keto acid which showed carbonyl absorptions at 1760, 1735, and 1710 cm^{-1}.

The crude keto acid was treated with ethereal diazomethane to give the keto ester **27a** (89% from **26a**) which was purified by preparative GLC: IR 1760, 1735, 1720, 1240, 1050 cm^{-1}; MS, *m/e* (relative intensity) 268 (M$^+$, 17), 208 (38), 170 (53), 125 (51), 43 (100); ^{1}H NMR δ 0.80–2.56 (m, 17 H, contains s at 2.00), 3.57 (s, 3 H). Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.59; H, 7.55.

Oxidative Degradation of 22a to Spiro[5.6]dodecane (25b). The degradation of **22a** to **25b** was carried out as described for **20a**. Lead tetraacetate oxidation of 1.00 g (5.10 mmol) of **22a** gave spiro[5.6]dodecane-1,9-dione (**24b**): 751 mg (76%); IR 1710, 1690, 1125 cm^{-1}. The subsequent thioketal reduction of 326 mg (1.68 mmol) of **24b** afforded the spiro hydrocarbon **25b**: 130 mg (47%); IR 2920, 2850, 1425 cm^{-1}; MS, *m/e* (relative intensity) 166 (M$^+$, 56), 96 (100), 81 (71), 67 (66); ^{13}C NMR δ 39.72 (t, 2 C), 38.79 (t, 2 C), 35.58 (s), 30.82 (t, 2 C), 26.70 (t), 22.75 (t, 2 C), 22.09 (t, 2 C).

Preparation of an Authentic Sample of 25b. The authentic sample of **25b** was prepared by the literature method.[15] Condensation of 20 g (0.18 mol) of cycloheptanone with 1,5-dibromopentane gave spiro[5.6]dodecan-7-one: 12.5 g (39%); IR 1690 cm^{-1}. The Wolff–Kishner reduction of 5.0 g (27.8 mmol) of the above ketone afforded 1.8 g (39%) of the spiro hydrocarbon which was identical (IR, MS, ^{13}C NMR) with **25b** obtained by the degradation of **22a**.

Oxidative Degradation of 23 to the Keto Ester 27b. The degradation of **23** was carried out in a manner similar to that of **20b**.

Dehydration of 640 mg (3.51 mmol) of **23** with thionyl chloride–pyridine gave tricyclo[5.3.2.0^{1,6}]dodec-5-en-7-yl acetate (**26b**): 457 mg (72%); IR 3050, 1740, 1250 cm^{-1}; MS, *m/e* (relative intensity) 220 (M$^+$, 21), 178 (44), 160 (100, M$^+$ – AcOH), 136 (68); ^{1}H NMR δ 1.16–2.12 (m, 17 H, contains s at 1.96), 2.20–2.64 (m, 2 H), 5.60 (t, 1 H); ^{13}C NMR δ 170.71 (s), 148.39 (s), 110.67 (d), 86.30 (s), 40.07 (s), 38.99 (t), 37.04 (t), 35.13 (t, 2 C), 33.27 (t), 24.36 (t), 21.87 (q), 20.40 (t), 20.11 (t). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.18; H, 9.33.

The oxidation of 235 mg (1.07 mmol) of **26b** by osmium tetraoxide gave the diol (IR 3500–3430, 1735, 1710,[22] 1255, 1075 cm^{-1}) which was subjected to lead tetraacetate oxidation to afford the keto aldehyde: IR 1760, 1735, 1720, 1250 cm^{-1}. Treatment of the crude aldehyde with saturated bromine–water gave the keto carboxylic acid (IR 1760, 1735, 1720, 1060 cm^{-1}), and the subsequent esterification with ethereal diazomethane afforded the keto ester **27b**: 172 mg (62% from **26b**); IR 1760, 1735, 1720, 1240 cm^{-1}; MS, *m/e* (relative intensity) 282 (M$^+$, 7), 184 (43), 55 (30), 43 (100); ^{1}H NMR δ 1.14–2.60 (m, 19 H, contains s at 2.00), 3.60 (s, 3 H). Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.85; H, 8.13.

Lithium Aluminum Hydride Reduction of 26b to i. A 122-mg sample of **26b** (0.55 mmol) was reduced by lithium aluminum hydride as described above to afford 98 mg of the unsaturated alcohol i (quantitative) which was purified by preparative GLC: IR 3370, 1170, 1140, 1060, 920 cm^{-1}; MS, *m/e* (relative intensity) 178 (M$^+$, 41), 149 (61), 136 (100), 135 (62); ^{1}H NMR δ 0.84–2.16 (m, 17 H), 5.32 (t, 1 H). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.47; H, 10.25.

Preparation of Spiro[4.7]dodecane. The Wolff–Kishner reduction of 3.5 g (19.4 mmol) of spiro[4.7]dodecan-6-one[24] afforded spiro[4.7]dodecane: 314 mg (10%); IR 2910, 2860, 1465, 1440 cm^{-1}; MS, *m/e* (relative intensity) 166 (M$^+$, 17), 95 (64), 82 (100), 67 (94), 41 (66); ^{1}H NMR δ 1.20–1.80 (m); ^{13}C NMR δ 45.97 (s), 39.39 (t, 2 C), 36.02 (t, 2 C), 28.87 (t, 2 C), 25.14 (t), 24.45 (t, 2 C), 24.00 (t, 2 C). Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.55; H, 13.54.

Registry No. 9, 5202-23-3; **10**, 42540-17-0; **11**, 38229-67-3; **12**, 38312-61-7; **13**, 88288-17-9; **13** semicarbazone, 88288-19-1; **14**, 42540-18-1; **15**, 88288-18-0; **16**, 88314-90-3; **17a**, 88288-20-4; **17b**, 51027-89-5; **18**, 38312-62-8; **19**, 88288-21-5; **20a**, 88314-91-4; **20b**, 88315-25-7; **22a**, 88314-92-5; **22b**, 88288-23-7; **23**, 88314-93-6; **24a**, 88288-25-9; **24b**, 88288-30-6; **24a** bis(ethylene thioketal), 88288-26-0; **25a**, 184-12-3; **25b**, 181-15-7; **26a**, 81843-01-8; **26a** diol, 88295-42-5; **26a** keto aldehyde, 88288-27-1; **26a** keto acid, 88288-28-2; **26b**, 81843-02-9; **26b** keto aldehyde, 88288-31-7; **27a**, 88288-29-3; **27b**, 88288-32-8; **28**, 88288-24-8; **29**, 88314-94-7; **30**, 88314-95-8; **31**, 88288-22-6; i, 88288-33-9; bicyclo[5.3.0]dec-1-(7)-en-8-one, 769-32-4; *cis-anti-trans*-dimethyl[4.3.2]propellanone, 38343-72-5; *cis*-2-butene, 590-18-1; ethane-1,2-dithiol, 540-63-6; spiro[4.6]undecan-6-one, 73223-32-2; 1,5-dibromopentane, 111-24-0; cycloheptanone, 502-42-1; spiro[5.6]dodecan-7-one, 4728-90-9; spiro[4.7]dodecane, 1197-84-8; spiro[4.7]dodecan-6-one, 3002-04-8.

