106–106.5 °C; IR (TF) 2.90 μm (broad); NMR ($CDCl_3$) δ 0.78, 0.97, 1.03 (three s, 9, C-5 and C-9 CH_3), 3.25 (m, 1, C-6α H), 3.92 (m, 4, OCH_2CH_2O); mass spectrum (70 eV) *m/e* 254 (M^+), 99 (base), 86. Anal. ($C_{15}H_{26}O_3$): C, H; also by HRMS.

Crude **16b** (prepared above and containing *10% or less* of the 6α epimer) was used directly to prepare **2**. To a solution of 2 mL of 1:5:6 concentrated hydrochloric acid–water–tetrahydrofuran under a nitrogen atmosphere was added 28 mg (0.11 mmol) of **16b**. The solution was stirred for 30 min. Extraction with ether, washing successively with water and brine, drying over anhydrous magnesium sulfate, and evaporation of solvents gave 22 mg of crude **2** contaminated with small amounts of its 6α epimer. Recrystallization from hexane produced 19 mg (82%) of crystalline **2** as a single isomer, mp 72–73 °C, whose spectral data were identical with those of the known compound: lit.[6] mp 72–73 °C. In a similar run, purified **16b** was hydrolyzed to **2** which was isolated as a crystalline sample in 96% yield: IR ($CHCl_3$, 10% solution) 2.77, 2.85, 5.90 μm; NMR ($CDCl_3$) δ 0.91, 1.04, 1.16 (three s, 9, C-5 and C-9 CH_3), 3.22 (m, 1, C-6α H).

Acknowledgments. We thank the National Institutes of Health (Grant GM-22978-02 to D.S.W.), the National Science Foundation (Grant CHE 76-16788 to D.S.W.), G. D. Searle and Co. (a grant to D.S.W.) and the Robert A. Welch Foundation (Grants F-345 and AX-637 to P.L.S.) for their generous financial support. We also thank the AMC Cancer Research Center, Lakewood, Colo., and the Robert A. Welch Foundation for predoctoral fellowships (to D.L.S. and C.L.E., respectively).

Registry No. 1, 16776-05-9; 2, 56985-41-2; **13**, 33760-61-1; **14a**, 70197-35-2; **14b**, 70197-36-3; **14c**, 69905-28-8; **15**, 70197-37-4; **16a**, 70197-38-5; **16b**, 70224-20-3; **17a**, 70197-39-6; **17b**, 70197-40-9; **18**, 70197-41-0; **19**, 70197-42-1; **16b** 6α-epimer, 70197-32-9.

Preparation of Benzocyclic [2.2.1] Azoxy Compounds

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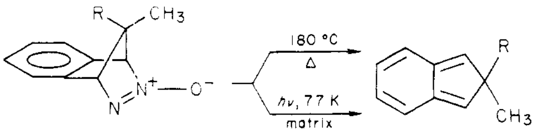
Received September 8, 1978

Benzobicyclic azoxy compounds, used as thermal and photochemical precursors of isoindenes, are synthesized from 2,2-dialkyl-1,3-indandiones via a four-step sequence in which the key step is a sequential hydrolysis–oxidation procedure in which the use of a vibromixer is absolutely essential.

Benzobicyclic azoxy compounds of the type **1**, where R = methyl, ethyl, cyclopropylcarbinyl, isopropyl, and benzyl, were required as thermal and/or photochemical precursors of the interesting series of isoindenes **2**.[1-3] The thermal stability of these azoxy compounds made them much more desirable precursors than the analogous azo compounds which should lose N_2 below room temperature.[4]

