1,2-diphenyl-3,5,5-trimethylcyclopentadiene, and 2,3-diphenyl-1,5,5-trimethylcyclopentadiene. The quantum yield of disappearance of the 3H-pyrazole was approximately 0.003. Separation of the mixture of the above four products from the sensitizer was effected by preparative high-pressure liquid chromatography.[29] Analysis of the faster moving bands by 270-MHz FT NMR revealed the presence of the same four compounds and the absence of any indene photoproducts (the threshold limit was approximately 0.01%).

Control Experiments

Photostability of 1,2-Diphenyl-3,5,5-trimethylcyclopentadiene. A solution of 159 mg (0.61 mmol) of 1,2-diphenyl-3,5,5-trimethylcyclopentadiene in 200 mL of benzene was irradiated through a Pyrex filter for 5.50 h on the Hanovia apparatus previously described. Upon concentration of the photolysate, no isomeric cyclopentadiene, indene, or vinylcyclopropene was detectable by 270-MHz FT NMR. It is estimated that 0.01% could have been detected. In addition to those of starting material, there were small peaks in the NMR spectrum indicative of a 2% conversion to 1,2-diphenyl-3,5,5-trimethylbicyclo[2.1.0]pent-2-ene.[15] The spectral data were as follows: 270-MHz FT NMR (CDCl₃) τ 3.580 (q, 1 H, J = 1.4 Hz, bridgehead CH), 8.167 (d, 3 H, J = 1.3 Hz, CH₃), 8.225 (s, 3 H, C(CH₃)₂), 8.273 (s, 3 H, C(CH₃)₂).

Photostability of 1-Phenyl-2-methyl-3-isobutenylindene. The irradiation was performed on the Wisconsin Black Box apparatus previously described, using filter B. A solution of 422 mg (1.62 mmol) of 1-phenyl-2-methyl-3-isobutenylindene in 240 mL of benzene absorbed 4.1 mEinsteins of light. Upon concentration of the solution no isomeric indene, cyclopentadienes, or vinylcyclopropenes were detectable by 270-MHz FT NMR. It is estimated that 0.01% conversion (Φ = 0.0004) could have been detected.

Photostability of 1,3-Diphenyl-2,5,5-trimethylcyclopentadiene. The irradiation was performed on the Wisconsin Black Box apparatus previously described, using filter B. A solution of 255 mg (0.98 mmol) of 1,3-diphenyl-2,5,5-trimethylcyclopentadiene, in 240 mL of benzene absorbed 2.55 mEinsteins of light. Upon concentration of the solution no isomeric cyclopentadienes, indenes, or vinylcyclopropenes were detectable by 270-MHz FT NMR. It is estimated that 0.01% (Φ < 10⁻⁴) could have been detected.

Photostability of 2,3-Diphenyl-1,5,5-trimethylcyclopentadiene. The irradiation was performed on the organic chemist's microoptical bench previously described, using a wavelength of 310 nm. A solution of 8.0 mg (0.031 mmol) of 2,3-diphenyl-1,5,5-trimethylcyclopentadiene in 30 mL of benzene absorbed 0.088 mEinstein of light. Concentration of the photolysate, followed by analysis using 270-MHz FT NMR, revealed a 35% conversion to isomeric 1,3-diphenyl-2,5,5-trimethylcyclopentadiene. The quantum yield was estimated by NMR integration to be 0.11. The internal standard used was *trans*-3,4-diphenyl-6-methyl-3,5-heptadien-2-one.

Photostability of 5,6-Diphenyl-3,3,7-trimethyl-3H-1,2-diazepine. The irradiation was performed on the organic chemist's microoptical bench previously described, using a wavelength of 320 nm. A solution of 35 mg (0.12 mmol) of 5,6-diphenyl-3,3,7-trimethyl-3H-1,2-diazepine in 30 mL of benzene absorbed 0.19 mEinstein of light. Upon concentration of the solution, no other products were detected by 270-MHz FT NMR analysis.