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(24) Krapcho, A. P.; McCullough, J. P. *J. Org. Chem.* **1967**, *32*, 2453.

Synthesis, Characterization, and Chemistry of Bridgehead-Functionalized Bicyclo[2.2.2]octanes: Reactions at Neopentyl Sites

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Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received July 13, 1983

This paper reports the synthesis and characterization of a series of 15 new, symmetric, 1,4-disubstituted bicyclo[2.2.2]octyl derivatives. Beyond detailing their syntheses and spectral properties, it describes the scope of synthetic transformations that can be effected at these neopentyl-like centers. The question of a possible direct displacement by hydride at such a site, as per an earlier literature report, is considered, and the limits of this and related substitution reactions are delineated. The scope of reactions at sp^2 centers attached to these positions is also defined.

In the course of a study of micelle-mediated organic reactions, we required a set of substrates that would provide two isolated but equivalent sites for reaction. These two reaction sites had to be separated by a rigid, nonaromatic, spacer group.[2] We have pursued a synthetic program that has led us to the synthesis and characterization of a variety of bridgehead-functionalized bicyclo[2.2.2]octanes and has allowed us to delineate some of the

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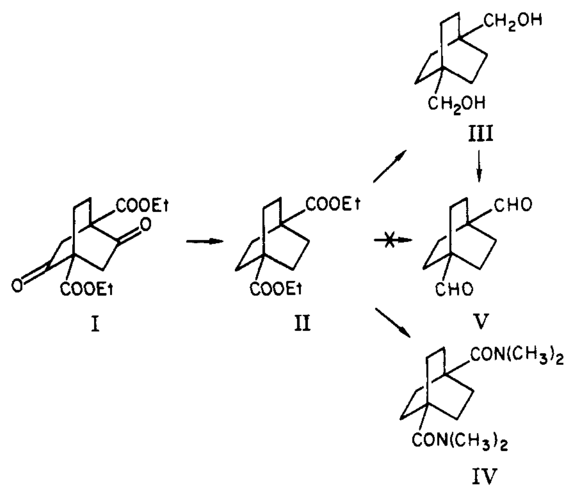
(1) NIH Research Career Development Awardee (1983–1988).

(2) The need for spacer rigidity and the preference for a nonaromatic spacer are best understood by reference to our earlier work: Link, C. M.; Jansen, D. K.; Sukenik, C. N. *J. Am. Chem. Soc.* **1980**, *102*, 7798. Sutter, J. K.; Sukenik, C. N. *J. Org. Chem.* **1982**, *47*, 4174.

0022-3263/84/1949-0665$01.50/0

Scheme I



chemistry that can be accomplished at these hindered reaction sites. We envisioned that the success of this program would yield not only an array of new materials with high symmetry and a well-defined geometric relationship between two identical reaction sites[3] but also an increased understanding of the scope of reactions that could be effected at such sites. We report below the realization of these goals as well as an amendment to a literature report on the chemistry of these systems.

The key entry to these compounds comes from the self-condensation of diethyl succinate, followed by alkylation/cyclization with 1,2-dibromoethane to yield diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (I).[4] Reduction of the ketones to methylenes is achieved either by Wolf–Kishner reaction[5] or by thioketalization followed by treatment with Raney nickel.[4c] This leaves a simple bicyclo[2.2.2]octyl skeleton with only bridgehead functionalization. It was with this diester II that we began our efforts.

Results

A limited number of transformations of II have been reported. Ester hydrolysis and subsequent reactions of the acid are well-known.[4c,6] Our initial interest focused on the three transformations of II shown in Scheme I. Treatment of II with LAH gives diol III in high yield.[7] Reaction of II with a mixture of $Al(CH_3)_3$ and $(CH_3)_2NH$[8] gives an excellent yield of the bis(amide) IV and is a preferred alternative to both the reported three-step sequence and the reported use of lithium dimethylamide.[3b] However, attempted conversion of II to dialdehyde V using DiBALH was unsuccessful. Though reported for a variety of esters,[9] with II, this reaction proceeded directly to diol III at either 0 °C or −78 °C. A low concentration of V and/or the monoaldehyde could be detected in the 0 °C reaction, but it never amounted to $\geq 10\%$. We were ultimately able to make V in high yield by the oxidation (oxalyl chloride, Me_2SO) of III.

Further elaboration of V resulted in the array of new materials outlined in Scheme II. The double aldol condensation of V with acetone produced the bis(enone) VI. This material was reduced with H_2/Pd on charcoal to give dione VII, which was further reduced with $NaBH_4$ to diol VIII. Wittig methylenation of V produced diene IX. This diene was transformed by hydroxymercuration to diol X, which was oxidized to dione XI. Similarly, methoxymethylation of V with $CH_3OCH_2PPh_3^+Cl^-$ allowed the homologation of V to XIII via acid hydrolysis of the bis(enol ether) XII. The new dialdehyde, XIII, was treated as had been done for V to yield XIV, XV, and XVI. The homologous relationship between dialdehydes V and XIII and dienes IX and XIV is readily noted, as should be a similar series among diols X, XV, and VIII and among diones XI, XVI, and VII.

Another set of compounds (Scheme III) emerged from the conversion of the bis(amide) IV to the diamine XVII. This could be effected with either $BH_3{:}(CH_3)_2S$ or with LAH. The LAH reaction[3b] produced a cleaner product and was the method of choice. Alkylation of XVII with 2 equiv of CH_3I or $CH_3OSO_2CF_3$ gave XVIII. The principal difference between XVIIIa (X = I) and XVIIIb ($X = CF_3SO_3$) was their solubility. Both XVIIIa and XVIIIb were soluble in water, but only the $CF_3SO_3^-$ salt could be dissolved in an organic solvent (acetone, methanol).

An alternate route to diamine XVII involved the conversion of diol III to ditosylate XIX (Scheme IV). This reaction is analogous to the conversion of III to its monotosylate reported by Stock.[4b] This is, however, an inferior route to XVII. Solutions of dimethylamine in water/dioxane showed sluggish reactivity; i.e., reaction of XIX with $(CH_3)_2NH$ at 65 °C for three days showed a 2:1 ratio of unreacted tosylate to product alkylamine. Reaction at 150 °C for 3 h was required for the conversion of XIX to XVII. The use of lithium dimethylamide in THF converted XIX back to diol III via a double S–O bond cleavage. Similarly, treatment of XIX with LAH in THF gave a mixture of C–O and S–O bond cleavage (40% alcohol XX and 60% diol III).

