The crystal structure of 2-(2′-acetoxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane (AETCNQ, 11) has been determined by X-ray diffraction, and the results will be published elsewhere.[8]

The cyclic voltammogram of **3**, obtained by Prof. Charles L. Hussey of the Department of Chemistry at The University of Mississippi, showed the usual two one-electron reduction waves characteristic of TCNQ-type electron acceptors. According to the half-wave reduction potentials (Table I), product **3** was a slightly poorer acceptor when compared with TCNQ (**1**) or the bromo derivative **2**.

Experimental Section

Melting points were run on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman Acculab 3 instrument. E. Merck silica gel (9385) was used in column chromatography. Cyclic voltammagrams were obtained by using an Amel Model 551 potentiostat programmed by a PARC 175 universal programmer. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

2-Hydroxyterephthalic Acid (6). The procedure given here was essentially that reported by Field and Engelhardt.[5] 2-Bromoterephthalic acid[4] (50.0 g, 0.204 mol) and 16.4 g (0.408 mol) of NaOH were dissolved in 940 mL of water. After the addition of 36.8 g (0.448 mol) of NaOAc, 0.26 g of Cu power, and a few drops of phenolphthalein, the aqueous mixture was stirred and heated to the reflux temperature. Aqueous KOH (5%) was added occasionally in order to keep the reaction mixture alkaline. Completion of the reaction was indicated by TLC after 3 days. After cooling, the mixture was filtered, and the filtrate was acidified with 1.2 N HCl. The white crystals were collected by filtration and then dried in a vacuum oven to afford 36.7 g (99%) of **6**: mp 315–319 °C (lit.[5] mp 320–322 °C). This product exhibits a blue fluorescence during irradiation with UV light.

2-(2′-Hydroxyethoxy)terephthalic Acid (7). 2-Chloroethanol (2.2 mL, 2.66 g, 33.0 mmol), was added in one portion to a stirred solution of 2.2 g (55.0 mmol) of NaOH, 2.0 g (10.98 mmol) of **6**, and 15 mL of water. The resultant mixture was stirred at room temperature for 2 days. The reaction mixture was then filtered, and the filtrate was acidified with 1.2 N HCl. The white precipitate was collected by filtration and dried (≅2.9 g). According to silica gel TLC (EtOAc–HOAc, 97:3), the white solid was a mixture of product, **7**, and starting material, **6**. Silica gel normal and reversed-phase column chromatography, preparative thin-layer chromatography, and recrystallization failed to separate this mixture. However, it was completely separated into its components with countercurrent chromatography[6] on an Ito Coil Planet centrifuge[9] [the solvent system was chloroform–MeOH–water (37:37:26); the upper phase was the mobile phase; the multilayer coiled column was 1.6-mm i.d., 130 m long, and 330-mL capacity; the flow rate was 180 mL/h at 800 rpm; the sample sizes for two runs were 1.5 and 1.42 g]. The product (**7**) was obtained as white crystals from acetone–hexane and weighed 1.88 g (76%): mp 223–224 °C; IR (KBr) 3550, 2650, 2550, 1695, 1245, 760 cm^{-1}. Anal. Calcd for $(C_{10}H_{10}O_6)_4 \cdot H_2O$: C, 52.05; H, 4.59. Found: C, 52.30; H, 4.41.

2-(2′-Acetoxyethoxy)terephthalic Acid (8). A mixture of 440 mg (1.95 mmol) of **7**, 1.0 mL (1.08 g, 10.6 mmol) of Ac_2O, a few drops of pyridine, and 5.0 mL of dry $CHCl_3$ was heated to the reflux temperature for 2 h. The reaction mixture was distilled at reduced pressure in order to remove all volatile materials. The residue sometimes required chromatography on a silica gel column with EtOAc–HOAc (96:4) or MeOH (100) as the eluant. The crystalline product (**8**) weighed 483 mg (92%) and could be recrystallized from EtOAc–acetone: mp 219–220 °C; IR (KBr) 2650, 2550, 1745, 1690, 1250, 760 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_7$: C, 53.73; H, 4.51. Found: C, 53.73; H, 4.41.

