residue obtained by evaporation of the benzene filtrates above was chromatographed on a column of neutral alumina (Fluka, type 507C, 47.5 g, shaken with 1.5 ml of water for 1 hr). After elutions with hexane and benzene, elution with anhydrous ether gave 0.4 g of solid. Recrystallization from benzene gave 0.25 g of white crystals, mp 118–119°, which showed a single peak upon gas chromatography: ir (Nujol) 1375, 1181, 1145, 1008, 963, 938, and 808 cm^{-1}; nmr [$(CD_3)_2SO$ + 2% DCl in D_2O] δ 0.85 (d, J = 6.2 Hz, 6, CH_3), 1.2–2.2 (m, 6, CH_2 and CH_3CH), 2.57 (quintet, CD_3SOCD_2H), 3.37 (unresolved m, 1, CHCHOH), 3.88 (quintet, 1, CH_2CHOH), and 4.1 (s, 2, OH). **4** is entered in Table I as diol B.

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found, C, 66.97; H, 11.11.

Continued elution with 19:1 ether–methanol gave a second fraction, 0.25 g, mp 139–141°, identified as diol **3**.

***r*-2,*c*-6-Dimethyl-*c*-4-hydroxycyclohexanone**[3] **(1)**.—To a solution of 0.40 g (3.4 mmol) of diol **3** in 15 ml of acetone (reagent grade, purified by distillation from $KMnO_4$), stirred vigorously in an ice–salt–water bath at −5°, was added dropwise 0.89 ml (1 equiv) of 2.5 *M* chromic acid solution[4] during 15 min. After stirring for an additional 15 min at −5°, a chilled solution of 1.3 g of $NaHSO_3$ in 40 ml of water was added and the mixture was extracted immediately with 6 × 100 ml of chilled ether. The ether layer was washed with 2 × 15 ml of cold 10% $NaHCO_3$ and then with 15 × 4 ml of cold water. The final washings were neutral. The ether layer was dried over anhydrous $MgSO_4$. Removal of solvent under reduced pressure gave a viscous oil which showed four peaks upon gas chromatography. One peak gave the same retention time as the starting material, diol **3**. The three expected products are hydroxy ketones **1** and **9** and dione **10**. Thin layer chromatography also showed four components.

The product was applied to three preparative thin layer chromatography plates, 20 × 20 cm, coated with a 2-mm layer of silica gel (E. Merck, PF_{254}). Double development with 1:1 anhydrous ether–benzene gave separation of the components. Each band was extracted with 10 × 20 ml of anhydrous ether. Filtration, removal of solvent under reduced pressure, and recrystallization from hexane gave from one band 0.12 g (30%) of fluffy white crystals, mp 66–66.5°, assigned structure **1**: nmr[2] (CD_3OD) δ 0.97 (d, J = 5.5 Hz, 6, CH_3), 1–3 (m, 6, CH_3CH-CH_2), 4.2 (nonet, 1, CHOH, band width 30.2 ± 0.2 Hz), and 4.7 (s, 1, OH); nmr[2] (benzene) 4.0 (nonet, 1, CHOH, band width 29.5 ± 0.2 Hz).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.72; H, 10.16.

Similarly, a second band yielded an oily residue, which after recrystallization from hexane gave 0.08 g (20%) of white, fluffy crystals, mp 53–54°, not fully characterized, but probably *r*-3,*c*-5-dimethyl-*c*-4-hydroxycyclohexanone (**9**).[14]

***cis*-2,6-Dimethyl-1,4-cyclohexanedione (10). A. Jones Oxidation of Diol 3.**—To 2.50 g (0.0173 mol) of diol **3** in 88 ml of acetone (distilled from $KMnO_4$) at 0° was added dropwise with vigorous stirring 18.7 ml (100% excess) of 2.48 *M* chromium oxide solution[4] during 15 min. The temperature was maintained at 0–5° during the addition and for 15 min of further stirring following the addition. Then 3.62 g of $NaHSO_3$ in 88 ml of water at 0° was added. The resulting green solution was immediately extracted with 3 × 290 ml of ether. Each ether extract was washed successively with 110 ml of 10% NH_4Cl, 110 ml of 10% $NaHCO_3$, and 66 ml of water. The ether extracts were combined and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure to give 2.2 g (90%) of a white solid, mp 85–87°. Two recrystallizations from hexane gave 1.3 g of cis dione **10**, mp 87.5–88°, containing *ca.* 1% of the trans epimer, detected by gas chromatography.[11]

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.73; H, 8.64.