The characterization of compounds V–XIX included the expected IR and mass spectral patterns. A useful diagnostic in the ^1H NMR was the sharp singlet of the CH_2 groups of the bicyclo[2.2.2]octyl skeleton which always appeared between δ 1.4 and δ 2.0. An interesting feature in the ^1H NMR of XVII is shown in Scheme V. We confirmed that the CH_2–N protons were *upfield* of the CH_3–N protons by making the monoalkylated compound XXI (Scheme V).[10] It should be noted that the bicyclo[2.2.2]octyl skeleton has the same effect as a neopentyl group. The CH_2 of diol III has the same chemical shift as the CH_2 of neopentyl alcohol and both are 0.4 δ upfield of the CH_2 in ethanol.[11] That this effect is a subtle one is evidenced by the fact that the alkylated sites of both XXI and XVIII have their CH_2–N^+ signals *downfield* of their CH_3–N^+ signals.

Discussion

Beyond the synthesis of new, symmetric, difunctional compounds for studying micelles, vesicles, and other organized media, it was our intent to probe the reactivity of

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(3) Two interesting applications of this skeleton as a spacer are: (a) photochemical donor–acceptor studies: Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933; (b) hypotensive activity of bis(ammonium) compounds: Cannon, J. G.; Yang, K. W.; Rodriguez, M.; Buckley, J. P. *J. Pharm. Sci.* **1971**, *60*, 1534 (also see: Yang, K. W.; Cannon, J. G.; Rose, J. G. *Tetrahedron Lett.* **1970**, 1791).

(4) (a) Wood, G.; Woo, E. P. *Can. J. Chem.* **1968**, *46*, 3714. (b) Holtz, H. D.; Stock, L. M. *J. Am. Chem. Soc.* **1964**, *86*, 5183. (c) Roberts, J. D.; Moreland, W. T.; Frazer, W. *Ibid.* **1953**, *75*, 637.

(5) Guha, P. C. *Chem. Ber.* **1939**, *72*, 1359.

(6) (a) Kauer, J. C.; Benson, R. E.; Parshall, G. W. *J. Org. Chem.* **1965**, *30*, 1431. (b) Mauret, P.; Roquefort, B.; Mermillod-Blardet, D. *Bull. Soc. Chim. Fr.* **1973**, *2*, 426.

(7) The reduction of the diketal of I to diol and the synthesis of III are reported in ref 4b.

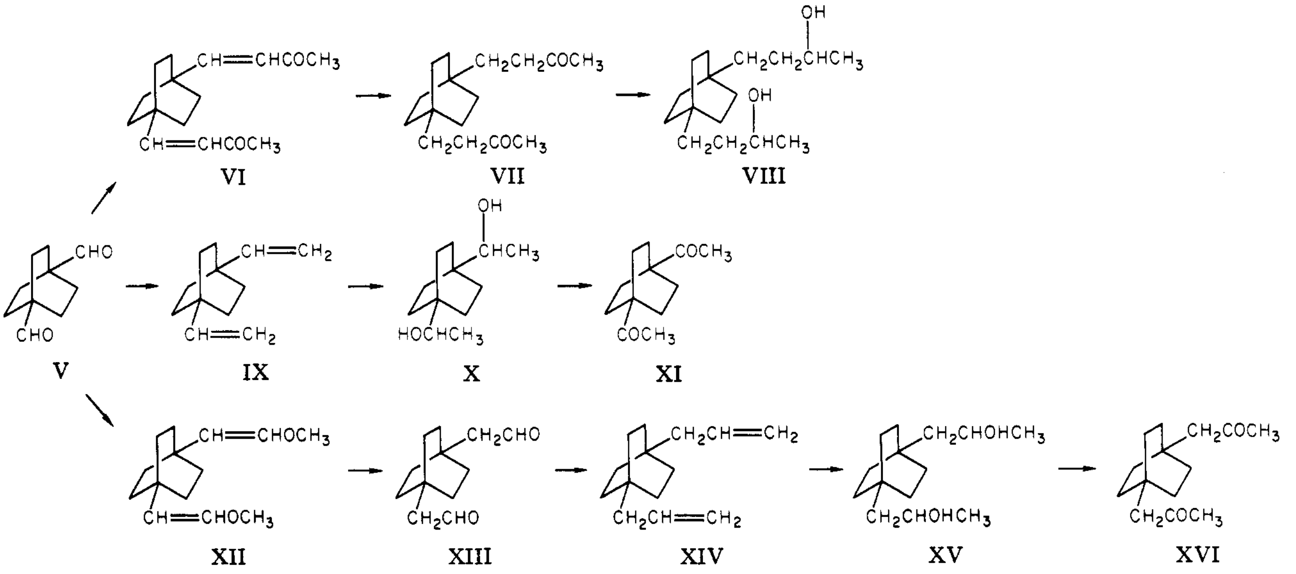
(8) Basha, A.; Lipton, M.; Weinreb, S. M. *Org. Synth.* **1979**, *59*, 49.

(9) Zakharkin, L. I.; Khorhina, I. M. *Tetrahedron Lett.* **1962**, 619.

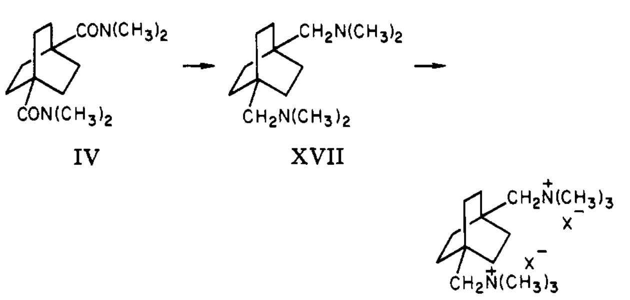
(10) The values in Scheme V were measured in CD_3OD at 200 mHz.

(11) Sadtler Standard NMR Spectra, *25*, no. 1897 and no. 16002.