In some runs, a faster moving product, **4**, was obtained in minor amounts from the silica gel column. It crystallized as colorless needles from EtOAc: mp 263–265 °C; IR (KBr) 2620, 1720, 1705, 1660, 1230, 740 cm^{-1}. Anal. Calcd for $C_{10}H_8O_5$: C, 57.70; H, 3.87. Found: C,57.63; H, 3.82.

2-(2′-Acetoxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane (11). One mL of $SOCl_2$ (1.64 g, 13.8 mmol) was added to a stirred solution of 0.399 g (1.49 mmol) of **8** in 10 mL of dry benzene. The resultant solution was heated to the reflux temperature for 2 h, after which the solvent and unreacted $SOCl_2$ were removed by distillation under reduced pressure. The residual viscous brown oil (the diacid chloride, **9**) was treated first with 1.0 mL of pyridine and then with 3.0 mL (2.23 g, 22.5 mmol) of trimethylsilanecarbonitrile, and this was stirred and heated to the reflux temperature under Ar for 5 h. The volatile material was removed by reduced pressure distillation, and the semisolid residue (**10**) was stored in a desiccator for 16 h. The latter was then treated with 1.3 mL (2.14 g, 13.9 mmol) of $POCl_3$ and 1.5 mL of dry pyridine, and this reaction mixture was stirred under Ar at room temperature for 20 min. The above was added to about 50 mL of EtOAc and 200 mL of ice water, the resultant mixture was shaken, and the phases were separated. The organic phase was washed with 50 mL of water and dried over anhydrous $MgSO_4$. The filtrate was distilled under reduced pressure, and the semisolid residue weighed 530 mg. Purification by silica gel column chromatography (EtOAc–hexane, 68:32) afforded 0.43 g (95%) of red crystals of **11**. These could be recrystallized from EtOAc–hexane: mp 156–158 °C; IR (KBr) 2210, 1725, 1220, 835 cm^{-1}. Anal. Calcd for $C_{16}H_{10}N_4O_3$: C, 62.74; H, 3.29; N, 18.29. Found: C, 62.55; H, 3.14; N, 18.38.

2-(2′-Hydroxyethoxy)-7,7,8,8-tetracyano-*p*-quinodimethane, HETCNQ (3). A solution of 50 mg (0.16 mmol) of **11**, 5.0 mL of CH_3CN, and 1.5 mL of 1.2 N HCl was stirred at 60 °C for 23 h. The reaction solution was poured into ≅10 mL of EtOAc, and the organic layer was washed with ≅5 mL of water. After drying, the EtOAc solution was distilled under reduced pressure, and the residue was chromatographed on silica gel (EtOAc–hexane, 30:70) to afford 31 mg (69%) of red crystals (**3**), which could be recrystallized from EtOAc: mp 173.0–174.5 °C de; IR (KBr) 3500–3300, 2230, 1605, 1550, 1530, 1240, 860, 825 cm^{-1}. Anal. Calcd for $C_{14}H_{18}N_4O_2$: C, 63.64; H, 3.05; N, 21.20. Found: C, 63.50; H, 2.80; N, 21.15. The cyclic voltammogram of **3** showed two one-electron reduction waves, and the half-wave reduction potentials are given in Table I.

Acknowledgment is made of support by the National Science Foundation, Solid State Chemistry (Grant DMR 84-17563). We also acknowledge the assistance of Prof. C. L. Hussey for the cyclic voltammogram of **3**.

Registry No. **3**, 111822-79-8; **5**, 586-35-6; **6**, 636-94-2; **7**, 111822-80-1; **8**, 111822-81-2; **9**, 111822-82-3; **10**, 111847-84-8; **11**, 111822-83-4; $Cl(CH_2)_2OH$, 107-07-3; $(H_3C)_3SiCN$, 7677-24-9.

(8) Miura, Y.; Laidlaw, R. K.; Panetta, C. A.; Metzger, R. M. *Acta Crystallogr.*, in press.
(9) Available from P. C. Inc., Potomac, MD.
(10) Anderson, J. R.; Orgensen, O. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3095.