Pyrolysis of *trans*-3,4-Diphenyl-6-methyl-3,5-heptadien-2-one Tosylhydrazone Conjugate Base. The method of Sharp[19] was used. Thus 109 mg (0.245 mmol) of *trans*-3,4-diphenyl-6-methyl-3,5-heptadien-2-one tosylhydrazone and 16.0 mg (0.296 mmol) of sodium methoxide in 20 mL of dry tetrahydrofuran were stirred for 5 h at room temperature under nitrogen while shielded from direct light. The resulting colorless slurry was vacuum pumped free of solvent, treated with 10 mL of dry toluene, and heated 8 h at reflux under nitrogen. Concentration in vacuo left colorless crystals plus a yellow oil which was triturated with hexane, filtered, and concentrated to afford 59 mg of a yellow oil (0.205 mmol, 84%) of 5,6-diphenyl-3,3,7-trimethyl-3H-1,2-diazepine, identified by its NMR and IR spectra. Analysis of the crude reaction product by 270-MHz FT NMR showed the absence of any hydrocarbon products (i.e., indenes, cyclopentadienes, or vinylcyclopropenes; vide supra). Injection on a ³/₈ in. × 1 ft high-pressure LC column[29] eluted with 20% anhydrous ether in anhydrous hexane also showed the absence of any hydrocarbon products.

The spectral properties of the 3H-1,2-diazepine are as follows: 270-MHz FT NMR (CDCl₃) τ 2.3–2.9 (m, 10 H, aromatic), 3.769 (s, 1 H, vinyl), 7.738 (s, 3 H, CH₃), 8.541 (s, 3 H, CH₃), 8.710 (s, 3 H, CH₃); IR (thin film) 6.21 (w), 6.37 (w) μm; high-resolution mass spectrometry for C₂₀H₂₀N₂ m/e (calcd) 288.163, m/e(found) 288.162.

Anal. Calcd for C₂₀H₂₀N₂: C, 83.29; H, 6.99. Found: C, 83.34; H, 7.11.

Regiospecific Synthesis of α,β-Unsaturated Azoxy Compounds (Diazene N-Oxides)[1]

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Received February 12, 1979

The regiospecific synthesis of α,β-unsaturated azoxyalkene 7 by the condensation of α,β-dihalonitroso compound 4 and N,N-dichlorourethane (5) followed by dehalogenation is described. Best results were obtained with the α-bromo-β-chloroazoxy precursor when subjected to iodide as promoter. The isomeric α-chloro-β-bromo compound was resistant to dehalogenation. Other dehalogenating agents were examined. The mechanistic features of dehalogenation by iodide are discussed.