Scheme II

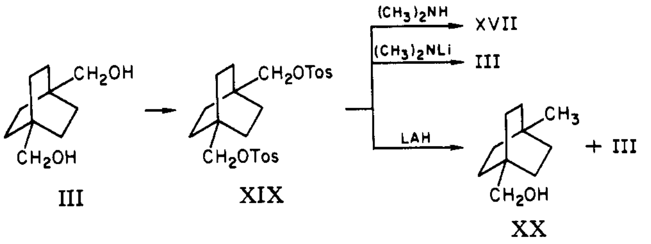


Scheme III

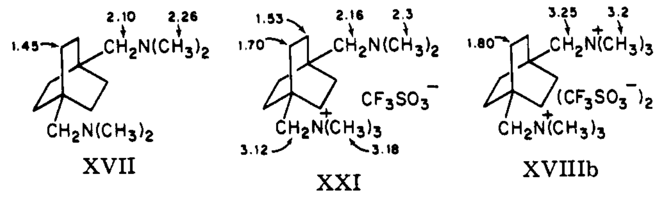


XVIIIa, X = I
XVIIIb, X = CF_3SO_3

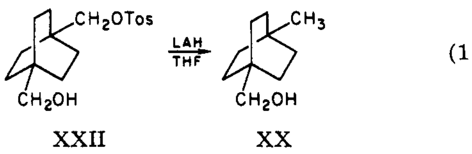
Scheme IV



Scheme V



these systems. The results reported in ref 3–6, among others, mostly show reactions at carbonyl derivatives. Notable exceptions are two reports by Holtz and Stock: a hydride displacement reaction[4b] (eq 1) and a study of the



(1)

S_N2 reaction of thiophenoxide with tosylates like XXII.[12]

Since our work with ditosylate XIX could not be reconciled with the reported results for XXII, we repeated the synthesis of XXII and found that, in our hands, its reduction by LAH in THF yielded only 40% XX with the remainder reverting to diol III.[13] We cannot reconcile this result[14] with the statement that "the neopentyl character of the tosylate (XXII) did not adversely influence the yield of XX obtained in the hydride displacement reaction."[4b] We suggest that nucleophilic attack at this position is badly disfavored. Depending on the nucleophile, this disfavoring of the normal S_N2 process can be seen in either of two ways. With soft nucleophiles like $(CH_3)_2NH$ in aqueous dioxane, the only result is a slow reaction rate. With hard nucleophiles like LAH or $LiN(CH_3)_2$, the steric hinderance to attack on carbon gives rise to S–O bond cleavage. The reported observation of C–O bond cleavage by using thiophenoxide in ethanol[12] suggests that those conditions are more like $(CH_3)_2NH$ in aqueous dioxane than like LAH or $LiN(CH_3)_2$ in THF. The possible role of Li^+ complexation in allowing S–O bond cleavage has been suggested[15] and is consistent with both these results and with a reportedly normal dispacement by NaCN on an analogous bicyclic tosylate.[16]

In terms of reactions on sp^2 carbons at such positions, we find that there is no inhibition of the initial attack of either nucleophiles (on C=O) or electrophiles (on C=C). There is, however, a profound effect on the *relative* rates of the formation and decomposition of the tetrahedral intermediate of carbonyl chemistry. This is best explained by reference to the reaction pathway shown in eq 2.

It seems clear that both in terms of ease of reaction and yield of product even bulky nucleophiles such as DiBALH and $(CH_3)_2AlN(CH_3)_2$ (Scheme I) and Wittig reagents (Scheme II) readily attack our neopentyl-like carbonyls.

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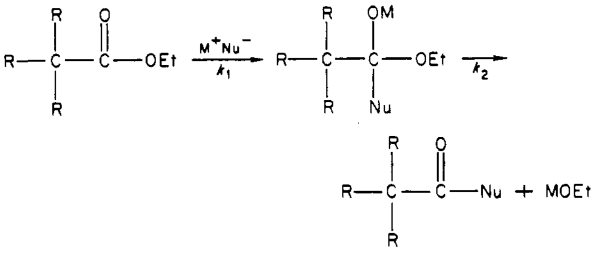
[12] Holtz, H. D.; Stock L. M. *J. Am. Chem. Soc.* **1965**, *87*, 2404.

[13] XIX and XXII give the same product mixture with LAH in THF. This observation is being explored.

[14] Prof. Stock has suggested (private communication) that differences in our two results might be due to trace impurities in different batches of LAH or to problems always inherent in reproducing results of heterogeneous systems. We can only report that our observation of mixed S–O and C–O bond cleavage instead of C–O cleavage alone persists, albeit to a lesser extent, even in homogeneous solutions of LAH in THF. As hinted in ref 13, this entire question of the balance between these two pathways is presently under investigation in our laboratory.

[15] Kraus, W.; Chassin, C.; Chassin, R. *Tetrahedron* **1969**, *25*, 3681.

[16] Sauers, R. R.; Gorodetsky, M.; Whittle, J. A.; Hu, C. K. *J. Am. Chem. Soc.* **1971**, *93*, 5520.



(2)

This suggests that the k_1 step in eq 2 is not adversely affected by the adjacent carbon skeleton. However, it seems that the primary effect of this carbon skeleton will be an enhancement of the relative rate of k_2, the reversion of the sp^3 intermediate back to an sp^2 center. This is important in the attempted conversion of an ester to an aldehyde with DiBALH. Instead of the tetrahedral alkoxy–aluminum acetal persisting until it is hydrolyzed on workup, it rapidly collapses to the aldehyde which is further reduced. In fact, only under the higher temperature (0 °C) reaction conditions could any aldehyde be isolated. The gentle, more selective, conditions of a −78 °C reaction temperature allow this k_2 to compete even more successfully and no aldehyde can be seen even at a low degree of ester conversion. This sterically enhanced collapse to a carbonyl seems to be the only significant consequence of the branched carbon skeleton and the only limitation on carbonyl chemistry at this site.

Experimental Section

A. General. Proton NMR spectra were obtained on Varian A-60A and Varian EM-360A spectrometers. They are reported as: NMR (solvent) chemical shifts in units δ (multiplicity, coupling constants, number of protons). Infrared spectra were recorded on a Beckman Model 10 spectrophotometer. Significant IR bands are reported in cm^{-1}. Analytical electron impact mass spectra were obtained on an AEI-MS 30 mass spectrometer. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were done by Galbraith Laboratories.

B. Synthesis.[17] **Diethyl 2,5-Dioxocyclohexane-1,4-dicarboxylate.** This compound was prepared in 78% yield, by the method of Wood;[4a] mp 125–127 °C (lit.[4a] 125.5–126.5 °C); NMR ($CDCl_3$) 1.46 (t, 7 Hz, 6 H), 4.37 (q, 7 Hz, 4 H), 3.30 (s, 4 H), 12.20 (s, 2 H); IR ($CHCl_3$) 3000, 1665, 1625.

Diethyl 2,5-Dioxobicyclo[2.2.2]octane-1,4-dicarboxylate (I). This compound was prepared in 78% yield by the method of Stock,[4b] and had properties identical with those reported in ref 4b,c and 6: NMR ($CDCl_3$) 1.28 (t, 7 Hz, 6 H), 4.25 (q, 7 Hz, 4 H), 1.95–3.28 (m, 8 H).

