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

Azimines. II. Reactions of Nitrenes with Azo Compounds

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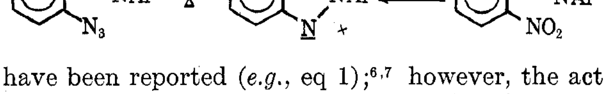
Syntheses of azimines by reaction of nitrenes with azo compounds are explored. The major product from the thermolysis of ethyl azidoformate in azobenzene is ethyl 2-(phenylazo)carbanilate, apparently formed by rearrangement of an azimine intermediate, **5**. No reaction occurred between *N*-phthalimidylnitrene 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.

nitrene with diethyl azodicarboxylate were reported by Hancock[10] and by Lwowski.[11] Photolysis of ethyl azidoformate in the presence of diethyl azodicarboxylate gave triethyl nitrilotricarboxylate; the intermediacy of a triaziridine or an azimine was postulated. However, an attempt to generate the singlet nitrene by α elimination in the presence of the azo compound failed to produce the same product, owing to decomposition of the azo compound.[11] It appeared to us that reaction of the electrophilic intermediate, carbethoxynitrene, with a more nucleophilic azo compound would have a better chance of success, and hence we chose to study initially the reaction of carbethoxynitrene with azobenzene. Thermolysis of the azide, which gives initially only the singlet nitrene, appeared preferable to photolysis, which gives both singlet and triplet.[12]

Reaction of Carbethoxynitrene with Azobenzene.—When ethyl azidoformate was thermolyzed in the presence of excess azobenzene at 115–117°, 78% of the azobenzene was recovered by chromatography on acid-washed alumina. The recovered azobenzene was found to contain a higher boiling contaminant by vpc. Isolation by preparative gas chromatography gave a red oil, which was identified by ir and uv as 2-(phenylazo)biphenyl (**1**).

An additional minor product eluted from the column after the azobenzene. This proved to be 4-(phenylazo)biphenyl (**2**), obtained in 0.4% yield. Initial identification by ir and melting point was supported by a mass spectrum which showed important peaks at *m/e* 258 (parent), 181 ($C_6H_5C_6H_4N_2^+$), 153 (base, $C_6H_5C_6H_4^+$), 105 ($C_6H_5N_2^+$), and 77 ($C_6H_5^+$), as reported elsewhere for **2**.[13]

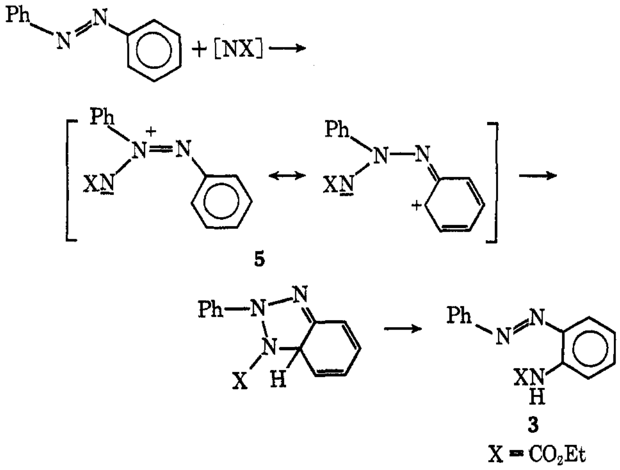
The only product directly arising from the nitrene was obtained as red-orange needles melting at 68.0–69.2°. The spectral data and microanalysis are consistent with structure **3**, ethyl 2-(phenylazo)carbanilate. The ir spectrum showed carbonyl absorption at 1736, a strong N–H stretch at 3311, and mono- and *o*-phenyl substitution at 773, 686, and 732 cm^{-1}, respectively. The pmr spectrum (CCl_4) showed an N–H absorption at τ 1.65, which disappeared after a solution of **3** was shaken with D_2O. The carbethoxy protons absorbed at τ 5.83 (q, $J \approx 7$ Hz, 2 H) and 8.73 (t, $J \approx 7$ Hz, 3 H). The aromatic region showed a one-proton doublet at τ 1.56 ($J \approx 8$ Hz), a three-proton multiplet at 2.3, a four-proton multiplet at 2.7, and another one-proton doublet at 3.03 ($J \approx 8$ Hz). The yield of **3** in a number of runs of the reaction fell in the 3–10% range.

Further elution of the column failed to yield any additional characterizable products. Comparisons of the eluate with an authentic sample (vpc, tlc) showed that it did not contain any ethyl *p*-(phenylazo)carbanilate (**4**). A quantity of **4** corresponding to 2% was readily detectable.

The formation of the carbanilate **3** was at first surprising, since singlet carbethoxynitrene does not ordinarily insert into aromatic C–H bonds.[14] Carbanilate products, when formed, have been found to arise primarily from acid-catalyzed rearrangement of initially formed azepines.[2,14] Since acidic alumina was used on work-up (**3** being unstable to basic alumina), we suspected that **3** might have been produced during chromatography. This possibility was excluded by demonstrating that (a) *N*-carbethoxyazepine could be recovered in 94% yield on chromatography on acidic alumina, no ethyl carbanilate being formed; and (b) **3** was present in the crude product prior to chromatography, as shown by vpc analysis. Again, **4** could not be detected. Formation of **3** by thermal rearrangement of an azepine under the reaction conditions cannot be absolutely excluded; however, the absence of any para isomer, **4**, makes this route (or direct insertion) seem improbable.