Previously we reported a novel, regiospecific synthesis of unsymmetrical azoxy compounds by the reaction of N,N-dichloroamino compounds with nitroso substrates in the presence of basic promoters.[4] Yields were low for
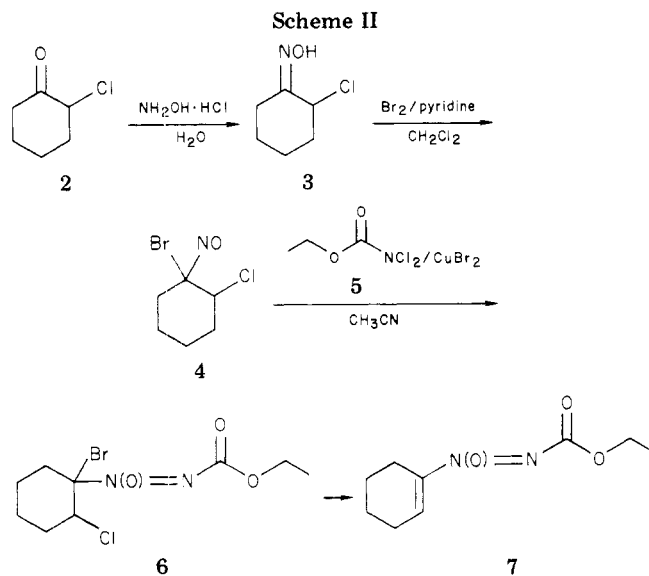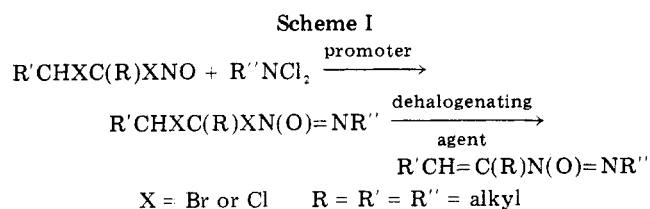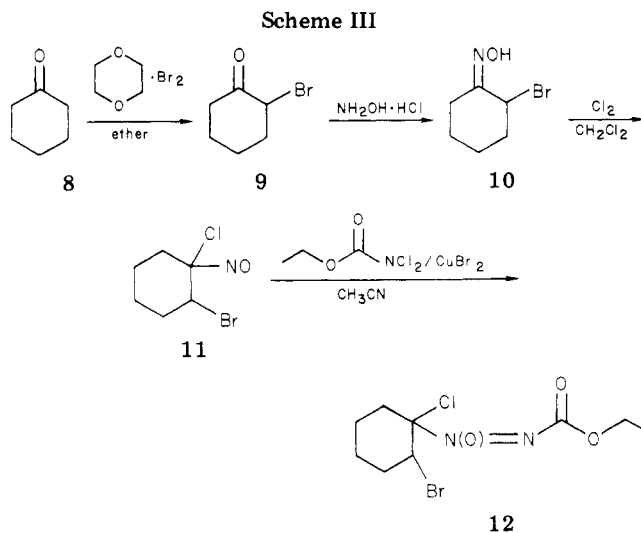
Scheme I

$$R'CHXC(R)XNO + R''NCl_2 \xrightarrow{\text{promoter}}$$

$$R'CHXC(R)XN(O)=NR'' \xrightarrow[\text{agent}]{\text{dehalogenating}}$$

$$R'CH=C(R)N(O)=NR''$$

X = Br or Cl   R = R' = R'' = alkyl

Scheme II

Table I. Conversion of 6 to 7: Variation in Dehalogenating Agent

agent	solvent	time, h	temp, °C	7, yield, %
NaI	acetone	6	0	96
CuCl/NH$_4$OH	MeCN	4	0-25	69
Zn/HOAc	ether	8	0	26
PPh$_3$	ether	0.5	0-25	0

Scheme III

reactions involving primary or secondary alkyl *N,N*-dichloroamines due to the competing elimination of hydrogen chloride. In subsequent studies, it was found that these yields, as well as reaction scope, could be substantially increased by use of cupric or cobaltous bromide as the promoter.[5,6]

The purpose of this study was to synthesize α,β-unsaturated azoxyalkenes through an extension of the above methods. The α,β-unsaturated analogues are of interest since a number of the naturally occurring members, such as elaiomycin (1), exhibit promising physiological activity.[7]

$$CH_3(CH_2)_5CH=CHN(O)=NCHCH_2OCH_3$$
$$\overset{|}{CH(OH)CH_3}$$

1
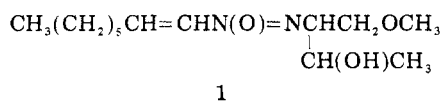
There are several published procedures available for the unsaturated types.[8,9]

Results and Discussion

Our prior attempts to condense α,β-unsaturated nitroso olefins directly with *N,N*-dichloroamines were unsuccessful since the nitroso precursors either polymerize readily or exist as stable dimeric azo dioxides.[5] Experiments aimed at dehydrohalogenation of α-haloazoxy compounds with strong base were also unfruitful.[5] In all instances, only

intractable tars were obtained. Moss and Matsuo have successfully dehydrohalogenated an α,β-dibromoazoxy precursor with DBU enroute to the synthesis of 1, in which the β-bromide was the leaving entity.[9] Obstacles are evident to such an approach in our case since it would require that the azoxy compound and its nitroso precursor contain an α-hydrogen. Primary and secondary alkyl nitroso monomers are not easily isolable due to facile isomerization to the corresponding oxime.[10] We then focused our attention on a pathway involving initial condensation of a *vic*-dihalonitrosoalkane with an *N,N*-dihaloamino compound in the presence of a promoter, followed by dehalogenation to the α,β-unsaturated species (Scheme I).