Diethyl Bicyclo[2.2.2]octane-1,4-dicarboxylate (II). Two dithioketals of I were prepared. The bis(dithiane) was prepared as follows. I (8 g, 28.3 mmol) was dissolved in $CHCl_3$ (18 mL) in a 250-mL three-necked flask. 1,3-Propanedithiol (12.1 g, 112 mmol) was added and hydrogen chloride was bubbled through the mixture for 7 h at 0 °C. The chloroform solution was washed with 2 N NaOH until no further reaction occurred and then washed with water and dried over anhydrous Na_2SO_4. The chloroform was removed in a ventillated hood and the resulting oil was boiled with hexane until a powdery white solid formed. The mixture was decanted hot and the solid product (11.1 g, 85%; mp 115–119 °C (lit.[4c] 115–118 °C) was used in the desulfurization reaction; NMR ($CDCl_3$) 1.33 (t, 7 Hz, 6 H), 4.23 (q, 7 Hz, 4 H); 1.78–3.50 (m, 20 H). The corresponding bis(dithiolane) was prepared (78%) using 1,2-ethanedithiol: mp 90–92 °C (lit.[4c] 91.8–92.7 °C); NMR ($CDCl_3$) 1.28 (t, 7 Hz, 6 H), 4.17 (q, 7 Hz, 4 H), 2.83–3.53 (m, 16 H). Raney Nickel desulfurization[4c] of the bis(dithiane) and bis(dithiolane) proceeded in 71% and 99% yield, respectively; NMR ($CDCl_3$) 1.23 (t, 7 Hz, 6 H), 1.8 (s, 12 H), 4.1 (q, 7 Hz, 4 H).

Bicyclo[2.2.2]octane-1,4-dimethanol (III). A 500-mL, three-necked flask, equipped with a reflux condenser, magnetic stirrer, pressure-equalized addition funnel, and a nitrogen inlet, was charged with 100 mL of dry diethyl ether and $LiAlH_4$ (8.5 g, 224 mmol). Diester II (21.12 g, 83 mmol) in 150 mL of dry ether was added dropwise to the reaction flask with stirring over 1.5 h. After the spontaneous reflux subsided, the mixture was heated at reflux for an additional 5 h. The reaction was quenched by dropwise addition of 8.5 mL of water, 2.5 mL of 15% NaOH, and 25.5 mL of water. The reaction mixture was filtered and the salts were washed with ether. The ether layers were combined and dried over anhydrous Na_2SO_4. After removal of the solvent, diol III was obtained (13.87 g, 98%): mp 106–108 °C (lit.[4b] 107–108 °C); NMR ($CDCl_3$) 1.43 (s, 14 H), 3.27 (s, 4 H).

***N,N,N′,N′*-Tetramethylbicyco[2.2.2]octane-1,4-dicarboxamide (IV).** A 500-mL, flame-dried, two-necked flask was equipped with a reflex condenser, a nitrogen inlet, a rubber septem, and a magnetic stirring bar. The flask was charged with freshly distilled toluene (75 mL), and a 2 M solution of trimethylaluminum (4.32 g, 60 mmol) in toluene (30 mL) was injected through the septum. The solution was stirred and cooled in an ice–salt bath at −10 to −15 °C, and dimethylamine (5.4 g, 120 mmol) was added (in 20 mL toluene) by syringe. The stirring was continued for an additional 30 min, the cooling bath was removed, and the contents of the flask were warmed to room temperature over 1 h. Diester II (5 g, 19.7 mmol) in dry toluene (20 mL) was injected. The resulting solution was heated to reflux for 2 h, cooled to room temperature, and hydrolyzed by the slow addition of 0.7 M HCl (171 mL). After stirring for 1 h, the organic layer was separated and the aqueous layer was extracted twice with ethyl acetate. The organic layers were combined, washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated. The solid product was washed with ether and the diamide, IV, was isolated (2.5 g). The water layer was further extracted with $CHCl_3$ and an additional 1.44 g of diamide was isolated (total yield 79%): mp 158–159 °C (lit.[3b] 161–162 °C); NMR ($CDCl_3$) 2.0 (s, 12 H), 3.83 (s, 12 H); IR ($CDCl_3$) 1610.

Bicyclo[2.2.2]octane-1,4-dicarboxaldehyde (V). A 250-mL, three-necked flask was equipped with a magnetic stirrer, two pressure-equalizing addition funnels, and a nitrogen inlet. The system was dried thoroughly and flushed with nitrogen. Freshly distilled CH_2Cl_2 (40 mL) and oxalyl chloride (1.6 mL, 2.24 g, 16.7 mmol) were added to the flask. In one of the funnels was placed Me_2SO (2.75 mL, 3.0 g, 38.8 mmol) in dry CH_2Cl_2 (15 mL) and in the other, diol III (1.4 g, 8.2 mmol) in a mixture of dry CH_2Cl_2 (5 mL) and Me_2SO (1.25 mL). The reaction flask was brought to −50 °C and the Me_2SO/CH_2Cl_2 was added dropwise while stirring. After this addition was complete, the reaction mixture was stirred for 5 min and then diol III in CH_2Cl_2–Me_2SO was added dropwise. Stirring at −50 °C was continued for 15 min. The reaction flask was warmed to −10 °C, triethylamine (12.74 mL, 9.25 g, 91.5 mmol) was added, and stirring was continued for 1 h. Water (80 mL) was added, the CH_2Cl_2 layer was separated, and the water layer was extracted with CH_2Cl_2. The organic layers were combined and washed with 1% HCl, 5% Na_2CO_3, water, and saturated aqueous NaCl. After drying over anhydrous $MgSO_4$, the solvent was removed under vacuum. The crude product V (1.27 g, 92.7%) was pure by NMR. It was distilled in a Kugelrohr apparatus at 172–75 °C (1.5 mm) and gave an isolated yield of 56.2% (0.768 g). As the dialdehyde is sensitive to air oxidation, it was freshly prepared and used without distillation for subsequent reactions: NMR ($CDCl_3$) 1.72 (s, 12 H), 9.44 (s, 2 H); IR 1730; MS 70 ev ($C_{10}H_{14}O_2$) calcd, 166.0994; obsd, 166.1019.

4,4′-Bicyclo[2.2.2]octane-1,4-diylbis[3-buten-2-one] (VI). To a mixture of dicarboxaldehyde V (1.0 g, 6 mmol) and acetone (1.4 g, 24 mmol) in methanol (10 mL) at 0 °C was added 10 mL of methanolic 6 N KOH. The reaction mixture was stirred for 15 min and then heated to 45 °C for 2 h. It was then diluted with water and extracted with ether. The combined ether extracts were washed with water (till neutral) and with saturated aqueous NaCl. They were dried over anhydrous Na_2SO_4 and concentrated. The resulting 1.36 g of crude product was distilled on a Kugelrohr apparatus at 160–70 °C (0.1 mm). The distillate solidified at room temperature. It was further purified on a silica gel column using hexane:ethyl acetate (100:20). The yield of pure VI was only 0.42 g (28.5%), mp 87–89 °C. Other products recovered from the

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[17] Nomenclature for these compounds was graciously provided by Dr. Robert White of Chemical Abstracts Service.

column were tentatively identified as the diacetal and monoenone and monoacetal of V. VI: NMR ($CDCl_3$) 1.62 (s, 12 H), 2.24 (s, 6 H), 5.92 (d, 16 Hz, 2 H), 6.68 (d, 16 Hz, 2 H); IR (CCl_4) 1715, 1695, 1635; MS 70 ev ($C_{16}H_{22}O_2$) calcd, 246.1620; obsd, 246.1690.