The exclusive formation of the ortho carbanilate **3** seems to us to suggest involvement of the azo group with the nitrene in the course of the reaction (Scheme I). We propose initial formation of the azimine **5**, which rearranges to **3** under the reaction conditions. Such a rearrangement is analogous to the well-known Wallach rearrangement of azoxybenzenes to 2-hydroxyazobenzenes.[15] The phenylazobiphenyl products produced must be formed by means of phenyl radicals arising from some reaction intermediate. (Azobenzene itself does not decompose to phenyl radicals below 600°.)[16]

SCHEME I



Decomposition of **5** by a route analogous to that proposed by Lwowski[11] and Hancock[10] would have yielded ethyl diphenylcarbamate, which could not be detected in the crude reaction product nor among the chromatographic fractions by tlc or vpc.

Attempted Reaction of *N*-Phthalimidylnitrene with Diethyl Azodicarboxylate.—A number of nucleophilic aminonitrenes have recently been shown to add to electrophilic alkenes, giving aziridines.[17] Since the simplest aminonitrenes, 1,1-dialkyldiazenes, apparently do not add in this fashion,[18] we chose to study the reaction of *N*-phthalimidylnitrene with the electrophilic diethyl azodicarboxylate (**6**). The nitrene was generated by *in situ* oxidation of *N*-aminophthalimide (**7**) with lead tetraacetate. The products obtained, phtha-

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[10] J. Hancock, *Tetrahedron Lett.*, 1585 (1964).

[11] W. Lwowski, *ibid.*, 1591 (1964).

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[13] N. S. Vul'fson, V. A. Puchkov, and Y. S. Nekrasov, *J. Gen. Chem. USSR*, **38**, 1337 (1968); *cf. Zh. Obshch. Khim.*, **38**, 1385 (1968).

[14] Reference 4, p 206.

[15] G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970).

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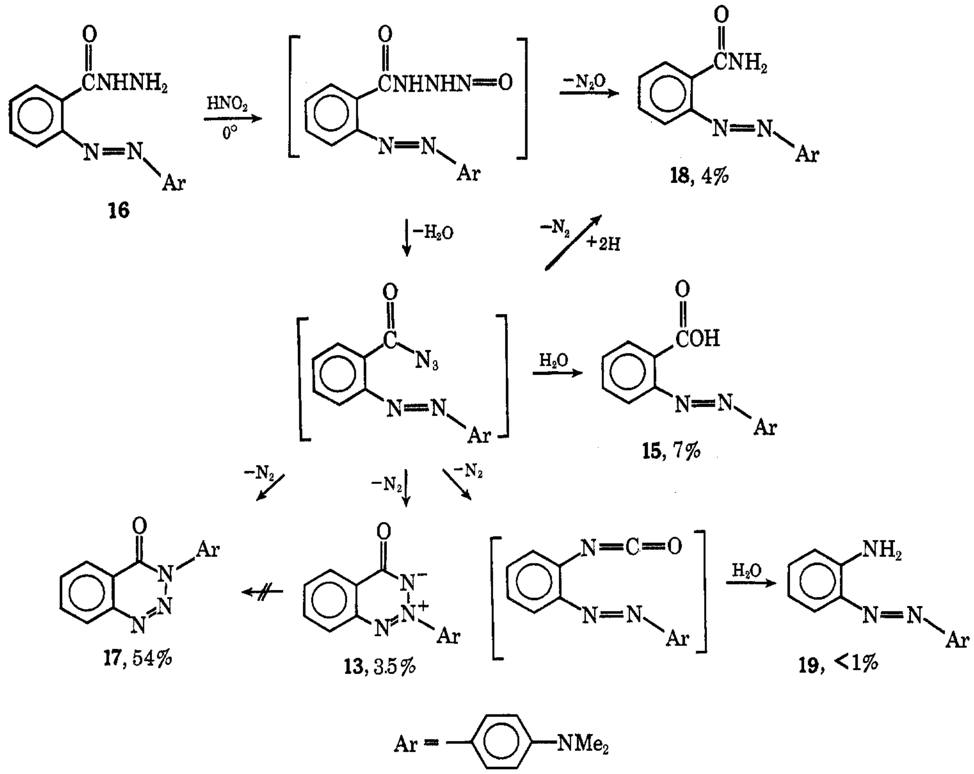
[18] D. M. Lemal, ref 4, p 363.

