^{79}Br for all bromine-containing peaks.

[47] L. Michaelis, *Ber.*, **26**, 2190 (1893).

(s), 10.59 (m), 12.15 and 12.30 μ (s, para-substituted). The nmr spectrum is given in the text.

Reaction of 9 with Indazolinone.—Indazolinone (2.68 g, 20.0 mmol) was suspended in 20 ml of methanol, and dissolved by adding 1.2 g (21 mmol) of KOH. A nitrogen atmosphere was established, and then a solution of 3.00 g (20.0 mmol) of **9** in 40 ml of methanol was added dropwise. After 2 hr, the methanol solvent was stripped off, the nearly black residue was added to 100 ml of water, and the mixture was extracted repeatedly with methylene chloride until the coloration of the organic layer was only light purple. The methylene chloride solutions were combined, dried with $MgSO_4$, and evaporated, leaving a dark purple residue. This was triturated with carbon tetrachloride, and the residue was recrystallized from chloroform and then dimethyl sulfoxide, giving a purple compound, mp *ca.* 186°. This was further purified by slow evaporation of a saturated 95% methanol–5% CCl_4 solution to give blue needles, mp 199–200° (lit.[25] mp for D, 198°).

Anal. Calcd for $C_{15}H_{14}N_4O$: C, 67.66; H, 5.26; N, 21.05. Found: C, 67.43; H, 5.37; N, 20.98.

Chromatography of the combined residue from evaporation of the CCl_4 triturate and the mother liquors from the recrystallizations on silica gel produced (1) *p,p'*-bis(dimethylamino)azobenzene, yield 0.21 g (8%), mp 264–268° (from benzene), identified by ir comparison with authentic[48] spectrum (lit.[49] mp 273°); (2) *N*-benzoyl-*N'*,*N'*-dimethyl-*p*-phenylenediamine, yield 0.14 g (3%), mp 220–225°, identified by ir and mixture melting point comparison with authentic material; (3) *N*,*N*-dimethyl-*p*-phenylenediamine, yield 0.25 g (9%), identified by vpc (150°, 15% SF-96 column) and ir comparison with authentic material; (4) additional D. Spectral data for D follow: ir (KBr disc) 3.35 (w, CH), 6.04 (s, C═O), 6.24 (s), 6.52 (m), 6.90 (s), 7.26 (s), 7.50 (m), 7.81 (s), 8.71 (s), 9.29 (s), 9.58 (s), 10.60 (m), 11.48 (m), 12.30 (s), 12.80 (m), 14.12 (m), 14.70 μ (m); nmr (DMSO-d_6), see text; nmr (CF_3COOH) τ 1.54 (d, $J \approx 10$ Hz, 2 H), 2.1 (m, 4 H), 2.78 (d, $J \approx 10$ Hz, 2 H), and 6.42 (s, 6 H); uv (95% EtOH) λ_{max} 548 nm (ε 86,000), 322 (sh, 5000), 298 (8800), 292 (9600), 238 (14,600), 228 (15,700) (The long-wavelength maximum appeared at 530 nm in $CHCl_3$, 522 nm in dioxane.); mass spectrum (direct inlet, 120°, 70 eV ionizing voltage) *m/e* (rel intensity) 267 (18.2, P + 1), 266 (100.0, P), 265 (9.4, P − H), 250 (2.9, P − H − CH_3), 238 (11.5, P − N_2 or CO), 237 (14.6, P − N_2 or CO − H), 223 (6.2, P − N_2 or CO − CH_3), 222 (5.7, P − N_2 or CO − CH_3 − H), 209 (7.8, P − N_2 − CO − H), 195 (15.6, P − N_2 − CO − CH_3), 167 (9.4, $C_6H_5NC_6H_4^+$), 134 (14.6, $Me_2NC_6H_4N^+$), 133 (16.2, P^{2+} or 134 H), 120 (43.2, $Me_2NC_6H_4^+$), 119 (19.8), 105 (26.0), 104.5 (9.9), 104 (18.8), 93 (9.4), 92 (8.9), 91 (9.9), 90 (10.4, $C_6H_4N^+$), 79 (13.5), 78 (13.0), 77 (24.5), 65 (7.8), 63 (10.4), 51 (4.2), 42 (31.8), 39 (9.9).