4,4′-Bicyclo[2.2.2]octane-1,4-diylbis[2-butanone] (VII). VI (100 mg, 0.4 mmol) was dissolved in 50 mL of absolute ethanol and slurried with 100 mg of 10% Pd/C in a Parr hydrogenator bottle. After 7 h under 20 psi of H_2, the solution was filtered and concentrated by vacuum to give a quantitative yield of crude product (VII): NMR ($CDCl_3$) 1.28 (s, 12 H), 1.15–1.53 (m, 4 H), 2.08 (s, 6 H), 2.30 (m, 4 H); IR (CCl_4) 1730; MS 13 ev ($C_{16}H_{26}O_2$) calcd, 250.1933; obsd, 250.1849.

***α,α′*-Dimethylbicyclo[2.2.2]octane-1,4-dipropanol (VIII).** Dione VII (70 mg, 0.28 mmol) was dissolved in 15 mL of absolute ethanol, and 106 mg of $NaBH_4$ in 5 mL of 3 N NaOH was added. After 6 h at room temperature, the reaction was diluted with water and extracted into ether. The ether solution was dried and concentrated to yield 62 mg (87%) of VIII as a slightly yellow oily solid: NMR ($CDCl_3$) 1.13 (d, 6 Hz, 6 H), 1.1–1.5 (m, 8 H), 1.30 (s, 12 H), 1.78 (br s, 2 H), 3.68 (m, 2 H); IR (CCl_4) 3410, 1055; MS 13 ev ($C_{16}H_{30}O_2$) calcd, 254.2246; obsd, 254.2235.

1,4-Diethenylbicyclo[2.2.2]octane (IX). A flame-dried, 3-neck, 500 -mL flask, equipped with a reflux condenser, a pressure equalized addition funnel, septum, an N_2 inlet, and a stirring bar, was charged with $CH_3Ph_3P^+I^-$ (4.12 g, 10.2 mmol) and dry THF (20 mL). The dialdehyde, V, (0.768 g, 4.62 mmol) in 10 mL of dry THF was placed in the dropping funnel. The flask was placed in an ice-water bath and *n*-BuLi (4.25 mL, 10.2 mmol, 2.4 M in hexane) was added dropwise by syringe with stirring. After the addition of *n*-BuLi was complete, the orange reaction mixture was brought to room temperature and stirred for an additional 20 min. The reaction flask was again cooled in ice-water and the dialdehyde in THF was added dropwise. The reaction mixture was stirred overnight at room temperature, dry ether was added to reaction flask, and the white precipitate was filtered off. The ether solution was concentrated under vacuum. NMR analysis of the crude product showed the presence of some Ph_3PO. This crude product was dissolved in pentane and filtered. An NMR pure sample of compound IX (0.67 g, 89%) was thus obtained: NMR ($CDCl_3$) 1.5 (s, 12 H), 4.64–5.0 (m, 4 H), 5.52–5.98 (4 lines, 2 H); IR (CCl_4) 3100, 2930, 2890, 1640, 1450, 1000, 920, 660; MS 70 ev ($C_{12}H_{18}$) calcd, 162.1409; obsd, 162.1429.

***α,α′*-Dimethylbicyclo[2.2.2]octane-1,4-dimethanol (X).** A 50-mL flask was fitted with a magnetic stirring bar and charged with mercuric acetate (1.6 g, 5.2 mmol). After the addition of 5 mL of water and 5 mL of THF, diene IX (0.4 g, 2.47 mmol) was added and the reaction mixture was stirred for 15 min at room temperature. Then 5 mL of 3 M NaOH was added, followed by 5 mL of a solution of 0.5 M $NaBH_4$ in 3 M NaOH. Solid NaCl was added to saturate the water layer. The THF layer was separated and concentrated to give NMR pure diol X (0.427 g, 87.5%). It was distilled on a Kugelrohr apparatus at 170–175 °C (0.1 mm) to give 0.38 g of X: NMR ($CDCl_3$) 1.00 (d, 6 Hz, 6 H), 1.35 (s, 14 H), 3.32 (q, 6 Hz, 2 H); IR ($CDCl_3$) 3620; MS 13 ev ($C_{12}H_{22}O_2$) calcd, 198.1620; obsd, 198.1651.

1,1′-Bicyclo[2.2.2]octane-1,4-diylbis[ethanone] (XI). Dione XI was prepared from diol X by the oxalyl chloride–Me_2SO oxidation described for compound V. 314 mg (1.3 mmol) of diol X gave 184 mg (60% yield) of purified product. It was distilled on a Kugelrohr apparatus at 125–130 °C (0.1 mm); NMR ($CDCl_3$) 1.80 (s, 12 H), 2.13 (s, 6 H); IR ($CDCl_3$) 1695; MS 70 ev ($C_{12}H_{18}O_2$) calcd, 194.1307; obsd, 194.1336.

1,4-Bis(2-methoxyethenyl)bicyclo[2.2.2]octane (XII). This bis(enol ether) was prepared from dialdehyde V (5.88 g, 35.47 mmol) and $CH_3OCH_2Ph_3PCl$ (42.51 g, 124 mmol) by a Wittig reaction similar to that described in the synthesis of diene IX. The crude product (10.75 g) which contained Ph_3PO was used without purification for the hydrolysis step (below). The following NMR data reflects the fact that XII was formed as a mixture of isomers: NMR ($CDCl_3$) 1.4 and 1.53 (singlets superimposed on a broad signal between them, 12 H), 3.30 and 3.40 (s, cis and trans OCH_3 groups, 6 H), 3.84 (d, 7 Hz), 4.42 (d, 13 Hz), 5.46 (d, 7 Hz), 5.96 (d, 13 Hz), sum of 4 vinyl (3.84–5.96) signals, 4 H; IR ($CDCl_3$) 1650.

Bicyclo[2.2.2]octane-1,4-diacetaldehyde (XIII). To the crude sample of XII (10.75 g) were added 150 mL of THF, 4 mL of C_2H_5OH and 50 mL of 1 N HCl and the mixture was stirred overnight. After addition of NaCl a THF layer was separated. The water layer was extracted with THF and the combined THF layers were washed with aqueous $NaHCO_3$ and aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated to yield dialdehyde XIII (6.38 g). NMR analysis of the crude product showed Ph_3PO contamination: NMR ($CDCl_3$) 1.6 (s, 12 H), 2.17 (d, 3 Hz, 4 H), 9.78 (t, 3 Hz, 2 H); IR ($CDCl_3$) 1720.