SCHEME II



lic anhydride (**8**), 4%, phthalimide (**9**), at least 53%, and 1,4-bisphthaloyltetrazene (**10**), 14%, were the same as obtained in the absence of **6**. The recovery of **6** was only 54% due to substantial decomposition. Some diethyl hydrazinedicarboxylate (**11**) was also formed, apparently by reaction of **6** with the intermediate, 1,4-diphthaloyltetrazane.[19,20]

Subsequent to this work, Koch and Fahr[21] reported successful reactions of even more nucleophilic 1,1-dialkyldiazenes with **6** and with the cyclic azo compound, 4-phenyl-1,2,4-triazoline-3,5-dione. From their results, it is probable that any azimine formed in our reaction would have decomposed to *N*-carbethoxyphthalimide[22] and ethyl azidoformate. The apparent absence of these products in our mixtures confirms the failure of *N*-phthalimidylnitrene to react with **6** to form an azimine. Dreiding[23] has reported the reaction of the nitrene with azoalkanes and azoarenes to form azimines, in contrast to **6**.

We next attempted to observe an intramolecular reaction of a nitrene with an azo group, because of the apparent greater stability of cyclic azimines.[1] Preparation of the previously examined,[1] stable azimine, *anhydro*-2-(*p*-dimethylaminophenyl)-3*H*-benzo-1,2,3-triazinium-4-one hydroxide (**13**), was therefore undertaken.

Synthesis and Decomposition of 2-(4′-Dimethylaminophenylazo)benzazide (14).—Numerous attempts to prepare azide **14** directly from the acid **15** (methyl red) failed. **15** could not be converted to its acid chloride using thionyl chloride, with or without sodium carbonate present,[24] or phosphorus pentachloride. In all cases only deeply colored tars were produced. An attempt to prepare the azide *via* the mixed carbonic anhydride[25] gave only recovered acid (92%). Consequently, an alternative route *via* the hydrazide **16** was used (Scheme II). **16** was synthesized from methyl anthranilate by standard reactions (overall yield 50%).

Inasmuch as photolysis of an acyl azide generally gives the nitrene whereas thermolysis gives Curtius rearrangement *via* a concerted route,[26] we proposed to study the former. However, the products obtained directly from the nitrosation of 2-(4′-dimethylaminophenylazo)benzhydrazide (**16**) were found to be the same as when the reaction was followed by photolysis. Evidently the azide **14** is susceptible to direct intramolecular thermal reaction (or is unstable even to room light). Facile intramolecular displacement of N_2 from *o*-arylazophenyl azides is well documented.[6,7]

When **16** was treated with nitrous acid at 0°, the azide **14** could not be detected by ir. The reaction mixture proved to contain 3-(4′-dimethylaminophenyl)-3*H*-benzo-1,2,3-triazin-4-one (**17**) as the major product (54%) and not the expected cyclic azimine **13**, which was obtained in 3.5% yield. A number of other minor products were also obtained (Scheme II). The carboxylic acid **15** presumably arises from nucleophilic displacement of the azide ion from **14** by water, whereas 2-(4′-dimethylaminophenylazo)benzamide (**18**) can be produced either by hydrogen abstraction by the nitrene or directly from the nitrosated benzhydrazide.[27] The 2-(4′-dimethylaminophenylazo)aniline (**19**) is envisioned as the final product of a Curtius rearrangement[26]

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[19] L. Hoesch and A. S. Dreiding, *Chimia*, **23**, 405 (1969).

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[25] J. Weinstock, *J. Org. Chem.*, **26**, 3511 (1961).

[26] Reference 4, pp 217–221.

[27] J. Honzl and J. Rudinger, *Collect. Czech. Chem. Commun.*, **26**, 2333 (1961).

followed by hydrolysis of the isocyanate. One unidentified material, **20**, was also obtained (see Experimental Section).

The mechanism of formation of the benzotriazinone **17** is under investigation at the present time. The "obvious" route, rearrangement of azimine **13**, is excluded by the thermal stability of **13**; moreover, photolysis of **13** under the same conditions as used in the photolytic reaction failed to convert **13** to **17**; **13** was quantitatively recovered.

Conclusions

Although reaction of nitrenes with azo compounds is on paper the simplest route to azimines, it appears to lack synthetic generality. Indeed, in the three cases we have examined, only the intramolecular reaction gives any isolable azimine at all. The failure to isolate azimines in the other cases evidently arises from too low reactivity of nitrene toward azo compound and instability of azimine toward reaction conditions. The latter is a particularly serious problem, since it appears that acyclic azimines may frequently be too unstable to survive the high-energy conditions (high temperatures or photolysis) necessary to generate nitrenes.

Experimental Section

All melting points were measured on a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137 NaCl spectrophotometer. Ultraviolet-visible spectra were obtained on a Beckman DK-2A and pmr spectra on a Varian Model A-60, using tetramethylsilane as internal standard unless otherwise noted. 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. Solutions were dried using sodium sulfate except as noted. The vapor phase chromatographic measurements were performed on a Varian Aerograph Series 1200 chromatograph equipped with a flame ionization detector. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Meade Microanalytical Laboratory, Amherst, Mass. Mass spectra were obtained from Morgan-Schaffer Corp., Montreal, on a Hitachi Perkin-Elmer RMU-6D.