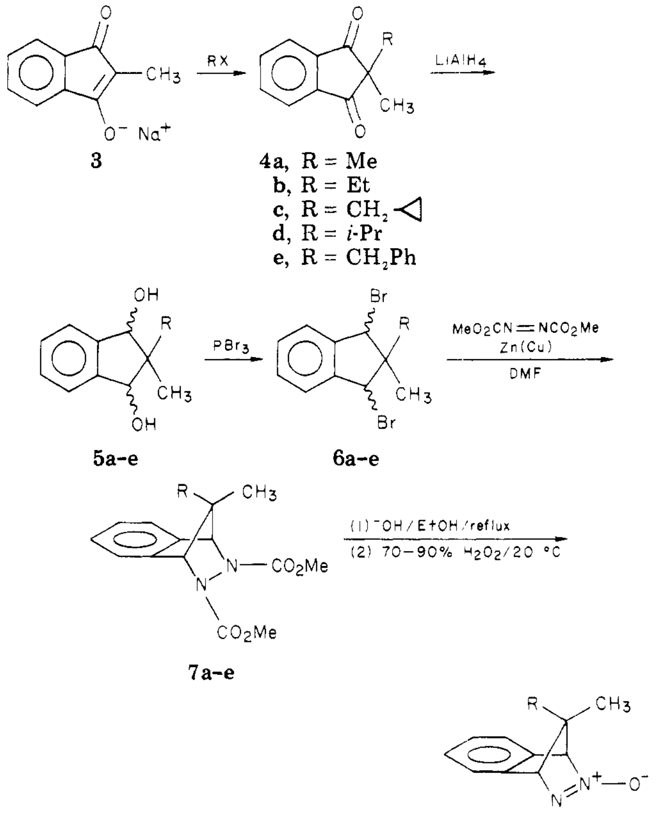


1a, R = Me
b, R = Et
c, R = CH_2-◁
d, R = *i*-Pr
e, R = CH_2Ph

2a–e

Snyder had previously prepared numerous cyclic, cis azoxy compounds by a combination hydrolysis–oxidation procedure.[5] Unfortunately, his method was not effective for the synthesis of the benzannelated series which we required. Our procedure is outlined in Scheme I.

Scheme I



Two features of our procedure proved to be *absolutely* essential for successful synthesis of the benzannelated azoxy compounds. First the vibromixer was found to be indispensable, particularly in the oxidation step where solubility of the organic species in the medium becomes a real problem.[6] Second, the oxidation procedure must, in all cases, be carried out as a *separate* step and at a temperature not to exceed room temperature. The oxidation of the presumed hydrazine intermediate, **8**, is quite exothermic; hence the addition of H_2O_2 must be very slow.

The major side products of these oxidative procedures were the keto alcohols **9** which are probably formed via

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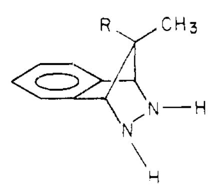
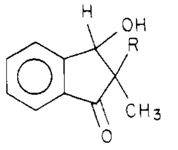
(6) The Vibromixer (Chemapec Inc., Hoboken, N.J., or Chemap Gmbh, Dusseldorf, West Germany) is an agitator, utilizing a vertical vibrating motion, which is particularly effective in dispersing heterogenous mixtures.

0022-3263/79/1944-2842$01.00/0



8a–e



9a–e

decomposition of intermediate azo compounds to isoindenes. Generally comparable amounts of **1** and **9** are formed, and separation is effected by column chromotography.

Azo compounds have traditionally been utilized as precursors to hydrocarbon species, and where the product is not a particularly stable entity loss of nitrogen provides facile entry into some interesting systems. Two very common examples of such extrusion reactions are the formation of carbenes from diazirines[7] and of trimethylene diradicals from 1-pyrazolines.[8] On the other hand, where stable products are to be formed and where the extrusion of N_2 is an allowed [2 + 4] retrocycloaddition, nitrogen loss is too facile a process for azo compounds to be considered as reasonable precursors.[4]

It has been noted by Snyder that azoxy compounds are much more thermally stable than their azo counterparts and that they seem to require about 200 °C *greater* temperature to extrude N_2O than was required by the analogous azo compounds to extrude N_2.[9] In line with this prediction, we have found that the azoxy compounds **1** require a temperature of about 180 °C to extrude N_2O to form the orthoquinoidal hydrocarbon species, the isoindenes. The syntheses presented here comprise the only presently known method of preparing these interesting azoxy compounds which until very recently[2,3,10–12] also were the *only* precursors which allowed isolation of isoindene species.