An Efficient Electrophile-Initiated Homoconjugate Addition of Acetate to Cyclopropyl Ketones

James H. Rigby* and Chrisantha Senanayake

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

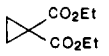
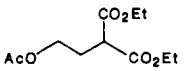
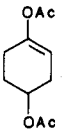
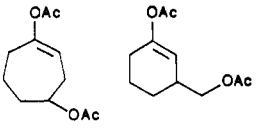
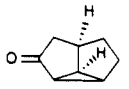
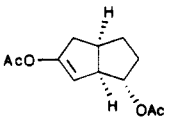
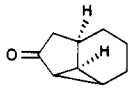
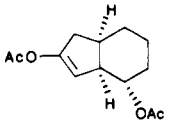
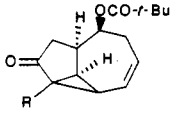
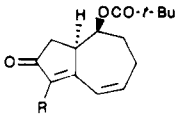
Received May 11, 1987

The homoconjugate addition of nucleophiles to cyclopropanes activated by a carbonyl substituent is a potentially powerful method for achieving 1,4-difunctionalization. A number of important strategies for effecting 1,5-additions of nucleophilic species to electron-deficient cyclopropanes have been reported,[1] and several cyclopropane

(1) (a) Danishefsky, S.; Singh, R. K. *J. Am. Chem. Soc.* **1975**, *97*, 3239. (b) Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66. (c) Wender, P. A.; Dreyer, G. B. *Tetrahedron Lett.* **1983**, *24*, 4543.

0022-3263/88/1953-0440$01.50/0 © 1988 American Chemical Society

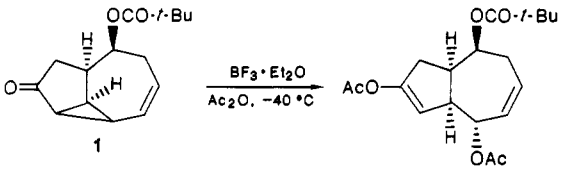
Table I. Homoconjugate Additions of Acetate to Cyclopropyl Ketone

entry	cyclopropyl ketone	conditions	product	yield,[a] %
1		rt, 1.5 h		85
2		rt, 1.5 h		71
3		rt, 0.5 h	 3:1	62
4		−20 °C, 1 h		87
5		0 °C, 1.5 h		80
6		rt, 2 h	 R = H R = Me	81 90

[a] All yields are for isolated, analytically pure product.

ring-opening reactions using heteroatom nucleophiles with the assistance of Lewis acid activation of the carbonyl group have been forthcoming in the recent literature.[2]

We report herein a new and experimentally convenient procedure for performing a homoconjugate addition to cyclopropyl ketones with concomitant regiospecific enol acetate formation. Typically, the reaction is carried out by the addition of a large excess of BF_3·Et_2O and acetic anhydride to a solution of substrate in dichloromethane. The reaction temperature can vary from −40 °C to room temperature depending on the type of carbonyl compound employed. For example, treatment of cyclopropyl ketone **1** under these conditions at −40 °C provided the highly functionalized acetoxyhydroazulene **2** in 93% isolated yield.[3]



1 **2**

Table I illustrates the generality of this method for a range of cyclopropyl ketone substrates. Several observations made during this study are particularly noteworthy. The regioselectivity of the cyclopropane cleavage in entries 2 and 3 is complimentary to that normally seen with several other acid mediated openings.[2] This difference in selectivity may reflect a greater degree of charge development during the course of the Ac_2O/BF_3·Et_2O reaction. Entry 6 demonstrates that additional conjugation can alter the course of the ring-opening process to give an $\alpha,\beta,\gamma,\delta$-unsaturated ketone as the exclusive product. In contrast to its behavior at low temperatures, cyclopropyl ketone **1** gives the corresponding dienone as the only observable product when exposed to the reaction conditions at room temperature. This interesting isomerization phenomena was not seen with any of the other simple cyclopropyl ketones examined. Furthermore, additional alkyl substitution at the α-carbon of the cyclopropyl ketone appears to completely suppress formation of the acetate addition product at any temperature, yielding only the corresponding dienone. This process, in conjunction with diazo ketone cyclization, could provide a convenient access to a variety of bicyclic dienone systems starting from monocyclic precursors.