1,4-Di-2-propenylbicyclo[2.2.2]octane (XIV). Wittig reaction (as described above for IX) of crude dialdehyde XIII (6.38 g) and $CH_3Ph_3P^+I^-$ (27.93 g) gave diene XIV (2.21 g) contaminated with Ph_3PO. It was purified on silica gel using pentane as eluent and 1.0 g of pure diene XIV was recovered: NMR ($CDCl_3$) 1.39 (s, 12 H), 1.73–2.0 (br d, 4 H), 5.42–6.17 (complex m, 2 H), 4.67–5.13 (m, 4 H); IR (neat) 920; MS 70 ev ($C_{14}H_{22}$) calcd, 190.1721; obsd, 190.1758.

***α,α′*-Dimethylbicyclo[2.2.2]octane-1,4-diethanol (XV).** By a procedure comparable to that used to synthesize X, diene XIV (156 mg, 0.82 mmol) was converted to XV (185 mg, 99%), a waxy white solid: NMR ($CDCl_3$) 1.15 (d, 6 Hz, 6 H), 1.25 (m, 4 H), 1.44 (s, 12 H), 1.60 (br s, 2 H), 3.95 (m, 2 H); IR ($CHCl_3$) 3640, 3480, 1110; MS 70 ev ($C_{14}H_{26}O_2$) calcd, 226.1933; obsd, 226.1901.

1,1′-Bicyclo[2.2.2]octane-1,4-diylbis[2-propanone] (XVI). A 25-mL, 2-neck flask was charged with XV (111 mg, 0.49 mmol) and 10 mL acetone. Freshly prepared Jones reagent was added dropwise using the color of the chromium salts to indicate sufficient oxidant. The reaction was left at room temperature for 5 h and partitioned between H_2O and ether; undissolved chromium salts were removed by centrifugation. The ether layer was dried over $MgSO_4$ and concentrated to yield 99 mg (91%) of dione XVI: NMR ($CDCl_3$) 1.52 (s, 12 H), 2.08 (s, 6 H), 2.2 (s, 4 H); IR ($CDCl_3$) 1725; MS 70 eV ($C_{14}H_{22}O_2$) calcd, 222.1620; obsd, 222.1586.

***N,N,N′,N′*-Tetramethylbicyclo[2.2.2]octane-1,4-dimethanamine (XVII).** The reduction of IV (2.9 g, 11.5 mmol) as per the procedure of Cannon et al.[3b] gave XVII. The crude product was purified by sublimation at 90–95 °C (2.5 mm); yield, 2.54 g (98%); mp 59–61 °C (lit.[3b] 60–61 °C); NMR ($CDCl_3$) 1.46 (s, 12 H), 2.17 (s, 4 H), 2.28 (s, 12 H); IR (CCl_4) 2970, 2880, 2820, 2790, 1465, 1275, 1050.

***N,N,N,N′,N′,N′*-Hexamethylbicyclo[2.2.2]octane-1,4-dimethanaminium Diiodide (XVIIIa).** A two-neck, 10-mL flask, equipped with a nitrogen inlet, magnetic stirrer, and a rubber septum, was flame dried and charged with diamine XVII (50 mg, 0.223 mmol) and dry, distilled CH_2Cl_2 (1 mL). Methyl iodide (0.127 g, 0.892 mmol) was added via syringe. After stirring for 1 h, the salt was filtered and washed with dry CH_2Cl_2: yield, 0.73 g (65%); NMR (CD_3OD) 1.77 (s, 12 H), 3.18 (s, 18 H), 3.22 (s, 4 H); IR (KBr) 3000, 2950, 2860, 1475, 950, 900.

***N,N,N,N′,N′,N′*-Hexamethylbicyclo[2.2.2]octane-1,4-dimethanaminium Bis(trifluoromethanesulfonate) (XVIIIb).** By use of the procedure described above for XVIIIa, diamine XVII (50 mg, 0.223 mmol) and methyl trifluoromethanesulfonate (0.15 g, 0.889 mmol) gave XVIIIb (0.11 g, 89.4%): NMR (CD_3OD) 1.8 (s, 12 H), 3.20 (s, 18 H), 3.25 (s, 4 H); IR (KBr) 1260, 1170, 1030, 640. Anal. Calcd for $C_{18}H_{34}N_2F_6S_2O_6$: C, 39.12; H, 6.20; N, 5.07. Found: C, 38.86; H, 6.23; N, 4.89.

4-[(Dimethylamino)methyl]-*N,N,N*-trimethylbicyclo[2.2.2]octane-1-methanaminium Trifluoromethanesulfonate (XXI). The procedure used to prepare XXI was identical with that used for the preparation of XVIIIb but instead of using 4 equiv of methyl triflate, only 0.8 equiv were used. This resulted in a mixture of unalkylated (XVII), monoalkylated (XXI), and dialkylated (XVIIIb) material. Separation was achieved by selective solubilization. The diamine (XVII) dissolved in dry diethyl ether while the two products did not. The mixed sample was thus freed of diamine by trituration with diethyl ether. The residue was triturated with $CHCl_3$ which removed the monoalkylated material (XXI) and left behind any XVIIIb as a final residue. The NMR data for XXI (in CD_3OD) are shown in Scheme V. IR (KBr) 1260, 1160, 1035, 645. Anal. Calcd for $C_{16}H_{31}N_2F_3SO_3$: C, 49.46; H, 8.04; N, 7.21. Found: C, 48.90; H, 8.11; N, 6.69.

Bicyclo[2.2.2]octane-1,4-dimethanol Bis(*p*-toluenesulfonate) (XIX). Diol (III) (200 mg, 1.176 mmol) was placed in a 25-mL, two-necked flask equipped with a drying tube and a septum. Dry pyridine (4.9 mL) was added followed by *p*-toluenesulfonyl chloride (627.7 mg, 4.7 mmol). The reaction was left in the refrigerator for 2 days. It was then poured into concentrated HCl and ice, extracted into ether, washed with saturated $NaHCO_3$ and water, and dried over anhydrous Na_2SO_4. After removal of the solvent, ditosylate (XIX) was obtained (540.6 mg, 96.2%). It was recrystallized from ether: mp 184–185 °C; NMR ($CDCl_3$) 7.74 (d, 4 Hz, 4 H), 7.32 (d, 4 Hz, 4 H), 3.60 (s, 4 H), 2.44 (s, 6 H), 1.34 (s, 12 H); IR ($CDCl_3$) 2980, 2900, 1200, 1190; MS 18 ev ($C_{24}H_{30}O_6S_2$) calcd, 478.1484; obsd, 478.1448.