B. Jones Oxidation of Diol 4.—As above, but on a smaller scale, 0.28 g (0.0019 mol) of diol **4** gave 0.24 g (89%) of white solid, mp 86–87.5°. Recrystallization from hexane gave 0.19 g of cis dione **10**, mp 87.5–88.5°. Reaction of **10** with excess 1,2-ethanedithiol and boron trifluoride–ether gave a product, mp 95–96° (from methanol).

Registry No.—**1**, 34958-40-2; **3**, 34958-41-3; **4**, 34958-42-4; **10**, 34958-43-5.

Bicyclo[3.2.1]oct-6-en-2-one. A Convenient Synthesis of Bridged Polycyclic, Homoconjugated Ketones[1,2]

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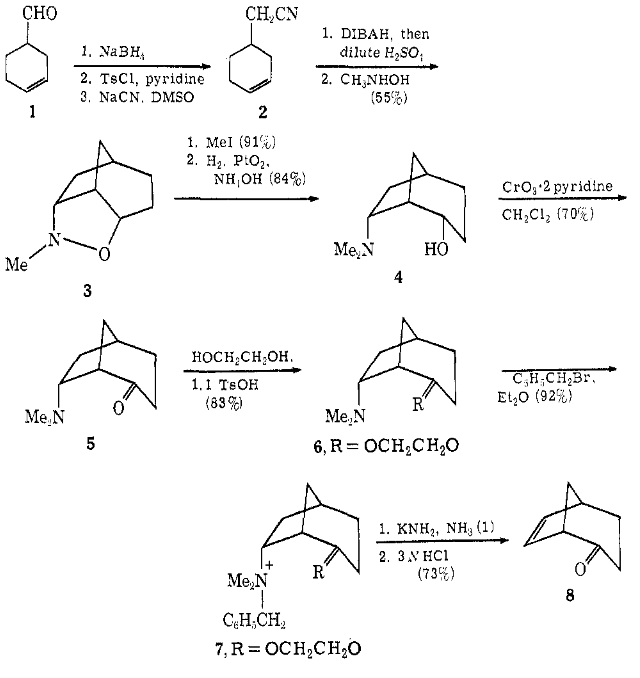
As part of a continuing program of exploration of the mechanistic nuances and the synthetic scope of intramolecular 1,3-dipolar cycloadditions of nitrones, we have prepared a variety of polycyclic isoxazolidines.[3] It is the purpose of this report to describe a simple and efficient degradation scheme which will allow conversion of certain of these products to homoconjugated (γ,δ-unsaturated) ketones. These latter are of both theoretical and preparative import.

The key compound of the present example is the tricyclic isoxazolidine **3**, which was prepared by the reaction of 3-cyclohexen-1-acetaldehyde with *N*-methylhydroxylamine. The aldehyde was obtained by diisobutylaluminum hydride reduction of 3-cyclohexen-1-acetonitrile (**2**). Quaternization of **3** with methyl iodide followed by hydrogenolysis gave the amino alcohol **4**, which was in turn oxidized to the *N*,*N*-dimethylamino ketone **5**.[4] The ethylene ketal **6** was then prepared, and it was benzylated to afford **7**.[5] Reaction with potassium amide in liquid ammonia and



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[1] This work was supported by the National Science Foundation under Grant No. GP 14114.

[2] For the previous paper in this series, see N. A. LeBel and E. G. Banucci, *J. Org. Chem.*, **36**, 2440 (1971).

[3] N. A. LeBel, *Trans. N. Y. Acad. Sci.*, **27**, 858 (1965); N. A. LeBel, G. H. J. Slusarczuk, and L. A. Spurlock, *J. Amer. Chem. Soc.*, **84**, 4360 (1962).

[4] The Collins oxidation procedure, ref 9, has proven superior in our hands; however, Jones, Kiliani, and Sarett oxidations were successful in varying degrees.

[5] Benzylation proved superior to methylation because the subsequent elimination reaction generated improved yields of product **8**.

subsequent hydrolysis of the ketal gave bicyclo[3.2.1]oct-6-en-2-one (**8**) directly. The overall yield of **8** from **2** was 16.3%, under conditions which involved the isolation of pure intermediates at each stage.[6]

The ketone **8** has not been described previously, and its homoconjugated nature is apparent from the ultraviolet spectrum [$\lambda_{\max}$ 212 nm (ϵ 3600) and 299 (180) in isooctane] which clearly shows the enhanced $n \rightarrow \pi^*$ transition relative to its saturated analog.