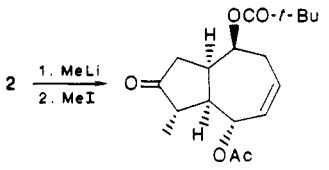
Of critical importance to the general utility of this procedure for complex synthetic applications is the capability of chemoselective manipulation of the resultant vinyl acetate in the presence of the alkylacetoxy group. Since a single enol acetate was obtained in each case examined during this study, the intriguing possibility of exploiting this group as a precursor for the corresponding enolate was considered.[4] Indeed, treatment of compound **2** with 2 equiv of MeLi at −50 °C followed by quenching with excess MeI gave ketone **3** as a single diastereomer in 61% yield.[5]

(2) (a) Dauben, W. G.; Schutte, L.; Wolf, R. E.; Deviny, F. J. *J. Org. Chem.* **1969**, *34*, 2512. (b) Demuth, M.; Rayhanan, P. R. *Helv. Chim. Acta.* **1979**, *62*, 2338. (c) Giacomini, E.; Loreto, M. A.; Pellacani, L.; Tardella, P. A. *J. Org. Chem.* **1980**, *45*, 519. (d) Miller, R. D.; McKean, D. R. *J. Org. Chem.* **1981**, *46*, 2412. (e) Dieter, R. K.; Pounds, S. *J. Org. Chem.* **1982**, *47*, 3174. (f) Demuth, M.; Mithail, G. *Tetrahedron* **1983**, *39*, 991.

(3) The regiochemistry of the ring-opening process was established in this case by performing COSY experiments on compound **3**.

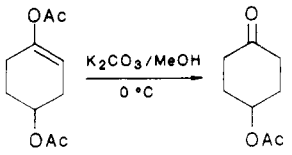
(4) (a) House, H. O.; Trost, B. M. *J. Org. Chem.* **1965**, *30*, 1341. (b) House, H. O.; Gall, M.; Olmstead, H. P. *Ibid.* **1971**, *36*, 2361.

(5) Much of the remaining material was the corresponding ketone which had not undergone methylation.



3

This important observation dramatically increases the applicability of this ring-opening method to synthesis, particularly in view of the difficulties that some workers have experienced in isolating similar intermediates from related reactions.[2c,d] The enol acetate unit can also be selectively cleaved with K_2CO_3/MeOH at 0 °C to provide the corresponding ketone as illustrated by the conversion of compound 4 to keto acetate 5.



4 5

The ring-opening methodology described herein clearly offers a number of interesting opportunities for 1,4-difunctionalization in a range of contexts and should prove to be a useful addition to the armory of methods available to synthetic chemists.

Experimental Section

General Procedure for Opening of Cyclopropyl Ketones. The cyclopropyl ketone (1 mmoL) in 1 mL of dichloromethane was placed in a two-necked flask under N_2 atmosphere. Acetic anhydride (1 mL) and $BF_3{\cdot}OEt_2$ (6 mmol) were added at the indicated temperature (see Table I), and stirring was continued for the appropriate reaction time. The reaction mixture was then poured into 20 mL of dichloromethane containing 5 g of solid sodium bicarbonate and stirred for 5 min, at which time 50 mL of saturated aqueous sodium bicarbonate solution was added. The mixture was extracted with 2 × 25 mL portions of dichloromethane, and the organic layer was washed with 10 mL of water, followed by 50 mL of brine, and dried over anhydrous sodium sulfate. The solution was concentrated in vacuo to yield crude product, which was purified by flash chromatography[7] to give corresponding γ-acetoxy enol acetate.

3,8-Diacetoxybicyclo[3.3.0]oct-2-ene: IR (CCl_4) 2957, 2874, 2857, 1767, 1737, 1667, 1441, 1371, 1250, 1220, 1195, 1155, 1140, 1044, 1019 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (m, 1 H), 1.68 (m, 1 H), 1.80–1.95 (m, 2 H), 1.97 (s, 3 H), 2.07 (s, 3 H), 2.12 (m, 1 H), 2.69–2.83 (m, 2 H), 3.81 (m, 1 H), 4.83 (m, 1 H), 5.31 (dd, J = 2.0, 4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.79, 21.09, 30.40, 31.98, 36.98, 38.78, 53.72, 79.99, 113.16, 150.76, 168.04, 170.43; mass spectrum, m/e (%) (no M^+), 181 (3), 165 (19), 122 (100), 95 (16), 79 (7), 43 (64). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.25; H, 7.19. Found: C, 64.39; H, 7.22.