Scheme II presents the synthesis of compound 6 used as a model in dehalogenation studies aimed at the preparation of 7. Oxime 3, made from α-chloro ketone 2, was brominated to form the α-bromo-β-chloronitroso compound 4. Compound 6 was then obtained by the reaction of 4 with *N,N*-dichlorourethane (5). When cupric bromide was substituted for cuprous cyanide as the promoter, a twofold increase in yield of 6 was achieved. This favorable effect with CuBr$_2$ or other bromide salts has been observed previously. The bromide ion appears to be the crucial reagent, forming the more reactive *N,N*-dibromoamino intermediate, unlike transition-metal salts, such as CuCN.[6,11]

Several attempts were then made to dehalogenate 6 with various promoters. The results are presented in Table I. The iodide reagent functioned best, affording the desired compound 7 in near-quantitative yield under mild conditions. Cuprous chloride/ammonium hydroxide provided 7 in good yield (69%). On the other hand, only a 26% yield resulted from zinc/acetic acid. The complete reduction of the azoxy function to primary amine is known to occur under similar conditions,[12a] which may account

(1) Paper 31 of the series "Chemistry of N-Halo Compounds".
(2) Undergraduate Research Participant.
(3) Postdoctoral Research Associate.
(4) F. R. Sullivan, E. Luck, and P. Kovacic, *J. Org. Chem.*, **39**, 2967 (1974).
(5) V. Nelson, A. Serianz, and P. Kovacic, *J. Org. Chem.*, **41**, 1751 (1976).
(6) R. Zawalski and P. Kovacic, *J. Org. Chem.*, in press.
(7) T. Miyadera, "The Chemistry of the Hydrazo, Azo and Azoxy Groups", S. Patai, Ed., Wiley, New York, NY, 1975, Part 1, pp 499-500.
(8) B. T. Gillis and J. D. Hagarty, *J. Org. Chem.*, **32**, 95 (1967); R. A. Moss and G. M. Love, *Tetrahedron Lett.*, 4701 (1973); J. P. Freeman, *J. Org. Chem.*, **27**, 1309 (1962); R. B. Woodward and C. Wintner, *Tetrahedron Lett.*, 2689 (1969).
(9) R. A. Moss and M. Matsuo, *J. Am. Chem. Soc.*, **99**, 1643 (1977).

(10) J. H. Boyer, "The Chemistry of the Nitro and Nitroso Groups", H. Feuer, Ed., Interscience, New York, NY, 1969, Part 1, p 255.
(11) R. Zawalski and P. Kovacic, *Synth. Commun.*, **8**, 549 (1978).

Scheme IV

X = I, Br, Cl
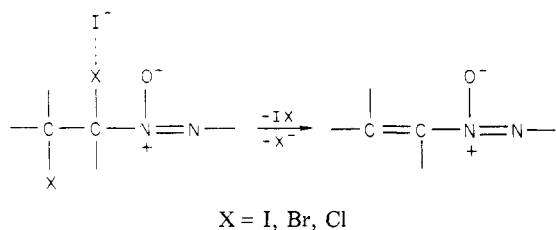
for the rather poor results. Dehalogenation with triphenylphosphine was not successful, although preliminary TLC evidence suggested that the desired compound was formed. However, upon examination of the crude reaction material, only the azoxy precursor, triphenylphosphine oxide, and small amounts of unidentified substances were present. Although we did not find the azo compound among the reaction products, azoxy compounds are known to undergo deoxygenation with triphenylphosphine.[12b]

We also synthesized **12** (Scheme III), the α-chloro-β-bromo isomer of **6**, in order to study the effect of interchanging the positions of the halogens. Cyclohexanone (**8**) was α-brominated with dioxane dibromide to yield **9**. Oximation to **10** proceeded in lower yield than in the case of **3**, perhaps due to competing displacement of halogen by hydroxylamine.[13] Chlorinative oxidation provided the α-chloro-β-bromonitroso derivative (**11**). Reaction of **11** with *N,N*-dichlorourethane in the presence of cupric bromide yielded **12** which was then subjected to iodide. We found that dehalogenation did not occur with **12** even under fairly vigorous conditions.