Thermolysis of Ethyl Azidoformate in Azobenzene.—Azobenzene (25.68 g, 141 mmol, mp 66–67.5°) and ethyl azidoformate (6.66 g, 57.9 mmol) were heated slowly in a flask equipped with a magnetic stirrer, thermometer, condenser with Nujol bubbler gas exit tube, and a dropping funnel. No appreciable N_2 evolution occurred until the temperature reached 115°. The contents of the flask were allowed to come to room temperature after a total reaction time of 3 hr at 115°, by which time nitrogen evolution had ceased. Chromatography of the resulting mixture on acidic alumina afforded, first, unreacted azobenzene, 19.97 g (77.6% recovery), eluted with benzene, and identical with starting material by ir and mixture melting point. However, a vpc analysis (5 × $^1/_8$ in. 5% SE-30 column, programmed from 130 to 230°) showed a higher boiling contaminant. Partial sublimation of the azobenzene fraction at 74–76° (0.20 Torr) gave a residue (18 mg) enriched in the unknown material (*ca.* 75%). Preparative vpc collection of this unknown (5 ft × $^1/_4$ in. 3% SE-30 on Varaport column) yielded 9.6 mg of red oil **1**: ir (neat film) 3.3 (m) and 3.45 (m, CH), 13.16 (m, monosubstituted), 13.65 (s, ortho-substituted), 14.35 (s), and 14.55 (s, monosubstituted) (lit.[28] mp 37–39°); uv (95% EtOH) λ_{max} 231 nm (ϵ 26,300), 322 (18,500), 440 (810).

Contained elution of the column with benzene increasingly rich in CCl_4 afforded a fraction (8.27 mg) of crude **2**, mp 50–83°. Recrystallization from CCl_4–pentane gave orange platelets: yield 14.68 mg (0.4%, based on azobenzene consumed); mp 154–155° (lit.[29] mp 154–155°); ir (Nujol) 3.32 (w, CH), 3.47 (w, CH), 11.80 (s, para-substituted), 12.98 (s, monosubstituted), and 14.5 (s, monosubstituted); uv (95% EtOH) λ_{max} 340 nm (ϵ 27,000) and 234 (14,300); mass spectrum[13] (indirect inlet at 250°, 70 eV ionizing voltage) *m/e* (rel intensity) 259 (8.1, P + 1), 258 (39.2, P), 230 (3.0, P − N_2), 228 (3.6, P − N_2 − H_2), 182 (1.9, P − C_6H_4), 181 (9.4, P − C_6H_5), 154 (13.3, P − $C_6H_4N_2$), 153 [100, P − $C_6H_5N_2$ ($C_{12}H_9^+$)], 152 (51.1, $C_{12}H_8^+$), 151 (13.3), 128 (1.8), 127 (7.1, $C_{10}H_7^+$), 105 (9.8, $C_6H_5N_2^+$), 78 (5.0), 77 (62.7, $C_6H_5^+$), 51 (13.4, $C_4H_3^+$), 43 (4.4), 28 (13.4), 18 (9.4).

Continued elution with carbon tetrachloride gave a red-orange oil, **3** (0.861 g, 3.20 mmol, 10%), which decomposed slowly in solution at room temperature. An analytical sample obtained by crystallization from ethanol–water was obtained as deep orange needles, mp 68.0–69.2°. (The reported melting points of the meta and para isomers of **3** are 102–103°[30] and 153°,[31] respectively.)

Anal. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.62; N, 15.60. Found: C, 66.74; H, 5.70; N, 15.36.

The ir spectrum (neat melt) showed bands at 3.02 (m, NH), 3.27 (w), 3.31 (m, CH), 5.76 (s, C=O), 12.93 and 14.57 (s, monosubstituted), and 13.62 μ (m, ortho-substituted). The pmr spectrum is given in the text; uv (95% EtOH) 227 nm (ϵ 16,300), 245 (sh, 13,700), 321 (12,200), 365 (sh, 7000), 450 (sh, 1250).

Further elution of the column with increasing amounts of ether in CCl_4 and then methylene chloride afforded a deep red oily fraction (*ca.* 1 g). Vpc analysis of this material (5% SE-30, 180°) showed that it contained at least five components. Attempts to isolate pure components failed. The ir spectrum of the mixture showed a broad carbonyl absorption at 5.82 μ and broad peaks at 13.1 and 14.4 μ. A comparison of this mixture with anticipated possible products by vpc and tlc showed the absence of ethyl phenylazocarboxylate, ethyl carbamate, ethyl carbanilate, ethyl diphenylcarbamate, and ethyl *p*-(phenylazo)-carbanilate.

Final elution of the column with increasing amounts of ethanol yielded 10.85 g of a tarry brown residue from which no characterizable materials could be obtained.

Various runs employing excess azobenzene gave 3–10% yields of **3**. Yields of **1** and **2** fell always below 1%. The recovery of azobenzene in all runs fell in the range of 78–89%.