Experimental Section

Boiling points and melting points were uncorrected, the latter taken on a Thomas–Hoover capillary melting point apparatus. Infrared spectral data were obtained from either a Perkin-Elmer Model 137 or a Beckman Model IR-10 spectrophotometer, and all absorption bands are listed in cm^{-1}. Nuclear magnetic resonance spectra were obtained from a Varian Model A-60A spectrometer, unless specified as the XL-100 model, utilizing Me_4Si as an internal standard. Mass spectral data were determined using an AEI-MS 30 high-resolution mass spectrometer, which was connected to a DS-30 data system. Exact mass data represent the mean of from 5 to 14 scans. Elemental analyses were performed by Atlantic Microlab, Inc. (Atlanta, Ga.).

All reagents which are not referenced were commercially available.

Sodium Enolate of 2-Methyl-1,3-indandione (3). This salt was prepared according to the procedure of Wislicenus and Kotzle.[13] A crude, dark red, solid product was obtained and used without purification. **2,2-Dimethyl-1,3-indandione (4a)** was also prepared by the procedure of Wislicenus and Kotzle.[13] The overall yield based upon the ethyl propionate used was 79%. **4a** was a white solid: mp 107 °C (lit.[13] mp 107–108 °C); NMR (CCl_4) δ 1.23 (s, 6 H), 7.86 (broad s, 4 H); IR (KBr) 2910 (m), 1745 (s), 1705 (s), 1595 (m), 1455 (m), 1280 (s), 1195 (m), 877 (m), 798 (m), 723 (s), 687 (m) cm^{-1}.[14]

2-Ethyl-2-methyl-1,3-indandione (4b). In a 3 L, three-neck flask was placed a solution of 174 g (<0.95 mol) of impure **3** in 1600 mL of EtOH. To this solution was added, over a 1-h period, 250 g (1.60 mol) of ethyl iodide. After the solution was gently refluxed for 48 h, most of the unreacted ethyl iodide and EtOH were removed by rotary evaporator. The dark red residue was added to a mixture of 250 mL of H_2O and 250 mL of ether and was extracted with ether four times. The combined ether extracts were washed with several portions of saturated aqueous Na_2CO_3 solution, until the aqueous wash layer, after shaking, became orange instead of red. Drying with Na_2SO_4 and evaporation of the ether gave a dark, red-brown oil which upon distillation (73–78 °C (0.1 mm)) resulted in a red crystalline solid. Recrystallization from hexane yielded 33.4 g (20.4%) of a white product: mp 46–47.5 °C (lit.[14] mp 46–47 °C); NMR ($CDCl_3$) δ 0.74 (t, 3 H), 1.26 (s, 3 H), 1.87 (q, 2 H), 7.70–8.14 (m, 4 H); IR (KBr) 2925 (m), 1745 (s), 1715 (s), 1603 (m), 1458 (m), 1385 (m), 1375 (m), 1335 (m), 1270 (s), 797 (m), 730 (s) cm^{-1}; exact mass calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0833.

2-Cyclopropylcarbinyl-2-methyl-1,3-indandione (4c). The procedure for making this compound was similar to that used in the synthesis of **4b**. Dione **4c** (bp 106–110 °C (0.4 mm)) was prepared in 22% yield, based on the amount of cyclopropylcarbinyl bromide[15] used as the alkylating agent: NMR ($CDCl_3$) δ 0.00–0.50 (m, 5 H), 1.27 (s, 3 H), 1.80 (d, 2 H, J = 6.5 Hz), 7.77–8.12 (m, 4 H).

2-Benzyl-2-methyl-1,3-indandione (4e). The procedure for making this compound was similar to that used in the synthesis of **4b**. Dione **4e** was prepared in 34% yield (based on the amount of benzyl bromide used: mp 78–79 °C (lit.[16] mp 78–79 °C); NMR ($CDCl_3$) δ 1.37 (s, 3 H), 3.13 (s, 2 H), 6.89 (s, 5 H), 7.45–7.85 (m, 4 H); IR (NaCl) 2990 (w), 2870 (w), 1740 (s), 1710 (s), 1580 (m), 1485 (m), 1440 (m), 1360 (m), 1325 (m), 1260 (s), 988 (s), 797 (m), 760 (s), 727 (m), 705 (s) cm^{-1}; exact mass calcd for $C_{17}H_{14}O_2$ 250.09930, found 250.09931.