Several mechanisms for dehalogenation with iodide are proposed in the literature. Winstein and co-workers postulated that *vic*-dibromides undergo a concerted trans elimination brought about by nucleophilic attack on bromine by iodide.[14a] It was later suggested that the reaction may initially involve an S_N2 displacement of Br$^-$ by I$^-$, followed by nucleophilic attack on iodine by another I$^-$.[15a] A recent study supports initial S_N2 displacement of bromide in the case of *vic*-bromochloro compounds.[14b] In our work the preference of **6** over **12** can be rationalized by the fact that a carbon–bromine bond is weaker than a carbon–chlorine bond, and hence that bromide is displaced more readily.[15b] This preference also suggests that breaking the α-carbon–halogen bond is the crucial step. The adjacent electron-withdrawing azoxy function would stabilize carbanionic character generated at the α-carbon in the transition state during a concerted elimination (Scheme IV).

Experimental Section

Infrared spectra were recorded (cm^{-1}) on a Beckman IR-8 spectrometer. NMR spectra were taken on a Varian T-60A with tetramethylsilane as an internal standard. Positive halogen content was determined by iodometric titration.[16] Melting and boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories.

2-Bromocyclohexanone (9). A literature procedure for the α-bromination of ketones with dioxane dibromide was used.[17] A

60% yield of the compound was obtained; bp 56–62 °C (1.5 mm) [lit.[18] bp 74 °C (3 mm)].

2-Bromocyclohexanone Oxime (10). 2-Bromocyclohexanone (3 g, 1.69×10^{-2} mol) and hydroxylamine hydrochloride (1.2 g, 1.74×10^{-2} mol) were stirred in 100 mL of C_2H_5OH–H_2O (10:1, (v/v)) at 0 °C for 3 h. The reaction mixture was poured into 300 mL of CH_2Cl_2, the aqueous layer was removed, and the organic contents were washed with dilute aqueous K_2CO_3 and then with H_2O to neutral pH. The CH_2Cl_2 phase was dried (Na_2SO_4) and the solvent was evaporated. Two recrystallizations from benzene/CH_2Cl_2 of the remaining light brown solid gave 2.05 g (64% of theory) of **10**: mp 87–89 °C; NMR ($CDCl_3$) δ 3.5–1.0 (m, aliphatic), 4.90 (m, 1, CHBr), 8.97 (s, 1, NOH); IR (CCl_4) 3570–2940 (OH), 1640 (C=N), 1000–885 (NO).

Anal. Calcd for $C_6H_{10}BrNO$: C, 37.52; H, 5.26; N, 7.29; Br, 41.60. Found: C, 37.74; H, 5.19; N, 7.25; Br, 41.40.

2-Chlorocyclohexanone Oxime (3). 2-Chlorocyclohexanone (**2**) (5 g, 0.04 mol) was added to a solution of hydroxylamine hydrochloride (3.55 g, 0.05 mol) and sodium acetate (5.63 g) in H_2O (15 mL). The mixture was vigorously shaken for 15 min and then was stored in a refrigerator. A light brown oil separated, which solidified. The solid was broken up, washed with cold H_2O, and dried under vacuum. Recrystallization from benzene/CH_2Cl_2 afforded 4.97 g (89% of theory) of **3**: mp 78–79 °C (lit.[19] mp 78–79 °C); NMR ($CDCl_3$) δ 3.4–1.0 (m, aliphatic), 4.67 (CHCl), 8.6 (NOH); IR (CCl_4) 3570–2940 (OH), 1640 (C=N), 1000–885 (NO).