Attempted Reaction of *N*-Phthalimidylnitrene with Diethyl Azodicarboxylate.—To a suspension of *N*-aminophthalimide[32] (**7**, 0.504 g, 3.11 mmol) in a 20-ml dichloromethane solution of diethyl azodicarboxylate (**6**) [Aldrich, distilled at 85° (3.5 Torr), 0.543 g, 3.11 mmol] was added 1.38 g (3.11 mmol) of lead tetraacetate in small portions over a 10-min period. The mixture was allowed to stir at room temperature for 1 hr, then evaporated to dryness to remove acetic acid. Addition of 50 ml of dichloromethane allowed the collection of precipitated lead diacetate (1.03 g, 100%). A concentrated benzene solution of the filtrate was then placed on a silica gel column. Elution with benzene, followed by mixtures increasingly rich in dichloromethane, afforded first a yellow band of unreacted **6**, 0.3119 g, from which 0.018 g (0.122 mmol) of phthalic anhydride (**8**) crystallized out upon standing (3.9% yield), mp 130–131° (lit.[33] mp 130.8°), ir spectrum identical with that of an authentic sample. The total recovery of unreacted **6** was 54%. Continued elution with dichloromethane and 1% ethanol in dichloromethane gave an oily solid (0.444 g). Fractional crystallization with CH_2Cl_2–PhH–ether afforded 0.243 g (53%) of phthalimide **9**, mp 230–238°. Recrystallization from ether gave mp 236–238° (lit.[34] mp 238.5–240°), ir spectrum identical with that of an authentic sample. The viscous filtrate (0.2 g) obtained from the recrystallization of **9** was shown by vpc analysis (5% SE-30, 160°) to contain additional phthalimide and a minimum of eight other components, two of which were identified as diethyl hydrazinedicarboxylate (**11**) and triethyl hydrazinetricarboxylate (**12**) by vpc comparison with authentic samples. Further elution with 5% ethanol in dichloromethane gave after drying a

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[33] "Handbook of Chemistry and Physics," 39th ed, C. D. Hodgman, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1958, p 1110.

[34] P. Hope and L. A. Wiles, *J. Chem. Soc.*, 4583 (1965).

semisolid (119 mg). Washing this material with anhydrous ether left a beige solid which gave long platelets from a slowly evaporating dichloromethane solution. Obtained was 73.6 mg (0.214 mmol, 14%) of 1,4-bisphthaloyltetrazene (**10**): mp 267–269° dec (lit.[19] mp 263–268° dec); ir (KBr) 3.32 (w, CH), 5.59 (m), 5.74 (s, C═O), 7.90 (s, br), 14.0 (s); nmr (CH_2Cl_2) τ 2.06 (symmetrical m). Evaporation of the ether washings from the crude **10** left 44 mg of residue which proved to contain more phthalimide and unknown material in about 1:1 ratio.

Additional experimental runs gave comparable yields of recovered azo compound **6** (50–56%). Yields of phthalimide **9** and tetrazene **10** fell in the ranges 40–55% and 9–15%, respectively. In all cases, small quantities of **11** and **12** were detected in the 150–225 mg of viscous material which eluted along with **9**. **12**, but not **11**, was produced by decomposition of **6** on the column; pure **6** could be recovered in 74% quantity from a silica gel column. **6** and **7** did not react spontaneously in 12 days at room temperature or in 3 hr at 80°, **7** being 92% recovered.

Methyl 2-(4′-Dimethylaminophenylazo)benzoate.[35]—In a 400-ml beaker were placed 7.0 g (46 mmol) of methyl anthranilate, 15 ml of H_2O, and 6 ml of concentrated HCl, followed by a slurry of 25 g of ice and 7 ml of concentrated HCl. When the temperature reached −5°, a solution of 3.6 g (50 mmol) of $NaNO_2$ in 10 ml of water was added dropwise, while the temperature was held at <5° (*ca.* 1 hr). To the clear yellow diazonium solution was then added 8.5 ml (8.1 g, 67 mmol) of *N*,*N*-dimethylaniline. The solution was stirred at 0–5° for 30 min, then treated with a solution of 6.80 g (83 mmol) of sodium acetate in 10 ml of water (a small amount of ethyl acetate was added to prevent foaming). The mixture was kept at 4° for 20 hr, then warmed to room temperature. The mixture was neutralized with sodium carbonate and left at room temperature for 8 hr. It was then extracted with four 50-ml portions of chloroform. The organic extracts were dried over $MgSO_4$ and evaporated, leaving a deep red oil, yield 17.6 g. A concentrated benzene solution of this material was placed on a basic alumina column, elution of which with benzene gave 1.1 g of unreacted *N*,*N*-dimethylaniline. Elution with ether–benzene mixtures afforded 6.76 g (52%) of red crystalline methyl 2-(4′-dimethylaminophenylazo)benzoate. Recrystallization from benzene–hexane gave mp 92–94°. Further recrystallization from hexane–CCl_4–$CHCl_3$ gave mp 94.5–96°; ir (KBr) 3.46 and 3.6 (w, CH), 5.8 (s, C═O), 12.08 (m, para-substituted), 13.0 μ (m, ortho-substituted); pmr ($CDCl_3$) τ 2.47 (m, 4 H), 2.17 (2 H, d, $J \approx 9$ Hz), 3.37 (2 H, d, $J \approx 9$ Hz), 6.17 (s, 3 H), 7.12 (s, 6 H).

Anal. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.83; H, 6.05; N, 14.82. Found: C, 67.75; H, 5.93; N, 14.91.