Reduction of 6c.—**6c** (0.205 g, 0.77 mmol) was reduced with tin in the same manner as **6b**, but no product was obtained from the ether extracts of the acidic solution. Therefore, the aqueous layers were made basic with sodium hydroxide and extracted with four additional 25-ml portions of ether. Drying and evaporating the latter ether layers left 0.107 g of liquid, which darkened rapidly on exposure to air. The infrared spectrum was essentially identical with that of *N*,*N*-dimethyl-*p*-phenylenediamine, but vpc analysis (SE-30, 135°) showed an additional, higher boiling component in addition to the diamine. The ir spectrum and air sensitivity suggested that the latter might be *p*-(dimethylamino)phenylhydrazine.[30] An attempt to obtain a hydrazone by reaction of the material with benzaldehyde[30] failed.

Registry No.—**6b**, 33986-95-7; *o*-aminobenzoyl-*p*-bromophenylhydrazide, 33986-96-8; *N*-benzoyl-*N*,*N'*-dimethyl-*p*-phenylenediamine, 33986-97-9; *N*,*N*-dimethyl-*p*-phenylenediamine, 99-98-9.

Acknowledgment.—We gratefully acknowledge support from Rohm and Haas Co. and from the Research Foundation of State University of New York.

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[48] Sadtler Standard Infrared Spectra, Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1970, No. 18592.

[49] D. Vorländer and E. Wolferts, *Ber.*, **56**, 1238 (1923).

Azimines. II. Reactions of Nitrenes with Azo Compounds

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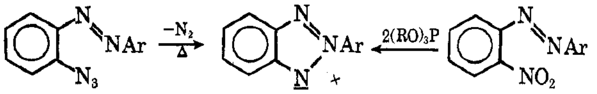
Syntheses of azimines by reaction of nitrenes with azo compounds are explored. The major product from the thermolysis of ethyl azidoformate in azobenzene is ethyl 2-(phenylazo)carbanilate, apparently formed by rearrangement of an azimine intermediate, **5**. No reaction occurred between *N*-phthalimidylnitrene and diethyl azodicarboxylate. The reaction of 2-(4'-dimethylaminophenylazo)benzhydrazide with nitrous acid did not give isolable 2-(4'-dimethylaminophenylazo)benzazide; the major product of the reaction was 3-(4'-dimethylaminophenyl)-3*H*-benzo-1,2,3-triazin-4-one (**15**). The expected azimine, *anhydro*-2-(4'-dimethylaminophenyl)-3*H*-benzo-1,2,3-triazinium-4-one hydroxide (**12**), was only obtained in low yield and did not undergo conversion to **15** under the reaction conditions.

Having studied a number of aromatic heterocycles containing the 1,3-dipolar azimine grouping,[1] $RN{=}N^{+}{-}(R)N^{-}R$, we wished to explore possible synthetic routes to acyclic azimines. One such route which appeared promising was addition of a nitrene to an azo group.

Electrophilic nitrenes add readily to pyridines, sulfides, and sulfoxides to give dipolar adducts.[2-5] Analogous addition to the azo group therefore appeared plausible, despite the low basicity of azo compounds. Formal intramolecular examples of such a reaction



(1)

have been reported (*e.g.*, eq 1);[6,7] however, the actual intermediacy of nitrenes in these reactions is not probable.[8] Moreover, the isolation of azobenzenes in good yields from reactions producing arylnitrenes[9] suggests that the reactivity of these nitrenes toward azobenzenes cannot be high.

Early attempts to study the reaction of carbethoxy-

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[1] R. C. Kerber, *J. Org. Chem.*, **37**, 1587 (1972).

[2] K. Hafner, D. Zinser, and K. L. Moritz, *Tetrahedron Lett.*, 1733 (1964).

[3] T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes, and Arynes," Appleton-Century-Crofts, New York, N. Y., 1969, p 98.

[4] W. Lwowski in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, p 216.

[5] D. S. Breslow, ref 4, pp 277–279.

[6] R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *J. Amer. Chem. Soc.*, **89**, 2618, 2633, 2638 (1967).

[7] J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 4831 (1965).

[8] P. A. S. Smith, ref 4, pp 138–141; J. H. Hall, 15th Annual Report on Research, Petroleum Research Fund, 1970, p 37.

[9] P. A. S. Smith, ref 4, pp 114–119.