5,8-Diacetoxybicyclo[4.3.0]non-7-ene: IR (CCl_4) 2934, 2862, 1759, 1737, 1682, 1445, 1370, 1245, 1312, 1034 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25–1.41 (m, 3 H), 1.77–1.86 (m, 3 H), 2.06 (s, 3 H), 2.09 (s, 3 H), 2.12–2.18 (m, 2 H), 2.51–2.53 (m, 2 H), 4.93 (m, 1 H), 5.21 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.17, 20.53, 20.89, 22.73, 26.94, 30.23, 31.85, 33.06, 71.30, 114.42, 149,18, 168.70, 169.92; mass spectrum, m/e (%) 238 (3), 196 (54), 136 (34), 108 (36), 43 (100); high-resolution mass spectrum calcd for $C_{16}H_{22}O_3$ 238.1205, found 238.1200.

1,4-Diacetoxycyclohexene: IR (CCl_4) 3022, 2961, 1758, 1737, 1680, 1441, 1371, 1253, 1222, 1199, 1016 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.88–1.90 (m, 2 H), 2.12 (s, 3 H), 2.25–2.50 (m, 4 H), 5.04 (quinter, J = 4.81 Hz, 1 H), 5.27 (m, 1 H); ^{13}C NMR (CDCl[3) δ 20.913, 21.224, 24.121, 26.971, 29.005, 68.118, 110.569, 147.598, 169.148, 170.585. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.57; H, 7.12. Found: C, 60.41; H, 7.15.

1-Acetoxy-3-(acetoxymethyl)cyclohexene: IR (CCl_4) 2943, 2861, 1760, 1737, 1680, 1369, 1100, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73–1.83 (m, 4 H), 2.01 (s, 3 H), 2.02 (s, 3 H), 2.03–2.20 (m, 2 H), 2.40–2.51 (m, 1 H), 3.86–3.99 (m, 2 H), 5.31 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.783, 24.69, 26.721, 29.97, 32.39, 36.20, 67.35, 114.11, 150.17, 169.32, 170.00.

1,4-Diacetoxycycloheptene: IR (CCl_4) 2943, 2861, 1758, 1737, 1687, 1454, 1439, 1430, 1368, 1246, 1225, 1172, 1101, 1024 cm^1; ^1H NMR ($CDCl_3$) δ 1.62–1.75 (m, 4 H), 1.99 (s, 3 H), 2.02 (s, 3 H), 2.22–2.40 (m, 4.73 (m, 1 H), 5.28 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.71, 21.17, 22.23, 30.23, 32.39, 36.20, 71.51, 111.31, 154.25, 169.32, 170.05.

Diethyl (2-acetoxyethyl)malonate: m.p. = 58–59 °C; IR (CCl_4) 2984, 2975, 1744, 1616, 1509, 1469, 1390, 1357, 1144, 1051 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.94 (t, J = 7 Hz, 6 H), 2.05 (s, 3 H), 2.62 (t, J = 5.99 Hz, 2 H), 4.05 (t, J = 5.99 Hz, 2 H), 4.43 (q, J = 7.10 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.938, 20.466, 20.916, 62.121, 65.118, 75.385, 170.488, 172.992. Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.63; H, 7.37, Found: C, 53.85; H, 7.35.

2,8-Diacetoxy-4-(trimethylacetoxy)-3,3aα,4,5,8,8aα-hexahydroazulene: IR (CCl_4) 3082, 2974, 2870, 1761, 1736, 1728, 1671, 1648, 1480, 1370, 1283, 1156, 1023 cm^{-1}; ^1H NMR ($CdCl_3$) δ 1.17 (s, 9 H), 2.03 (s, 3 H), 2.08 (s, 3 H), 2.27–2.86 (m, 5 H), 3.24 (m, 1 H), 5.19 (m, 1 H), 5.65 (d, J = 2 Hz, 1 H), 5.49 (m, 2 H), 5.65 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.80, 20.88, 26.89, 32.40, 32.91, 38.73, 40.44, 48.73, 71.32, 72.87, 113.17, 125.60, 130.99, 150.46, 167.85, 170.04, 177.72; mass spectrum, m/e (%) (no M^+), 291 (31), 249 (100), 189 (23), 117 (5), 57 (14), 43 (10). Anal. Calcd $C_{19}H_{26}O_6$: C, 65.11; H, 7.48. Found: C, 65.09; H, 7.51.