1-Bromo-1-nitroso-2-chlorocyclohexane (4). A mixture of oxime **3** (3.0 g, 0.02 mol), pyridine (1.58 g, 0.02 mol), and CH_2Cl_2 (45 mL) was stirred at 0 °C in the absence of light. Bromine (3.2 g, 0.02 mol) in CH_2Cl_2 (15 mL) was added dropwise over a 5-min period (the colorless solution immediately turned blue). After 20 min, the reaction mixture was washed with water to neutral pH and dried (Na_2SO_4), and the solvent was evaporated. The resulting oil was chromatographed [Skelly B–CH_2Cl_2 (9:1 (v/v)) on silica] to yield 3.43 g (76% of theory) of **4** as a blue oil: NMR ($CDCl_3$) δ 3.2–1.2 (m, aliphatic), 5.61 (t, 1, CHCl); IR (neat) 1560 (N–O).

Anal. Calcd for $C_6H_9BrClNO$: C, 31.81; H, 4.01; N, 6.19. Found: C, 31.67; H, 4.16; N, 6.38.

1-Chloro-1-nitroso-2-bromocyclohexane (11). Chlorine gas was bubbled into CH_2Cl_2 (15 mL) until a weight increase of 0.37 g (5.21×10^{-3} mol) of dissolved chlorine was obtained. The chlorine solution was then added dropwise to a stirred solution of the oxime **10** (1.0 g, 5.21×10^{-3} mol) in CH_2Cl_2 (20 mL) at 0 °C in the absence of light. After 20 min, the blue solution was washed with H_2O to neutral pH and dried (Na_2SO_4), and the solvent was evaporated. The resulting oil was chromatographed [Skelly B–CH_2Cl_2 (9:1 (v/v)) on silica] to yield 1.1 g (92% of theory) of **11** as a blue oil: NMR ($CDCl_3$) δ 3.1–1.3 (m, aliphatic), 5.24 (t, 1, CHBr); IR (neat) 1570 (N–O).

Anal. Calcd for $C_6H_9BrClNO$: C, 31.81; H, 4.01; N, 6.19. Found: C, 31.92; H, 4.05; N, 6.09.

N,N-Dichlorourethane (5) was prepared according to a published procedure[20] (yields of at least 85%). Iodometric titrations showed the crude products to have positive halogen contents of 95–100% of theory.

N-Carbethoxy-*N'*-(1-bromo-2-chlorocyclohexyl)diazene *N'*-Oxide (6). A. Cupric Bromide as Promoter.[6] A mixture of nitroso compound **4** (2.27 g, 0.01 mol), *N,N*-dichlorourethane (2.36 g, 0.012 mol), CuBr$_2$ (2.33 g, 0.01 mol), and CH$_3$CN (25 mL) was stirred at room temperature for 5 h. The green-black solution was then added to H_2O (200 mL) and repeatedly extracted with ether until the aqueous phase was light blue. The ether extract was washed once with dilute aqueous $Na_2S_2O_3$ and once with water and then dried (Na_2SO_4), and the solvent was evaporated to provide a light yellow oil. Crystallization from Skelly B–CH_2Cl_2 provided 2.87 g (92% of theory) of **6** as a white solid: mp 43.5–45 °C; NMR ($CDCl_3$) δ 3.4–1.0 (m, aliphatic), 1.40 (t, 3.1, OCH$_2$CH$_3$), 4.40 (q, 2.1, OCH$_2$CH$_3$), 5.05 (t, 1, CHCl); IR (CCl_4) 1750 (C=O), 1505

(12) J. March, "Advanced Oranic Chemistry: Reactions, Mechanisms, and Structures", 2nd ed., McGraw-Hill, New York, NY, 1977: (a) p 1132; (b) p 1129.

(13) L. B. Volodarskii and Yu. G. Putsykin, *J. Org. Chem. USSR (Engl. Transl.)*, 3, 1642 (1967); we thank a referee for this reference.

(14) (a) S. Winstein, D. Pressman, and W. G. Young, *J. Am. Chem. Soc.*, 61, 1645 (1939); (b) P. E. Sonnet and J. E. Oliver, *J. Org. Chem.*, 41, 3284 (1976).