2-(4′-Dimethylaminophenylazo)benzhydrazide (16).—Methyl 2-(4′-dimethylaminophenylazo)benzoate (3.25 g, 11.5 mmol) and 2.00 ml (62 mmol) of hydrazine (95+%) were dissolved in 25 ml of methanol, and the solution was refluxed for 90 min while being magnetically stirred. By this time a voluminous, bright red precipitate had separated. The mixture was cooled to room temperature, then filtered to give 3.15 g (97%) of fluffy red needles, mp 170–171°. An analytical sample obtained by recrystallization from chloroform–carbon tetrachloride had mp 173–174°; ir (KBr) 3.0 (w, NH), 3.21 (w, NH), 3.52 (w, CH), 6.08 (m, C═O), 12.38 (m, (para-substituted), and 13.21 μ (w, ortho-substituted); pmr (DMSO-d_6) τ 0.48 (br s, 1 H, NH), 2.48 (m, 6 H), 3.21 (2 H, d, $J \approx 9$ Hz), *ca.* 5.4 (very broad), 6.92 (s, 6 H).

Anal. Calcd for $C_{15}H_{17}N_5O$: C, 63.58; H, 6.05; N, 24.72. Found: C, 63.87; H, 6.12; N, 24.93.

Nitrosation of 16. Method A.—2-(4′-Dimethylaminophenylazo)benzhydrazide (**16**, 1.75 g, 6.18 mmol) was dissolved in 75 ml of water by the addition of about 1.5 ml of 12 *M* HCl. Dichloromethane (60 ml) was added. While the heterogeneous mixture was stirred and kept below 5°, a solution of 0.621 g (9.0 mmol) of $NaNO_2$ in 6 ml of cold water was added. A red precipitate formed and was extracted into the CH_2Cl_2 layer. The organic layer was separated and the aqueous layer was washed with three 50-ml portions of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and filtered to yield a deep red solution. The solution was then flushed with nitrogen and irradiated for 3 hr through the Pyrex flask using a GE UA-3 360-W medium pressure mercury lamp. The solvent was allowed to reflux. During this time only a slight amount of gas was evolved through a bubbler. The solution was then evaporated to dryness, and a suspension of the red-brown material in benzene was chromatographed on a silica gel column. Elution with benzene and 2% ether in benzene afforded 7.8 mg (<1%) of 2-(4′-dimethylaminophenylazo)aniline (**19**) as orange platelets: mp 104–106° (lit.[36] mp 105–106°); ir (KBr) 3.03 (w, br, NH), 3.5 (w, CH), 3.59 (sh, w), 12.18 (m, para-substituted), 13.29 μ (w, ortho-substituted).

Further elution with 2% ether in benzene afforded a minor yellow product, 8.9 mg, fluffy needles, mp 240–241° dec (EtOH), which was not identified: ir (KBr) 3.03 (m, br), 3.5 (w, br), 4.28 (w), 6.00 (m), 6.30 (m), 6.62 (s), 6.94 (m), 13.11 μ (m). Elution with 5–40% ether in benzene gave 0.7493 g (46%) of a deep orange solid, mp 242–244° dec. Recrystallization from dichloromethane gave 0.330 g (1.24 mmol) of 3-(4′-dimethylaminophenyl)-3*H*-benzo-1,2,3-triazin-4-one (**17**): mp 246–247° dec [(lit.[37] mp 249–250° (EtOH)]; ir (KBr) 3.34 (w, CH), 3.54 (w), 5.99 (s, C═O), 12.29 (m, para-substituted), 13.71 (m, br), and 14.6 (m, br); visible ($CHCl_3$) λ_{max} 362 nm (ϵ 5260); pmr ($CDCl_3$) τ 1.45–2.28 (m, 4 H), 2.49 (d, $J \approx 9$ Hz, 2 H), 3.17 (d, $J \approx 9$ Hz, 2 H), and 6.96 (s, 6 H). The red-colored filtrates from the recrystallizations contained (by tlc analysis) additional **17**. Crystallization of the residue from these filtrates from dioxane gave 9 mg of deep red needles, mp 240–242°. Comparison of ir spectra and tlc behavior (neutral alumina, CH_2Cl_2) demonstrated that this material was impure **20** (see below).

Elution of the column with ether and dichloromethane–ether mixtures brought down a deep red-brown band which weighed 0.443 g; the crude melting point was 176–194°. Tlc (silica gel) showed four major components. Crystallization of this material from CH_2Cl_2–CCl_4 afforded 0.1384 g of crude 2-(4′-dimethylaminophenylazo)benzamide (**18**), mp 186–189° (8%). Recrystallization from CH_2Cl_2–methylcyclohexane gave 0.120 g of **18**: mp 196–197°; ir (KBr) 3.09 (m, NH), 3.22 (w), and 3.50 (w, CH), 6.05 (m, C═O), 6.28 (s), 12.09 (m, para-substituted), 13.08 μ (w, ortho-substituted); visible (95% EtOH) 443 nm (ϵ 44,700). Upon addition of concentrated HCl, λ_{max} shifted to 527 nm and the absorbance more than doubled.[38]

Anal. Calcd for $C_{15}H_{16}N_4O$: C, 67.15; H, 6.01; N, 20.87. Found: C, 66.93; H, 6.30; N, 20.64.