1-Methyl-4-(trimethylacetoxy)-3aα,4α,5,6-tetrahydroazulen-2(3*H*)-one: IR(CCl_4) 3031, 2967, 2930, 2866, 1729, 1702, 1631, 1637, 1477, 1262, 1156, 1101, 1091cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (s, 9 H), 1.79 (s, 3 H), 2.06–2.62 (m, 6 H), 3.23 (m, 1 H), 5.27 (m, 1 H), 6.25 (dt, J = 6.1, 12.2 Hz, 1 H), 6.58 (d, J = 12.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 8.08, 24.97, 27.04, 31.52, 38.53, 39.07, 45.03, 71.86, 125.42, 138.10, 139.34, 163.31, 178.63, 207.48; mass spectrum, m/e (%) 162 (7), 234 (12), 191 (11), 178 (26), 161 (25), 145 (21), 132 (16), 117 (34), 104 (18), 85 (8), 57 (100); high-resolution mass spectrum calcd for $C_{16}H_{22}O_3$ 262.1568, found 262.1561.

8-Acetoxy-1-methyl-4-(trimethylacetoxy)-1β,3aα,4β,5,8β,8aα-hexahydroazulen-2(3*H*)-one (3). A solution of 350 mg (1 mmol) of enol acetate **2** in 4 mL of 1,2-dimethoxyethane was cooled to −78 °C, and 1.35 mL (2 mmol) of methyllithium (1.5 M in diethyl ether) was added dropwise with stirring over 1.5 h. The resulting lithium enolate solution was warmed to about −50 °C, and 347 μL (2 mmol) of HMPA in 1 mL of dimethoxyethane was added. Finally, 1.55 mL (25 mmol) of methyl iodide was added rapidly with vigorous stirring. After the reaction had been stirred for 1 h at this temperature, the mixture was poured into 50 mL of cold (0–10 °C) saturated aqueous ammonium chloride solution and extracted with diethyl ether. The ether extract was dried over anhydrous sodium sulfate and concentrated. Flash chromatography on 12 g of silica gel (1:1 ether/hexane) yielded 196.5 mg (61%) of acetoxy methyl ketone **3**: IR (CCl_4) ν 2977, 2935, 1747, 1737, 1730, 1487, 1366, 1235, 1152, 1031 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (d, J = 7 Hz, 3 H), 1.18 (s, 9 H), 212 (s, 3 H), 2.24–2.54 (m, 6 H), 2.90 (m, 1 H), 5.24 (m, 1 H), 5.26–5.78 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 14.87, 21.01, 26.97, 31.50, 37.62, 38.73, 40.08, 45.87, 48.17, 71.66, 71.97, 129.05, 129.31, 170.25, 177.61, 218.40; mass spectrum, m/e (%) 322 (1), 263 (38), 221 (13), 161 (100), 133 (25), 85 (23), 57 (77); high-resolution mass spectrum calcd for $C_{18}H_{26}O_5$ 322.1780, found 322.1785.

4-Acetoxycyclohexanone (5). To a suspension of anhydrous potassium carbonate (100 mg, 0.75 mmol) in 1 mL of methanol at 0 °C was added 100 mg, (0.5 mmol) of acetoxy enol acetate (**4**), and the reaction mixture was stirred at 0 °C for 1 h. The resultant mixture was treated with 3 mL of water and acidified to pH 4 with 5% aqueous hydrochoric acid. The reaction mixture was extracted with three 20-mL portions of diethyl ether, and the organic layer was washed with 20 mL of saturated solution of aqueous sodium chloride and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure to give crude acetoxy ketone. The crude product was purified by flash chromatography on 5 g of silica gel with 1:1 ether/hexane as eluent

(6) For an example, see: Rigby, J. H.; Senanayake, C. *J. Am. Chem. Soc.* **1987**, *109*, 3147.

(7) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2023.

to give 70 mg (90%) of the acetoxy ketone **5**: IR (CCl_4) 2964, 2894, 1739, 1725, 1440, 1365, 1234, 1089 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84–2.04 (m, 4 H), 2.05 (s, 3 H), 2.27–2.36 (m, 2 H), 2.45–2.55 (m, 2 H), 5.12 (quintet, 1 H); ^{13}C NMR δ 21.08, 30.30, 37.13, 68.50, 170.24, 209.50; CI mass spectrum, *m/e* (%) (M + 1), 157 (4), 97 (18).