The synthetic scheme described in this report is applicable to large-scale work and is quite general.

Experimental Section

Methods.—Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Ir spectra were measured with a Perkin-Elmer Model 237B grating infrared spectrophotometer. Nmr spectra were obtained with a Varian Associates Model T-60. Analyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind.

3-Cyclohexenyl-1-acetonitrile (2).—3-Cyclohexenyl-1-methanol was prepared in good yield by reduction of 3-cyclohexene-1-carboxaldehyde (1) with $NaBH_4$ in methanol, bp 65–67° (4 Torr), $n^{25}\mathrm{D}$ 1.4817 [lit.[7] bp 79–83° (12 Torr), $n^{20}\mathrm{D}$ 1.4852]. Reaction of the alcohol with *p*-toluenesulfonyl chloride in pyridine followed by the usual work-up gave a 97% yield of the crude tosylate. The tosylate (500 g, 1.99 mol) was added to a solution of NaCN (1.2 molar equiv) in 600 ml of freshly distilled DMSO at 80°. The addition required 15–20 min, during which time the temperature rose to about 95°. The oil bath was removed and stirring was continued for 3 hr at room temperature followed by the usual aqueous work-up; there was obtained after distillation 218 g (90%) of 3-cyclohexenyl-1-acetonitrile (**2**), bp 61–66° (2.5 Torr), $n^{24.2}\mathrm{D}$ 1.4726.

Anal. Calcd for $C_8H_{11}N$: C, 79.34; H, 9.09; N, 11.57. Found: C, 79.55; H, 9.09; N, 11.80.

3-Methyl-2-oxa-3-azatricyclo[4.2.2.0^{4,9}]decane (3).—Diisobutylaluminum hydride (40 g, 0.28 mol) was slowly added to a mechanically stirred solution of 3-cyclohexenyl-1-acetonitrile (27.61 g, 0.23 mol) in 200 ml of hexane under a nitrogen atmosphere while the temperature was maintained at 10–20°. After addition was completed, the solution was stirred for 1 hr, and the excess hydride was destroyed by careful addition of cold 10% H_2SO_4. Dropwise addition of the dilute acid was continued, keeping the temperature below 30° until about 200 ml had been added. The white precipitate was removed by filtration and washed thoroughly with ether. The aqueous layer was separated and extracted with ether. The combined ether extract was washed with brine, dried ($MgSO_4$), and concentrated on a rotary evaporator to give 25.25 g of crude 3-cyclohexen-1-acetaldehyde.

Purification of the aldehyde can be effected by distillation; however, because of extensive formation of nonvolatile residues, this is not desirable or necessary. 3-Cyclohexen-1-acetaldehyde shows bp 46–52° (3.7 Torr), $n^{25}\mathrm{D}$ 1.4702.

Anal. Calcd for $C_8H_{12}O$: C, 77.43; H, 9.67. Found: C, 77.14; H, 9.72.

The 2,4-dinitrophenylhydrazone melted at 120–121° (lit.[8] mp 125–126°). To a refluxing solution of the crude aldehyde in 500 ml of toluene was added dropwise a solution of methylhydroxylamine in 15 ml of methanol. The water produced was collected in a Barrett receiver and the first 20 ml of liquid was readded to the reaction mixture. Refluxing was continued for 16 hr. The cooled reaction mixture was extracted with 10% HCl (4 × 100 ml). The combined aqueous layers were extracted with ether, basified with 20% NaOH, and continuously extracted with ether for 24 hr. The organic layer was dried and concentrated to give a dark residue which was distilled to afford 19.3 g (55.4%) of **3**: bp 50–60° (0.3 Torr), 67–69° (1.25 Torr); $n^{27.5}\mathrm{D}$ 1.4995; ir (neat) 2940, 1450, and 1438 cm^{-1}; nmr (CCl_4) δ 4.20 (d of t, 1 H), 3.65–3.27 (m, 1 H), 3.10–2.80 (m, 1 H), 2.47 (s, 3 H), and 2.25–1.00 (m, 9 H).