(15) J. Hine, "Physical Organic Chemistry", McGraw-Hill, New York, NY, 1956: (a) pp 186–187; (b) p 167.

(16) P. Kovacic and S. S. Chaudhary, *Org. Synth.*, 48, 4 (1968).

(17) P. B. Terentiev, A. N. Kost, N. P. Lomakina, and V. G. Kartev, *Org. Prep. Proced.*, 6, 115 (1974).

(18) E. J. Corey, *J. Am. Chem. Soc.*, 75, 2301 (1953).

(19) W. Pritzkow, H. Schaefer, P. Pabst, A. Ebenroth, and J. Beger, *J. Prakt. Chem.*, 29, 123 (1965).

(20) R. E. White and P. Kovacic, *J. Am. Chem. Soc.*, 96, 7284 (1974).

(N=N), 1440 (NO), 1215 (CO).

Anal. Calcd for $C_9H_{14}BrClN_2O_3$: C, 34.41; H, 4.51; N, 8.93; total halogen, 36.78. Found: C, 34.41; H, 4.47; N, 8.94; total halogen, 36.58.

B. Cuprous Cyanide as Promoter.[5] A mixture of nitroso compound 4 (2.27 g, 0.01 mol), N,N-dichlorourethane (1.68 g, 0.01 mol), CuCN (1.79 g, 0.02 mol), and CH_3CN (60 mL) was stirred at 0 °C (color change from olive green to black). The reaction mixture was warmed to room temperature, stirred overnight, added to 300 mL of H_2O, and then repeatedly extracted with ether until the aqueous layer was light blue. The ether extract was washed once with saturated aqueous NaCl and dried ($CaCl_2$), and the ether was evaporated. The remaining yellow green oil was chromatographed [Skelly B–benzene (7:3 (v/v) on silica] providing 1.37 g (44% of theory) of 6.

N-Carbethoxy-N'-(1-chloro-2-bromocyclohexyl)diazene N'-Oxide (12). The procedure described for 6 was used with $CuBr_2$ promoter: 62% yield of white solid; mp 30–31 °C; NMR ($CDCl_3$) δ 3.10–0.95 (m, aliphatic), 1.39 (t, 3.2, OCH_2CH_3), 4.42 (q, 2.2, OCH_2CH_3), 5.00 (t, 1, CHBr); IR (CCl_4) 1755 (C=O), 1505 (N=N), 1430 (NO), 1210 (CO).

Anal. Calcd for $C_9H_{14}BrClN_2O_3$: C, 34.41; H, 4.51; N, 8.93. Found: C, 34.36; H, 4.45; N, 8.90.

Dehalogenation. With Sodium Iodide.[21] Azoxy compound (6 or 12) (0.26 g, 8.3×10^{-4} mol) was stirred in 20 mL of dry acetone at 0 °C with a large excess (1.2 g) of NaI. Compound 6 was stirred for 6 h; compound 12 was warmed to room temperature and stirred for 72 h. Workup consisted of adding the reaction mixture to ether (60 mL) and washing once with dilute aqueous $Na_2S_2O_3$ and then once with saturated aqueous NaCl. The ether phase was dried (Na_2SO_4) and the solvent was evaporated. Compound 6 yielded 0.16 g (96% of theory) of the dehalogenated product 7: bp 110 °C (0.25 mm); NMR ($CDCl_3$) δ 2.9–1.2 (m, aliphatic), 1.38 (t, 3.2, OCH_2CH_3), 4.40 (q, 2.1, OCH_2CH_3), 7.22 (m, 1, C=CH); IR (neat) 1755 (C=O), 1670 (C=C), 1480–1430 (N=N, NO), 1220 (C—O), 925, 855 (C=C).

Anal. Calcd for $C_9H_{14}N_2O_3$: C, 54.53; H, 7.12; N, 14.13. Found: C, 54.26; H, 7.17; N, 14.32.

Compound 12 did not undergo reaction and was recovered.