The filtrate from the first recrystallization of **18** was concentrated; on addition of benzene, 70 mg of a material melting at 161–163° was obtained. Recrystallization from a slowly evaporating benzene–methylcyclohexane solution gave 20 mg of deep violet needles, mp 174–175°. This material was identical (ir, tlc comparison, and mixture melting point) with authentic methyl red, mp 175–176° (Pfaltz & Bauer, recrystallized from acetic acid, then benzene–methylcyclohexane), crude yield 4%.

Continued elution of the column with methanol yielded a deep violet material. Recrystallization from slowly evaporating dichloromethane–benzene afforded 9 mg of blue-black material, mp 198–200°. Recrystallization from slowly evaporating 95% methanol–5% CCl_4 solution gave deep blue needles of *anhydro*-2-(*p*-dimethylaminophenyl)-3*H*-benzo-1,2,3-triazinium-4-one hydroxide (**13**), mp 199–200°, yield 8.6 mg (<1%). The spectral data were identical with those previously described.[1]

The filtrate from **13** was evaporated; successive recrystallization (CH_2Cl_2–CCl_4) gave 45 mg of **20**, mp 238–241°. Recrystallization from a slowly evaporating 5% CH_2Cl_2–95% ethanol mixture gave orange needles: yield 25 mg; mp 250–251° dec; ir (KBr) 3.25 (w) 3.52 (w) (CH), 6.29 (s), 12.14 (m, para-substituted), 13.1 μ (w, ortho-substituted); uv–visible (EtOH–$CHCl_3$) 471, 315 (sh), 280 nm; after addition of concentrated HCl, λ_{max} shifted to 493 nm, absorption doubled in intensity; uv ($CHCl_3$) 483 nm.

Anal. Calcd for $C_{16}H_{16}N_4O_2$: C, 64.80; H, 5.44; N, 18.90. Found: C, 64.85; H, 5.41; N, 19.02.

The mass spectrum (70 eV ionizing voltage, 220° direct inlet) exhibited an apparent parent peak at *m/e* 290 (14.7%). The peak at *m/e* 291 had a relative intensity of 3.1%. Although **20** remains unidentified, the intact skeletal structure of **16** is substantiated by fragments appearing at *m/e* (rel intensity) 224 (16.7, $ArN{=}NC_6H_4^+$), 148 (28, ArN_2^+), 134 (19.7, $Me_2NC_6H_4N^+$), and 120 (100, $Ar^+ = Me_2NC_6H_4^+$). Other important fragments appeared at *m/e* (rel intensity) 268 (7.3), 254 (15.2), 253

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(35) Synthesis adapted from H. T. Clarke and W. R. Kirner, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 374.

(36) W. C. J. Ross and G. P. Warwick, *J. Chem. Soc.*, 1724 (1956).

(37) J. J. Jennen, *Meded. Vlaam. Chem. Ver.*, **18**, 43 (1956).

(38) Analogous behavior is reported for the methyl ester: B. Majee and S. K. Chakravarti, *Z. Phys. Chem.* (*Frankfurt am Main*), **57**, 89 (1968).

(46), 252 (43), 239 (10.7), 238 (13.4), 210 (10.4), 181 (16.3), 147 (46), 146 (36.5), 145 (12.7, P^{2+}?), 136 (82.3), 135 (79), 132 (20), 122 (53), 121 (56), 119 (38), 108 (18.7), 107 (37), 106 (14.5), 105 (23), 104 (17.6), 94 (16.3), 93 (31), 92 (41), 78 (16.3), 77 (41), 76 (19.5), 65 (34), 42 (26.8), 39 (21.4), 28 (31), and 18 (18.7).

The pmr spectrum (CF_3CO_2H) follows: τ 2.05–3.55 (m, 8H), 6.92 (s, 6H); two doublets can be discerned within the multiplet, at τ 2.55 and 3.30 ($J \approx 9$ Hz).

Method B (in the Dark).—The previous reaction was performed with the flask wrapped in aluminum foil. An ir spectrum of the crude product mixture showed no azide absorption in the 4.0–5.0 μ region. The same work-up procedure was performed, giving **17** (54.5%), unknown **20** (96 mg), and acid **15** (7.5%), amide **18** (4%), and **13** (3.5%). The higher yield of **17** is obtainable if **17** is not left in solution for prolonged periods.[39] The aniline **19** was not detected in this run.

Photolysis of 13.—Azimine **13** (0.5866 g, 2.2 mmol) in 250 ml of N_2-saturated dichloromethane was photolyzed for 3 hr. During this time the solution was allowed to reflux. No appreciable gas evolution was observed through the N_2 bubbler. The solution showed no visible color change. Evaporation of the solvent gave back **13** (0.585 g, >99%).

Synthesis of 17.[37] **A. *N'*-Anthranilyl-*N*,*N*-dimethyl-*p*-phenylenediamine.**—Isatoic anhydride (Aldrich, 1.35 g, 8.30 mmol) and *N*,*N*-dimethyl-*p*-phenylenediamine (Eastman, 1.15 g, 8.50 mmol) were heated together on a steam bath until gas evolution ceased (15 min). This left a black solid mass (2.10 g, 99%), mp 134–138°. Two recrystallizations from ethanol gave a gray solid (0.94 g, 45%): mp 147–148° (lit.[37] mp 146–148°); ir (KBr disc) 2.85 and 2.96 μ (m, NH_2), 3.30 (w, NH), 3.40 and 3.49 (w, CH), 6.06 (vs, C=O), 12.22 and 12.39 (s, para), and 13.35 (s, ortho); pmr ($CDCl_3$) τ 2.3 (br, s, 1 H), 2.7 (m, 4 H), 3.3 (m, 4 H), 4.7 (broad s, 2 H), 7.10 (1 s, 6 H).