Anal. Calcd for $C_9H_{15}NO$: C, 70.58; H, 9.80; N, 9.15. Found: C, 70.40; H, 9.68; N, 9.28.

The methiodide of isoxazolidine **3** was obtained in 91–100% yield by stirring an ether solution of **3** with a threefold excess of methyl iodide. Crystallization from a mixture of ethanol and ether gave the pure salt, mp 151–152°.

Anal. Calcd for $C_{10}H_{18}NOI$: C, 40.68; H, 6.10; N, 4.75. Found: C, 40.61; H, 6.15; N, 4.70.

***endo,endo*-7-(*N,N*-Dimethylamino)bicyclo[3.2.1]octan-2-ol (4).**—The methiodide of **3** (9.43 g, 3.2 mmol) was hydrogenated over 0.9 g of prereduced PtO_2 in 100 ml of absolute ethanol containing four drops of concentrated NH_4OH at 2 atm for 16 hr. The catalyst was removed and the filtrate was concentrated. The residue was taken up in 10% NaOH and ether, and the aqueous layer was extracted thoroughly with ether. The combined ether extract afforded a viscous liquid, which was distilled to give 4.54 g (84%) of the amino alcohol **4**: bp 66–67° (0.5 Torr); $n^{24}\mathrm{D}$ 1.4912; mp 171–173° (crystallized from a mixture of methanol and ether); ir (neat) 3425 cm^{-1} (br); nmr (CCl_4) δ 3.33 (br, 2 H), 2.28 (s, 6 H), 2.6–1.0 (m, 11 H).

Anal. Calcd for $C_{10}H_{19}NO$: C, 71.01; H, 11.24; N, 8.28. Found: C, 70.92; H, 11.48; N, 8.27.

***endo*-7-(*N,N*-Dimethylamino)bicyclo[3.2.1]octan-2-one (5).**—To a mixture of pyridine (12.0 g, 0.15 mol) and 75 ml of CH_2Cl_2 was added dry CrO_3 (7.62 g, 76.2 mmol) in several portions.[9] The mixture was stirred for 15 min, and the amino alcohol **4** (2.15 g, 12.7 mmol) was added in one batch. After 30 min of stirring, the solvent was removed on a rotary evaporator. The residue was taken up in ether and 5% NaOH, and the aqueous layer was continuously extracted with ether for 24 hr. The extract was concentrated to give an oil which was distilled. There was obtained 1.48 g (70%) of amino ketone **5**: bp 67–69° (0.5 Torr); ir (neat) 1710 cm^{-1}; nmr (CCl_4) δ 2.10 (s, 6 H), 2.8–1.0 (m, 11 H).

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.86; H, 10.18; N, 8.38. Found: C, 71.57; H, 10.35; N, 8.49.

***endo*-7-(*N,N*-Dimethylamino)2-ethylenedioxybicyclo[3.2.1]octane (6).**—The amino ketone **5** (4.69 g, 28.1 mmol) was refluxed in 100 ml of benzene with 4 ml of ethylene glycol and 1.1 equiv of *p*-toluenesulfonic acid. The cooled solution was basified and continuously extracted with ether for 24 hr. The extract, after concentration and distillation, afforded 4.94 g (83%) of the amino ketal **6**, bp 60–65° (0.5 Torr).

The benzylammonium bromide salt of **6** was prepared by stirring a solution of the amino ketal **6** with benzyl bromide in a mixture of ether and acetone for 3 days. The solid was washed well with ether and recrystallized from a mixture of absolute ethanol and ether to give 92% of **7**, mp 222–224° dec.

Anal. Calcd for $C_{19}H_{28}NO_2Br$: C, 59.69; H, 7.38; N, 3.66. Found: C, 59.60; H, 7.40; N, 3.51.