With Cuprous Chloride/Ammonium Hydroxide. A procedure similar to a literature one was used.[22] Azoxy compound 6 (0.25 g, 8.0×10^{-4} mol) and CuCl (0.16 g, 1.6×10^{-3} mol) were stirred in CH_3CN (9 mL) at 0 °C. Addition of aqueous NH_4OH (10%, 3 mL) over a 5-min period caused the faint yellow solution immediately to turn dark blue. The reaction mixture was warmed to room temperature and after 4 h was added to 70 mL of $CHCl_3$. Water (15 mL) was added and the phases were separated. The $CHCl_3$ phase was washed to neutral pH with H_2O and dried (Na_2SO_4), and the solvent was evaporated to yield 0.11 g (69% of theory) of 7.

With Zinc/Acetic Acid. A procedure similar to a published one was used.[9] Azoxy compound 6 (0.26 g, 8.31×10^{-4} mol) and powdered Zn (0.1 g, large excess) were stirred with 25 mL of a solution of ether–30% (w/w) aqueous acetic acid (25:1 (v/v)) at 0 °C. After 8 h the reaction mixture was added to CH_2Cl_2 (100 mL), the solid was filtered, the CH_2Cl_2 solution was dried (Na_2SO_4), and solvent was evaporated. Preparative TLC (CH_2Cl_2 on silica) was carried out on the remaining oil to yield 7 (42 mg, 26% of theory).

Attempted with Triphenylphosphine. A procedure similar to a published one was used.[23] Azoxy compound 6 (0.26 g, 8.3×10^{-4} mol) was stirred in dry ether (17 mL) at 0 °C. To this was added an equimolar amount of Ph_3P (0.27 g) in 10 mL of ether. Immediately upon addition, a white solid precipitated. After 30 min, TLC indicated that all of the Ph_3P had been consumed. After the solid was filtered, solvent was evaporated. Spectral evidence indicated that the desired product 7 was not present.

(21) A. J. Solo and B. Singh, J. Org. Chem., 30, 1658 (1965).

(22) K. A. Kurginyan, R. G. Karapetyan, and G. A. Chakhadzhyan, Arm. Khim. Zh., 27, 1065 (1974); Chem. Abstr., 82, 139177 (1975).

(23) C. J. Devlin and B. J. Walker, J. Chem. Soc., Perkin Trans. 1, 1249 (1972).

Reactions of Alkylbenzyldimethylammonium Halides with Amide in Liquid Ammonia

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Competitive elimination and rearrangement reactions of alkylbenzyldimethylammonium ions with amide ion in liquid ammonia have been investigated. Elimination is largely dependent on the geometry of the alkyl group. Cyclohexyl- and tert-butylbenzyldimethylammonium halides undergo more Stevens than Sommelet–Hauser rearrangement with amide ion in liquid ammonia. The results are interpreted in light of the reactivity of the intermediate ylide. The structure of the rearrangement product from isopropylbenzyldimethylammonium iodide has been reassigned.

When treated with base, quaternary ammonium salts may undergo various reactions. If the salt contains a hydrogen atom β to the nitrogen atom, elimination to produce an alkene usually is important. Under certain conditions a γ proton may be removed resulting in formation of a cyclopropane derivative.[1] Base may also abstract a proton α to the nitrogen atom forming an ylide which in certain cases can isomerize to a tertiary amine.[2]

In the case of benzyltrimethylammonium ion two ylides are possible, one resulting from removal of a proton from a methyl group and one from the benzyl position.[3] The ylide generated by the latter process merely returns to starting material, whereas the methyl ylide may isomerize by two different pathways—the Stevens rearrangement[4]

(1) C. L. Bumgardner, J. Am. Chem. Soc., 83, 4420 (1961).
(2) For an excellent review, see S. H. Pine, Org. React., 18, 403 (1970).

(3) W. H. Puterbaugh and C. R. Hauser, J. Am. Chem. Soc., 86, 1108 (1964).
(4) T. S. Stevens, E. M. Creighton, A. B. Gorden, and M. Mac Nicol, J. Chem. Soc., 3193 (1928).