B.—The amide (0.724 g, 2.84 mmol) was dissolved in 30 ml of 1 *M* H_2SO_4, cooled to 0°, and treated with 0.20 g (2.84 mmol) of $NaNO_2$. After 10 min, the solution was neutralized with $NaHCO_3$ and filtered. The precipitate was washed with water and air dried, leaving 0.762 g (100%) of yellow powder, mp 235–238° dec. Recrystallization from acetone gave **17**, mp *ca.* 245° dec (lit.[37] mp 249–250°). The mixture melting point with **17** from nitrosation of **16** was 244–245° dec. The ir spectra were identical.

Registry No.—**3**, 33986-91-3; **13**, 33986-92-4; **16**, 33986-93-5; **18**, 33986-94-6; methyl 2-(4'-dimethylaminophenylazo)benzoate, 20412-23-1; methyl red, 493-52-7.

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[39] Benzotriazinones are unstable to light: E. M. Burgess and G. Milne, *Tetrahedron Lett.*, 93 (1966).

Reactions of the Nitrosonium Ion. IV. Nitrosative Cleavage of the Carbon–Nitrogen Double Bond. The Reaction of *N*-Arylimines and Ketimines with Nitrosonium Salts[1a]

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N-Benzylideneanilines react with nitrosonium salts at or below room temperature to produce benzaldehydes and benzenediazonium salts. These reactions proceed with initial N-nitrosation and are proposed to involve the intermediacy of N-substituted oxadiazetine compounds. Competing reactions are observed only with *p*-methoxy substituents. When a proton is produced in these reactions, as when benzophenonimine undergoes nitrosative cleavage, protonation of the imine occurs to the exclusion of further reaction with the nitrosonium ion.

Reactions of nitrosonium compounds with compounds containing the carbon–carbon double bond have been well characterized.[2] Similar reactions with other functional groups, however, have received less attention. Although imines represent the simplest class of organic compounds for use in a study of the reactions of nitrosonium compounds with the carbon–nitrogen double bond, few examples of such reactions have been reported.[3–5] Turcan in 1935 reported that nitrosyl chloride, dinitrogen tetroxide, and nitrosyl sulfuric acid react with *N*-benzylideneaniline under mild conditions to produce benzaldehyde and the corresponding benzenediazonium salt (eq 1).[3] Since these reactions were run under anhydrous conditions in benzene or ether, the production of benzaldehyde and the benzenediazonium salt could not have involved prior hydrolysis of the imine followed by diazotization of aniline. Similar results were obtained when *N*-heptylideneaniline, *N*-benzylidene-*p*-bromoaniline, and *N*-benzylidene-α-naphthylamine were treated with nitrosyl chloride under mild conditions, although no yields were given.[3] The reaction of *N*-benzylideneaniline with dinitrogen tetroxide was recently shown, however, to proceed in high yield to benzaldehyde and benzenediazonium nitrate.[4]

$$C_6H_5CH{=}NC_6H_5 + XNO \longrightarrow C_6H_5CHO + C_6H_5N_2^+X^- \quad (1)$$
$$X = Cl,\ NO_3,\ HSO_4$$

Unlike the carbon–carbon double bond, which undergoes initial electrophilic addition with nitrosyl halides and related compounds,[2] aldimines react with nitrosonium compounds with cleavage to form carbonyl and diazonium compounds.[6] Since aldimines are formed from aldehydes and amines and the parent aldehyde re-formed, the net effect of the reaction of aldimines with nitrosonium compounds is an efficient diazotization of the amine. The mechanism of carbon–nitrogen double bond cleavage may be represented as involving the intermediacy of an N-substituted oxa-

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[1] (a) For part III, see M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, in press; (b) National Science Foundation Undergraduate Research Participant, summer 1969.

[2] (a) L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 319 (1951); (b) J. Meinwald, Y. D. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, **86**, 4074 (1964); (c) H. C. Hamann and D. Swern, *ibid.*, **90**, 6481 (1968); (d) E. F. Schoenbrunn and J. H. Gardner, *ibid.*, **82**, 4905 (1960).

[3] J. Turcan, *Bull. Soc. Chim. Fr.*, **2**, 627 (1935).

[4] R. M. Scribner, *J. Org. Chem.*, **29**, 3429 (1964).

[5] (a) C. J. Thoman and I. M. Hunsberger, *ibid.*, **33**, 2852 (1968); (b) J. Jappy and P. N. Preston, *Tetrahedron Lett.*, 1157 (1970).

[6] Only one example of an apparent addition reaction has been reported: E. P. Goldberg and H. R. Nace, *J. Amer. Chem. Soc.*, **75**, 6260 (1953).