Acknowledgment. We thank the National Institutes of Health (Grant GM-30771) for their support of this research.

Registry No. 1, 112067-98-8; 2, 112067-99-9; 3, 112021-68-8; 4, 41043-90-7; 5, 41043-88-3; diethyl 2,2-cyclopropanedicarboxylate, 1559-02-0; bicyclo[3.1.0]hexan-2-one, 4160-49-0; bicyclo[4.1.0]-heptan-2-one, 5771-58-4; tricyclo[3.3.0.$0^{2,8}$]octan-3-one, 20826-85-1; (1α,6β,7α)-10-methyl-6-(trimethylacetoxy)tricyclo[5.3.0.$0^{2,10}$]-dec-3-en-9-one, 112021-61-1; diethyl(2-acetoxyethyl)malonate, 110281-43-1; 1,4-diacetoxycycloheptene, 112021-62-2; 1-acetoxy-3-(acetoxymethyl)cyclohexene, 112021-63-3; (1α,5α,8α)-3,8-diacetoxybicyclo[3.3.0]oct-2-ene, 112021-64-4; (1α,5α,6α)-5,8-diacetoxybicyclo[4.3.0]non-7-ene, 112021-65-5; 4-(trimethylacetoxy)-3aα,4α,5,6-tetrahydroazulen-2(3*H*)-one, 112021-66-6; 1-methyl-4-(trimethylacetoxy)-3aα,4α,5,6-tetrahydroazulen-2-(3*H*)-one, 112021-67-7.

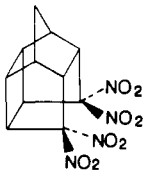
Synthesis of 8,8,11,11-Tetranitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane

Alan P. Marchand,* Benny E. Arney, Jr., and Paritosh R. Dave

Department of Chemistry, North Texas State University, Denton, Texas 76203-5068

Received July 16, 1987

There is considerable current interest in the synthesis and chemistry of polynitropolycyclic "cage" molecules.[1] As part of a program that is involved with the synthesis of novel, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes,[2] we have synthesized the title compound, 1. Compound

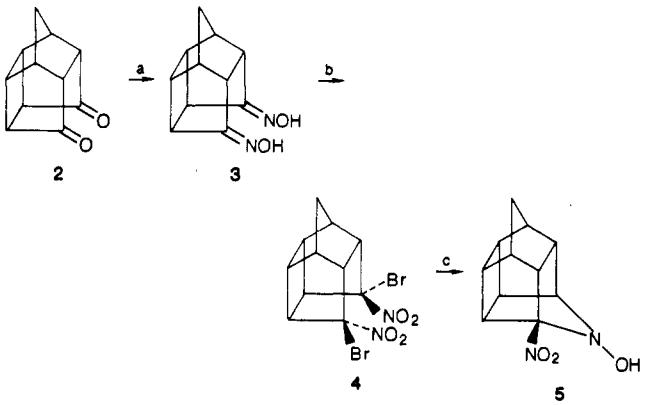


1

1 is of interest as a new, strained energetic material. Strain in this compound potentially can arise from the following sources: (i) deformations of the carbon–carbon framework bonds that are associated with the norbornyl moiety and the cyclobutane ring in 1 and (ii) nonbonded interactions that may occur between the *endo*-8- and *endo*-11-nitro groups in 1.