2-Methyl-1,3-indandione (10). In a 2-L separatory funnel was placed 180 g of crude **3** in 1.1 L of H_2O. Most of the salt dissolved, and an opaque, dark red suspension resulted. Extraction four times with ether removed various impurities, after which the aqueous mixture was placed in a 2 L Erlenmeyer flask equipped with a magnetic stirrer. The enolate was then acidified with 6 N HCl until a pH of 2 was reached (ca. 250 mL of acid). A dark red oil separated during the acidification. Extracting the oil four times with 250 mL of ether, washing the combined ether extracts with saturated NaCl solution, drying the extracts with $MgSO_4$, and evaporating the ether led to a clear, dark red oil which may crystallize upon standing. Distillation (98–115 °C (0.12 mm)) led to an orange-yellow product which crystallized. Recrystallization (2:1, EtOH–H_2O) led to 28.8 g of creamy white crystals (20.7%, based on ethyl propionate): mp 83–84.5 °C (lit.[14] mp 86–87 °C); NMR ($CDCl_3$) δ 1.40 (d, 3 H), 3.07 (q, 1 H), 7.70–8.20 (m, 4 H); IR (neat, NaCl) 2920 (m), 1775 (m), 1745 (s), 1720 (s), 1600 (m), 1468 (m), 1453 (m), 1370 (m), 1345 (m), 1283 (m), 1235 (m), 743 (m) cm^{-1}.[13]

2-Isopropyl-2-methyl-1,3-indandione (4d). A solution of NaOEt was freshly prepared from 2.3 g (0.10 mol) of Na and 100 mL of EtOH. It was added to 12.0 g (0.075 mol) of **10** in 100 mL of EtOH. This deep red enolate solution was then added to an 800 mL Pyrex pyrolysis tube along with 40 g (0.235 mol) of isopropyl iodide. Additional EtOH (50 mL) was used to wash down the sides of the tube, which was sealed under N_2. Thermolysis at 150 °C for 10 h in a tube furnace led to a clear yellow-orange solution which, after opening the tube, was poured into 750 mL of H_2O in a 2-L separatory funnel. Three 250 mL extractions with ether were combined and washed with saturated aqueous Na_2CO_3 solution and then aqueous NaCl solution and

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(15) Cyclopropylcarbinyl bromide (bp 108.5–110.5 °C (760 mm)) was made in 48% yield by treating cyclopropylcarbinol with triphenylphosphine and bromine.

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dried over $MgSO_4$, and the ether was removed in vacuo to give 8.2 g of a brown oil. Distillation (73–84 °C (0.1 mm)) led to 6.7 g (44%) of product:[14] NMR ($CDCl_3$) δ 0.94 (d, 6 H), 1.28 (s, 3 H), 1.84–2.56 (m, 1 H), 7.72–8.12 (m, 4 H); IR (neat, NaCl) 2975 (m), 2945 (m), 2885 (m), 1745 (s), 1710 (s), 1600 (m), 1465 (m), 1390 (m), 1375 (m), 1335 (m), 1270 (s), 1160 (m), 988 (m), 785 (m), 730 (m) cm^{-1}; exact mass calcd for $C_{13}H_{14}O_2$ 202.0993, found 202.0996.

2,2-Dimethyl-1,3-indandiol (5a). This diol was prepared by the procedure of Alder and Fremery,[17] involving the reduction of **4a** with $LiAlH_4$ in 91% yield. The white solid had mp 145–150 °C: NMR ($CDCl_3$) δ 0.93–1.27 (m, 6 H), 1.73–2.45 (m, 2 H), 4.45–5.07 (m, 2 H), 7.30–7.70 (m, 4 H); IR (NaCl) 3360 (s), 2960 (m), 2875 (m), 1460 (m), 1380 (w–m), 1215 (w–m), 1100 (m), 1030 (s), 995 (m), 760 (m), 740 (m) cm^{-1}.