Bicyclo[3.2.1]oct-6-en-2-one (8).—To a suspension of 4 equiv of KNH_2 in liquid ammonia was added the quaternary ammonium salt **7** (2.00 g, 5.11 mmol) in several portions, and the mixture was stirred for 3.5 hr. A small amount of NH_4Cl was added to destroy excess amide. The ammonia was allowed to distil and was replaced by ether. Water was added, the layers were separated, and the aqueous layer was extracted with ether. The combined ether extract yielded a liquid which was stirred with a two-phase, ether–3 *N* HCl mixture for 16 hr. The layers were separated and the aqueous layer was extracted with ether. The combined organic layer contained 466 mg (73%) of the ketone **8**: mp 65–81° (after sublimation); mass spectrum m/e 122 (M^+); ir (CCl_4) 3065 (w), 2495, 2865, 1720, 1590 (w), 1220, 1085, 727, and 710 cm^{-1}; nmr (CCl_4) δ 6.15 (d of q, 2 H), 2.90 (sextet 2 H), 2.7–2.1 (m, 3 H), 2.05–1.55 (m, 3 H). The nmr spectrum of **8** may be contrasted with that of bicyclo[3.2.1]oct-6-en-3-one,[10] which shows the vinyl protons as a rather narrow, unresolved multiplet at δ 6.20.

The 2,4-dinitrophenylhydrazone melted at 151–152° after recrystallization from ethanol.

Anal. Calcd for $C_{14}H_{14}N_4O_4$: C, 55.63; H, 4.67; N, 18.54. Found: C, 55.36; H, 4.61; N, 18.39.

The ketone **8** was hydrogenated to the known bicyclo[3.2.1]octan-2-one and it was shown by glpc to be the major ketone from

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(6) We have shown that it is quite feasible to introduce a resolution step in the sequence at the amino alcohol stage, allowing for the generation of optically active homoconjugated ketones similar to **8**: M. A. Sciaraffa, unpublished work.

(7) J. Edelson, C. G. Skinner, J. M. Ravel, and W. Shive, *Arch. Biochem. Biophys.*, **80**, 416 (1959).

(8) M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

(9) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*. 3363 (1968); R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

(10) N. A. LeBel and R. N. Liesmer, *J. Amer. Chem. Soc.*, **87**, 4301 (1965).

the deaminative ring expansion of 2-aminomethylbicyclo[2.2.1]-oct-5-en-2-ol.

Registry No.—**2**, 34956-61-1; **3**, 34956-62-2; **3** MeI, 34956-63-3; **4**, 34956-64-4; **5**, 34956-65-5; **6**, 34956-66-6; **7**, 34956-67-7; **8**, 34956-68-8; **8** 2,4-DNP, 34956-69-9; 3-cyclohexen-1-acetaldehyde, 24480-99-7.

Reactions of Bicyclo[3.2.1]octan-8-ylidene and Bicyclo[3.2.1]oct-2-en-8-ylidene

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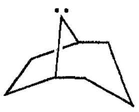
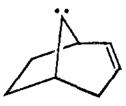
The "nonclassical" stabilization of singlet carbenes by olefinic bonds has been suggested by Hoffmann and Gleiter[1] for systems in which the molecule is constrained in such a way that addition to the double bond cannot occur. This has been termed a "foiled methylene" and is commonly referred to as a nonclassical carbene. Fisch and Pierce[2] and Moss, Dolling, and Whittle[3] have recently described such potential cases with the bicyclo[3.3.1]non-2-en-9-ylidene[2] and 7-norbornenylidene[3] systems. We would like to report work on some related carbenes, bicyclo[3.2.1]octan-8-ylidene (**1**) and bicyclo[3.2.1]oct-2-en-8-ylidene (**2**), the latter providing an excellent example of the foiled methylene reaction.



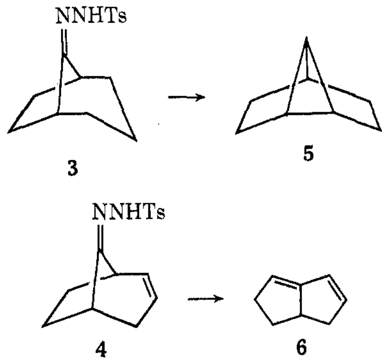
1



2

Carbenes **1** and **2** were generated by the sodium methoxide catalyzed decomposition of the corresponding tosylhydrazones **3** and **4** at 150° in dry diglyme. Hydrocarbon products were isolated in 80-90% yield by pentane extraction of the water-diluted reaction mixture and analyzed by capillary gas chromatography (gc). Decompositions were carried out using both 2 and 4 equiv of base with no significant effect on product composition.[4]