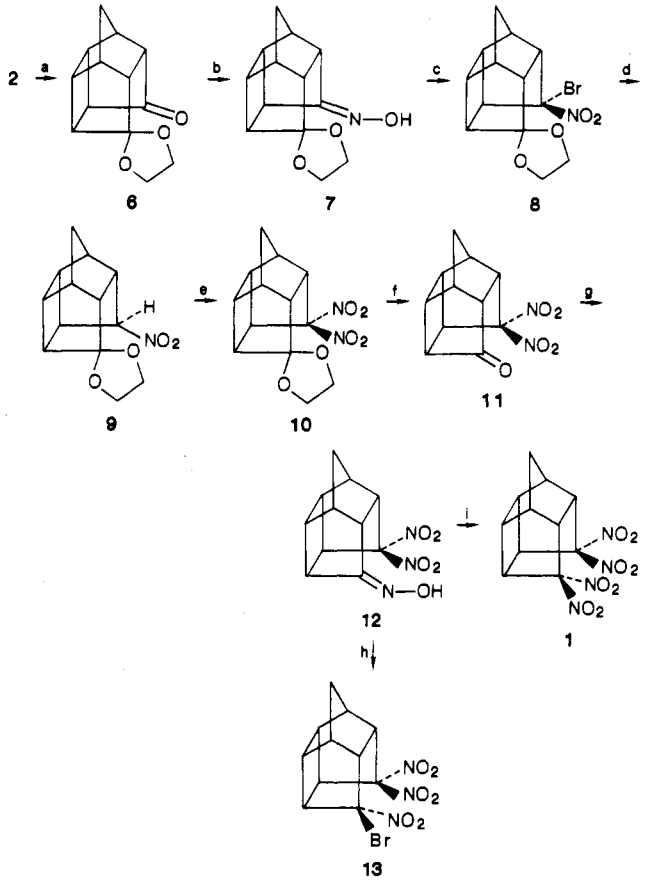
Our initial attempt to synthesize 1 from the readily available cage diketone 2[3] is summarized in Scheme I.

Scheme I[a]



[a] (a) NH_2OH·HCl, NaOAc, EtOH (87%); (b) NBS, $NaHCO_3$, dioxane, room temperature, 48 h (49%); (c) $NaBH_4$, 60% aqueous EtOH, room temperature, 45 min (28%).

Scheme II[a]



[a] (a) $HOCH_2CH_2OH$, TsOH, benzene, Dean–Stark tube (92%); (b) NH_2OH·HCl, NaOAc, EtOH, room temperature, overnight (79%); (c) Br_2, $NaHCO_3$, DMF, 0 °C, and then O_3, CH_2Cl_2, 0 °C (80%); (d) $NaBH_4$, 60% aqueous EtOH, room temperature, 0.5 h (97%); (e) $K_3Fe(CN)_6$, $NaNO_2$, aqueous MeOH, NaOH, room temperature, 0.5 h (73%); (f) concentrated H_2SO_4, CH_2Cl_2, room temperature, overnight (73%); (g) NH_2OH·HCl, NaOAc, EtOH, room temperature, overnight (89%); (h) NBS, $NaHCO_3$, 5% aqueous dioxane, room temperature, 72 h (65.7%); (i) 98% red HNO_3, NH_4NO_3, CH_2Cl_2, reflux 1 h, then 30% H_2O_2, reflux 1 h (31%, 64% based on recovered 11).

Conversion of 2 to the corresponding *exo,exo*-8,11-dibromo-*endo,endo*-8,11-dinitro derivative, 4, was straightforward. Subsequent reaction of 4 with sodium borohydride in methanol was expected to result simply in reduction of the carbon–bromine bonds.[4] However, this

(1) (a) Sollott, G. P.; Gilbert, E. E. *J. Org. Chem.* **1980**, *45*, 5405. (b) Eaton, P. E.; Ravi Shankar, B. K.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J. Sandus, O. *J. Org. Chem.* **1984**, *49*, 185. (c) Marchand, A. P.; Suri, S. C. *J. Org. Chem.* **1984**, *49*, 4078. (e) Paquette, L. A.; Fischer, J. W.; Engel, P. *J. Org. Chem.* **1985**, *50*, 2524. (f) Paquette, L. A.; Nakamura, K.; Engel, P. *Chem. Ber.* **1986**, *119*, 3782. (g) Marchand, A. P.; Annapurna, G. S.; Vidyasagar, V.; Flippen-Anderson, J. L.; Gilardi, R.; George, C.; Ammon, H. L. *J. Org. Chem.* **1987**, *52*, 4781. (h) Marchand, A. P.; Sharma, G. V. M.; Annapurna, G. S.; Pednekar, P. R. *J. Org. Chem.* **1987**, *52*, 4784.

(2) Marchand, A. P. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI: Greenwich, CT, Volume 1, in press.

(3) Marchand, A. P.; Allen, R. W. *J. Org. Chem.* **1974**, *39*, 1596.

0022-3263/88/1953-0443$01.50/0 © 1988 American Chemical Society