Similarly, **2-ethyl-2-methyl-1,3-indandiol (5b)** (crude mp 68–95 °C), **2-cyclopropylcarbinyl-2-methyl-1,3-indandiol (5c)** (yellow oil), **2-isopropyl-2-methyl-1,3-indandiol (5d)** (white sticky solid), and **2-benzyl-2-methyl-1,3-indandiol (5e)** (crude mp 43–51 °C) were also prepared, in 80–99% yields. In general, the diols were used in the next synthetic step without purification.

1,3-Dibromo-2,2-dimethylindan (6a). This compound was prepared according to the procedure of Alder and Fremery.[17] An 84% yield of light yellow oil was obtained: bp 109–112 °C (0.5 mm); NMR ($CDCl_3$) δ 1.20–1.49 (m, 6 H), 5.09–5.30 (m, 2 H), 7.14–7.56 (m, 4 H); IR (NaCl) 2975 (s), 2940 (m), 1470 (s), 1395 (m), 1375 (m), 1220 (s), 1185 (s), 1155 (m), 890 (s), 865 (m), 840 (m), 765 (s), 700 (s), 655 (m), 637 (m), 605 (m) cm^{-1}.

Similarly, **1,3-dibromo-2-ethyl-2-methylindan (6b)** (bp 101–104 °C (0.125 mm)), **1,3-dibromo-2-cyclopropylcarbinyl-2-methylindan (6c)**, **1,3-dibromo-2-isopropyl-2-methylindan (6d)** (bp 94–96 °C (0.045 mm)), and **1,3-dibromo-2-benzyl-2-methylindan (6e)** (bp 152–158 °C (0.10 mm)) were prepared in 46–95% yields. In general, the dibromoindans were not completely purified. Also, the distillation of **6e** caused slight decomposition, but the crude product was of adequate purity for the next reaction.

Dimethyl 7,7-Dimethyl-5,6-diaza-2,3-benzobicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate (7a). Using 20 mesh Zn, 12 g of Zn–Cu couple were freshly prepared according to the method of LeGoff.[18] The 12 g of couple were then placed in a 500-mL, three-neck flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel. In the flask was also placed 30 mL of dimethylformamide (previously dried by standing for 1 week over 4A molecular sieves). A solution containing 10 g (0.033 mol) of dibromoindan **6a**, 9.8 g (0.067 mol) of dimethyl azodicarboxylate,[19] and 30 mL of dry dimethylformamide was added dropwise over a 30-min period to the rapidly stirred Zn–Cu couple. The reaction mixture immediately began to turn green, and it became warm. After the addition of the reagents was completed, stirring of the reaction mixture was continued for about 1 h, until it cooled to room temperature. The Zn–Cu couple was filtered off, using a Celite pad. Ether and water were then added to the filtrate, along with a few milliliters of dilute HCl, in order to dissolve the $ZnBr_2$ precipitate. The resultant mixture was separated, and the aqueous layer was extracted three times with ether. The combined extracts were washed with water and then dried by filtration through anydrous $MgSO_4$. Solvent removal under vacuum resulted in 8.7 g (91% yield of crude product) of a light yellow glassy solid. Sublimation (at 100 °C and a pressure of <0.005 mm) gave a white solid: mp 105–106 °C; NMR ($CDCl_3$) δ 0.75 (s, 3 H), 1.23 (s, 3 H), 3.73 (s, 6 H), 4.93 (broad s, 2 H), 7.05–7.49 (m, 4 H); IR (CCl_4, KBr liquid cell) 2980 (w), 2945 (m), 1755 (s), 1705 (very s), 1435 (s), 1330 (s), 1220 (m), 1135 (m), 1110 (m), 1065 (m), 945 (m), 762 (s), 682 (m) cm^{-1}; exact mass calcd for $C_{15}H_{18}N_2O_4$ 290.127, found 290.129.

Anal. Calcd for $C_{15}H_{18}N_2O_4$: C, 62.05; H, 6.25; N, 9.65. Found: C, 62.14; H, 6.29; N, 9.63.