The two carbenes follow strikingly different reaction paths. **1** gave a product mixture containing three components in the relative amounts of 1.5, 98, and *ca.* 0.5% (in order of elution from the gc column). The major product was identified as tricyclo[3.3.0.0^{2,8}]-octane (**5**), the result of a 1,3-insertion reaction, by a comparison of its gc retention time and ir and nmr spectra with those of an authentic sample of the known hydrocarbon.[5,6] The unsaturated carbene **2** gave two products in the relative amounts of 3 and 97%. The major product is an unstable, colorless liquid and is assigned the structure of the 1,2-rearrangement product, bicyclo[3.3.0]octa-1,7-diene (**6**), on the basis of



3 → **5**

4 → **6**

its hydrogenation to bicyclo[3.3.0]octane and the following spectral data: nmr (CCl_4) δ 5.23 (m, 1 H, vinyl), 6.16 (AB, 2 H, J = 7 Hz, five-membered ring vinyl[7]), 3.0 (m, broad, 1 H, bridgehead), 1.2-2.8 (6 H, envelope of peaks); uv (pentane) λ_{max} 247 nm (heteroannular conjugated diene)[8]; ir (CCl_4) 3110 and 3050 (vinyl CH), 1648 (C=C), 720 cm^{-1} (out of plane CH bend for cis alkene); mass spectrum (70 eV) M^+ 106. No attempt was made to identify the minor products of these reactions.

The contrasting behavior of carbenes **1** and **2**—insertion *vs.* rearrangement—is similar to but far more dramatic than that found for the related C_7 and C_9 carbenes.[2,9] Apparently the saturated carbene **1** has the carbenoid center well situated for insertion into the axial C_2–H bond. It shows a much greater propensity for insertion compared to rearrangement (98%) than the homologous carbenes, norbornan-7-ylidene (12%)[9] and bicyclo[3.3.1]nonan-9-ylidene (80%).[2]

The preference for rearrangement in the unsaturated carbene **2** can be explained in several ways. Since models indicate that the axial hydrogen in **2** is farther away from the carbenoid center than it is in **1**, it is possible that the insertion reaction is simply less favorable than rearrangement in this case. Alternatively, the difference in behavior can be rationalized very nicely in terms of a "foiled methylene." A stabilizing interaction of the carbenoid center with the double bond would further discourage the insertion reaction, because it tends to twist the axial hydrogen even farther away from the reacting center. Since addition to the double bond is also discouraged by the nature of the strained tetracyclic hydrocarbon **7**[10] which would result, the most favorable reaction of the nonclassical carbene becomes the 1,2 rearrangement to the diene **6**. Presumably, double-bond interaction in the stab-

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[1] R. Gleiter and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 5457 (1968).

[2] M. H. Fisch and H. D. Pierce, Jr., *Chem. Commun.*, 503 (1970).

[3] R. A. Moss, U.-H. Dolling, and J. R. Whittle, *Tetrahedron Lett.*, 931 (1971).

[4] Variation in the number of equivalents of base present has been observed to strongly affect product composition. See R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Amer. Chem. Soc.*, **89**, 1442 (1967).

[5] M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

[6] The decomposition of **3** serves as an excellent synthetic route to **5**.

[7] (a) O. L. Chapman, *J. Amer. Chem. Soc.*, **85**, 2014 (1963); (b) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); (c) P. Laszlo and P. v. R. Schleyer, *ibid.*, **85**, 2017 (1963).

[8] The λ_{max} calculated for compound **6** using Woodward's rules is 234 nm. The discrepancy between the calculated value and the observed value (bathochromic shift) can be attributed to the strain of the double bond at the ring juncture. Consider, for example, $\Delta^{3,5}$-*B*-norcholestadiene: ψ_{max}^{calcd} 234 nm, λ_{max}^{obsd} 245 nm. L. F. Fieser, *J. Amer. Chem. Soc.*, **75**, 4386 (1953). Bicyclo[3.2.0]hepta-1,6-diene: λ_{max}^{calcd} 234 nm, λ_{max}^{obsd} 255 nm.[3]

[9] R. A. Moss and J. R. Whittle, *Chem. Commun.*, 341 (1969).

[10] This hydrocarbon would contain a carbon atom having all four bonds on one side of a plane. For the synthesis and properties of such compounds, see, for example, K. B. Wiberg, *et al.*, *J. Amer. Chem. Soc.*, **93**, 246 (1971); **91**, 3372 (1969); *Tetrahedron Lett.*, 5855 (1968); 317 (1969). For theoretical discussions see M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 773 (1972), and W.-D. Stohrer and R. Hoffmann, *ibid.*, **94**, 779 (1972).