The analogous **dimethyl 7-alkyl-7-methyl-5,6-diaza-2,3-benzobicyclo[2.2.1]hept-2-ene-5,6-dicarboxylates (7b–e)**, where alkyl = ethyl, cyclopropylcarbinyl, isopropyl, and benzyl, respectively, were prepared as viscous oils or glassy solids by identical procedures in 86–94% yields. The following exact mass data were obtained for these diaza diester adducts: **7b**: calcd for $C_{16}H_{20}N_2O_4$ 304.1422, found 304.1415; **7d**: calcd for $C_{17}H_{22}N_2O_4$ 318.1579, found 318.1581; **7e**: calcd for $C_{21}H_{22}N_2O_4$ 366.1578, found 366.1578.

7,7-Dimethyl-5,6-diaza-2,3-benzobicyclo[2.2.1]hepta-2,5-diene 5-*N*-Oxide (1a). A solution containing 10.0 g (0.0345 mol) of diester **7a** in 100 mL of absolute EtOH was placed in a reaction vessel designed to accommodate a vibromixer,[6] a reflux condenser, gas inlet and outlet tubes, a solid addition funnel, and a rubber septum (fitted on a side arm). After placing 10 g (0.18 mol) of KOH in the solid addition funnel, the solution and the reaction vessel were flushed with argon for 1.5 h. From this point on, a positive argon pressure and the vibromixing were maintained. The solution was heated to reflux, followed by the rapid addition of the KOH pellets. After 3.5 h of refluxing, the hydrolysis step was completed (as indicated by TLC, using Al_2O_3, $CHCl_3$, and I_2), and the reaction mixture was cooled to room temperature. A fairly rapid flow of argon was passed through the vessel during the next part of the reaction sequence. Using a syringe, 50 mL of 70% H_2O_2 were gradually added over a 15-h period. The slow rate of addition prevented the reaction mixture from rising above room temperature, a condition which is important to the success of the reaction. For convenience, it was possible to leave the reaction overnight at room temperature, under an argon atmosphere. The mixture was extracted with five portions of CH_2Cl_2. After filtering the combined extracts through $MgSO_4$, solvent removal under vacuum resulted in 5.3 g of a yellow oil. The GLC analysis (2.5 ft. × 0.25 in. column containing 1% SE-30 on Chromosorb W, silanized, operating at 140 °C) indicated that 55% of the crude product was the desired azoxy compound.

The other 45% consisted largely of the keto alcohol side product, **9a**. The azoxy compound was separated and partially purified by column chromatography, using 300 g of 80/200 mesh Al_2O_3 as the absorbent and CH_2Cl_2 as the elution solvent. The Al_2O_3 was coated with Dupont 906 luminescent indicator (5% w/w) which, under ultraviolet irradiation, showed the development of three bands during the elution. The relatively small first band contained nothing of interest, but the large second band consisted of 2.37 g of partially pure azoxy compound. Material obtained from the third band weighed 3.25 g, but GLC analysis indicated that only 20% of it was the desired product. Further purification of the azoxy fraction (from band 2) was done by triturating the solid several times in pentane. The resulting white powder weighed 1.7 g (26%): mp 71–73 °C (with gas evolution); NMR ($CDCl_3$) δ 0.85 (s, 3 H), 1.43 (s, 3 H), 5.04–5.17 (m, 1 H), 5.20–5.37 (m, 1 H), 7.17–7.67 (m, 4 H); IR (KBr) 3040 (m), 2990 (m), 1510 (s), 1465 (m), 1360 (m), 1275 (m), 1215 (m), 915 (m), 785 (m), 740 (s), 707 (m) cm^{-1}; exact mass ($M^+ - N_2O$) (no parent peak) calcd for $C_{11}H_{12}$ 144.0938, found: 144.0937.

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.10; H, 6.45; N, 14.89.

7-Ethyl-7-methyl-5,6-diaza-2,3-benzobicyclo[2.2.1]hepta-2,5-diene 5-*N*-Oxide (1b). This azoxy compound was prepared from **7b** by essentially the same procedure used to make azoxy **1a**, except that the oxidizing agent was 90% H_2O_2. The product was a viscous oil, formed in 22% yield: NMR ($CDCl_3$) δ 0.55–1.45 (overlapping multiplets, 8 H), 4.92–5.18 (m, 1 H), 5.19–5.38 (m, 1 H), 7.00–7.63 (m, 4 H); IR (NaCl) 3040 (w), 2980 (m), 2895 (m), 1510 (s), 1465 (s), 1360 (m), 1220 (m), 925 (m), 780 (m), 735 (s), 708 (m) cm^{-1}; exact mass ($M^+ - N_2O$) calcd for $C_{12}H_{14}$ 158.1095, found 158.1088.

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.33; H, 7.00; N, 13.78.

7-Cyclopropylcarbinyl-7-methyl-5,6-diaza-2,3-benzobicyclo[2.2.1]hepta-2,5-diene 5-*N*-Oxide (1c). The procedure for preparing **1c** from diester **7c** was essentially identical with that used in making azoxy **1a**. The creamy-white solid was made in 29% yield: mp 81–85 °C (with gas evolution); NMR ($CDCl_3$) δ –0.11 to –0.35 (τ 10.11–10.35) (m, 1 H), 0.10–1.33 (overlapping multiplets, 6 H), 1.37–1.84 (m, 3 H, including a tall singlet at 1.49), 5.08–5.49 (m, 2 H), 7.07–7.68 (m, 4 H); IR (NaCl) 3090 (m), 3015 (m), 2950 (m), 1512 (s), 1465 (s), 1390 (w-m), 1362 (m), 1220 (m), 1188 (m), 1163 (m), 1024 (m), 980 (m), 915 (m), 830 (w-m), 788 (m), 775 (m), 740 (s), 710 (m) cm^{-1}; exact mass ($M^+ - N_2O$) calcd for $C_{14}H_{16}$ 184.1251, found 184.1257.

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Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.61; H, 7.08; N, 12.25.

7-Isopropyl-7-methyl-5,6-diaza-2,3-benzobicyclo[2.2.1]hepta-2,5-diene 5-*N*-Oxide (1d). The synthesis of azoxy **1d** from diester **7d** involved essentially the same procedure as that used in making **1a**. However, the oxidation was carried out with 90% H_2O_2. The purified product, a white powder, was isolated in 24% yield: mp 108–110 °C dec; NMR ($CDCl_3$) δ 0.75 (t, 6 H (on a Varian Model XL-100 spectrometer, this signal consists of two doublets)), 0.98–1.64 (m, 4 H, including a large singlet at 1.24), 5.08 (d, 1 H), 5.20–5.47 (m, 1 H), 7.05–7.67 (m, 4 H); IR (KBr) 3040 (w), 2975 (m), 2890 (w), 1515 (s), 1460 (s), 1365 (w), 775 (m), 730 (s), 710 (m) cm^{-1}; exact mass ($M^+ - N_2O$) calcd for $C_{13}H_{16}$ 172.1251, found 172.1252.

Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.21; H, 7.47; N, 13.00.

7-Benzyl-7-methyl-5,6-diaza-2,3-benzobicyclo[2.2.1]hepta-2,5-diene 5-*N*-Oxide (1e). This azoxy compound was prepared from diester **7e** using an almost identical procedure as that involved in the synthesis of **1a**. The oxidizing agent was 90% H_2O_2, and a 28% yield of white powder was obtained, mp 122–124 °C (with gas evolution): NMR ($CDCl_3$) δ 1.28 (s, 3 H), 2.36 (s, 2 H), 5.01 (d, 1 H), 5.10–5.38 (m, 1 H), 6.69–7.74 (m, 9 H); IR (NaCl) 3070 (w), 3040 (m), 2950 (w), 1605 (w), 1515 (s), 1465 (m), 1350 (w), 1215 (m), 765 (s), 740 (m), 708 (s) cm^{-1}; exact mass ($M^+ - N_2O$) calcd for $C_{17}H_{16}$ 220.1251, found 220.1256.

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.13; H, 6.14; N, 10.54.

Keto Alcohol Side Product (9a): NMR ($CDCl_3$) δ 1.13 (s, 3 H), 1.25 (s, 3 H), 3.94–4.28 (m, 1 H), 4.89 (broad s, 1 H), 7.05–7.79 (m, 4 H); IR (NaCl) 3420 (broad, m), 3020 (w), 2925 (m), 1710 (s), 1615 (m), 1520 (w), 1455 (m), 1380 (m), 1325 (m), 1240 (m), 1065 (m), 762 (m), 725 (m) cm^{-1}; exact mass calcd for $C_{11}H_{12}O_2$ 176.084, found 176.086.

Acknowledgments. The authors wish to acknowledge, with thanks, the donors of the Petroleum Research Fund, administered by The American Chemical Society, for partial support of this research.

Registry No. 1a, 54963-23-4; **1b**, 70355-72-5; **1c**, 70355-73-6; **1d**, 70355-74-7; **1e**, 70355-75-8; **3**, 70355-76-9; **4a**, 17190-77-1; **4b**, 70292-52-3; **4c**, 70355-77-0; **4d**, 70355-78-1; **4e**, 70355-79-2; **5a**, 70355-80-5; **5b**, 70355-81-6; **5c**, 70355-82-7; **5d**, 70355-83-8; **5e**, 70355-84-9; **6a**, 70355-85-0; **6b**, 70355-86-1; **6c**, 70355-87-2; **6d**, 70355-88-3; **6e**, 70355-89-4; **7a**, 70355-90-7; **7b**, 70355-91-8; **7c**, 70355-92-9; **7d**, 70355-93-0; **7e**, 70355-94-1; **9a**, 59269-93-1; **10**, 876-83-5; dimethyl azodicarboxylate, 2446-84-6.

Thermal [1,5] Sigmatropic Alkyl Shifts of Isoindenes

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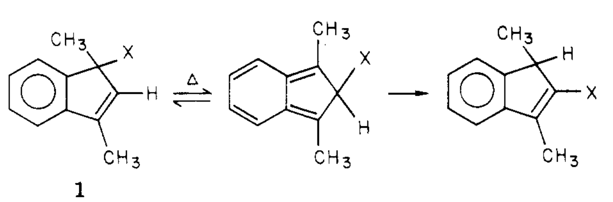
Received September 8, 1978

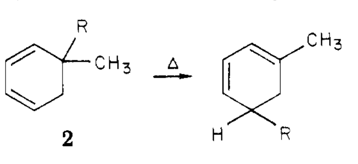
2,2-Dialkylisoindenes are generated by the thermal extrusion of N_2O from bicycloazoxy compounds at 180 °C. Such isoindenes undergo facile 1,5-alkyl shifts which allow the determination of relative migratory aptitudes of a number of alkyl groups: Me:Et:*i*-Pr:cyclopropylcarbinyl:benzyl = 1:6.2:5.3:7.9:55.6. Isolation of dimethylisoindene allowed the determination of activation parameters for its methyl-shift process: log A = 11.0, E_a = 26.1 kcal/mol. The results are discussed in terms of a pericyclic mechanism with the migrating group taking on a significant degree of radical character in the transition state.

Differences in migratory aptitudes of various unsaturated groups in [1,5] sigmatropic rearrangements have been examined by a number of groups in recent years.[1-7] Studying racemization rates of indenes (**1**), Field, Jones, and Kneen concluded that substituent effects were in the order: CHO > COR > H > CH=CH$_2$ > CONHMe > CO$_2$Ph > CO$_2$Me > CN ≈ C≡CH > alkyl.[5,6] Similarly, Schiess and Funfschilling examined [1,5] sigmatropic shifts in the 5-methylcyclohexa-1,3-diene system (**2**) and found CHO >> H ≈ COCH$_3$ > CO$_2$CH$_3$. The former workers rationalized their results in terms of a concerted migration involving an interaction of the HOMO of the diene system with the LUMO of the migrating group, a conclusion which was consistent with their most recent results in which it was shown that electron-poor vinyl groups migrate faster than electron-rich vinyl groups.[7]



1

X = -CHO, -COR, -CO$_2$R, -CH=CH$_2$, -C≡CH, -CN, etc.



R = CO$_2$CH$_3$, CHO, COCH$_3$

In other studies, Miller and Boyer determined that phenyl underwent 1,5 migration slower than H but faster than methyl in an indene system,[8] while Paquette and Carmody discovered a very facile 1,5 shift of a 1,3-butadienyl group.[9]

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