Bicyclo[2.2.2]octane-1,4-dimethanol *p*-Toluenesulfonate (XXII). III (150 mg, 0.498 mmol) was placed in a 25-mL, two-neck flask equipped with a drying tube. Then 1.4 mL of dry pyridine was added followed by *p*-toluenesulfonyl chloride (94.9 mg, 0.498 mmol) in 0.7 mL of pyridine. After 2 days in the refrigerator the reaction was poured into concentrated HCl and ice, extracted with ether, washed with saturated $NaHCO_3$ and water, and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was chromatographed on silica gel. Elution with benzene/acetone (10:1) yielded a small amount of ditosylate (XIX). Elution with benzene/acetone (5:1) gave the product (XXII) (115 mg, 74.2%). Elution with acetone gave a small amount of diol (III). The product (XXII) was recrystallized from benzene: mp 122–123 °C (lit.[4b] 128–129 °C); NMR ($CDCl_3$) 7.76 (d, 4 Hz, 2 H), 7.34 (d, 4 Hz, 2 H), 3.64 (s, 2 H), 3.26 (s, 2 H), 2.44 (s, 3 H), 1.38 (s, 12 H); IR ($CDCl_3$) 3660, 2970, 2900, 1200, 1190.

C. Attempted S_N2 Reactions on Mono- and Ditosylates. (a) $(CH_3)_2NH$ with XIX. Ditosylate (XIX) (50 mg) was mixed with 40% aqueous $(CH_3)_2NH$ (30 mL) and dioxane (20 mL) in a 100-mL flask. This reaction was heated at 60–65 °C for 3 days under a reflux condenser. After cooling to room temperature, it was extracted with $CHCl_3$, dried over $MgSO_4$, and concentrated by vacuum. NMR analysis showed the mixture of products and unreacted starting material indicated above.

Modification of the above procedure by the use of a 20-mL stainless steel bomb was effected with 30 mg of XIX in 4.5 mL of aqueous dimethylamine and 2.5 mL of dioxane. Heating at 150 °C for 3 h, followed by cooling and workup as above, gave a sample of XVII which was at least 80% pure by NMR and showed no unreacted tosylate.

(b) $(CH_3)_2NLi$ with XIX. A 50-mL, three-neck flask was fitted with two septa, a dry ice condenser, a magnetic stirring bar, and a nitrogen inlet. Gaseous $(CH_3)_2NH$ (1 mL) was condensed into the flask and dry THF (5 mL) was added followed by *n*-BuLi (0.83 mL, 2.4 M in hexane). This mixture was stirred for 15 min at −63 °C and then warmed to room temperature for another 15 min. After cooling to −40 °C, a solution of XIX (200 mg) in 5 mL of dry THF was added. The reaction was warmed to room temperature and stirred for 2 h. The reaction was poured into water and extracted with $CHCl_3$. After passage through a short silica gel column, the $CHCl_3$ solution was concentrated and analyzed by NMR. This analysis showed <10% unreacted tosylate with the remainder of the product being diol (III).

(c) $LiAlH_4$ with XIX. A 100-mL, 3-neck flask was equipped with a magnetic stirring bar, a reflux condenser, and a nitrogen inlet. The flask was charged with a slurry of LAH (400 mg, 10.5 mmol) in dry THF (30 mL). A solution of XIX (30 mg, 0.06 mmol) in a minimal amount of dry THF was added and the reaction was allowed to reflux for 20–21 h. Workup with water, aqueous NaOH, and saturated aqueous NaCl was followed by drying with solid anhydrous Na_2SO_4. The solvent was removed by vacuum and the product was analyzed by both gas chromatography (15% SE-30; 140–180 °C) and by NMR for the ratio of diol (III) to alcohol (XX). Two independent analyses of each of two runs showed 60% ± 3% III and 40% ± 3% XX. XX: NMR ($CDCl_3$) 0.78 (s, 3 H), 1.38 (s, 12 H), 1.50 (br s, 1 H), 3.26 (s, 2 H); IR ($CHCl_3$) 3660, 3510, 1045, 920.

(d) $LiAlH_4$ with XXII. In an attempt to repeat the results of Stock et al.[4b] the procedure described above for the reaction of LAH with XIX was used with monotosylate XXII (30 mg, 0.09 mmol). Using the same workup and analysis as above, the product mixture again showed a 60:40 mixture of III:XX.[13]

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Registry No. I, 843-59-4; I (bis(dithiane) ketal), 41034-55-3; I (bis(dithiolane) ketal), 1686-98-2; II, 1659-75-2; III, 826-45-9; IV, 28673-85-0; V, 84774-84-5; VI, 88393-16-2; VII, 88393-17-3; VIII, 88393-18-4; IX, 88393-19-5; X, 88393-20-8; XI, 88393-21-9; XII, 88393-22-0; XIII, 88393-23-1; XIV, 88393-24-2; XV, 88393-25-3; XVI, 88393-26-4; XVII, 34131-02-7; XVIIIa, 88393-27-5; XVIIIb, 88393-29-7; XIX, 88412-20-8; XX, 28305-83-1; XXI, 88393-31-1; XXII, 898-81-7; $(CH_3)_2NH$, 124-40-3; CH_3Ph_3PI, 2065-66-9; $CH_3OCH_2Ph_3PCl$, 4009-98-7; diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate, 787-07-5; 1,2-dibromoethane, 106-93-4; 1,3-propanedithiol, 109-80-8; 1,2-ethanedithiol, 540-63-6; acetone, 67-64-1.

Synthesis of Methyl- and Nitro-Substituted Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-diones

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Diels–Alder cycloaddition of an appropriately substituted cyclopentadiene to an appropriately substituted *p*-benzoquinone (**1a–c**) followed by photocyclization of the resulting endo cycloadduct **2a–d** was employed to synthesize the following monomethylated pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-diones: 1-methyl (**3a**), 2-methyl (**3b**), and 3-methyl (**3c**). Single-crystal X-ray structural analysis was performed on **3c**. 2-Nitrobenzoquinone, generated via silver(I) oxide promoted oxidation of 2-nitrohydroquinone, was trapped in situ by cyclopentadiene, affording four products: 4a-nitro-1,4,4a,8a-tetrahydro-*endo*-1,4-methanonaphthalene-5,8-dione (**4**, 40%), 4a-nitro-1,4,4a,8a-tetrahydro-*exo*-1,4-methanonaphthalene-5,8-dione (**5**, 7%), and two 2:1 diene:dienophile cycloadducts [**6** (2%, from further reaction of **4** with cyclopentadiene) and **7** (4%, from further reaction of **5** with cyclopentadiene)]. The assignment of endo configuration for **4** was confirmed via its facile intramolecular photocyclization to 9-nitropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (**8**). Attempted column chromatographic purification of **4** on either alumina or silica gel resulted in the formation of 1,4-dihydro-1,4-methano-5,8-naphthoquinone (**10**) via elmination of nitrous acid from **4**. Reduction of **4** with methanolic sodium borohydride in the presence of cerous chloride afforded 4a-nitro-1,4,4a,8a-tetrahydro-*endo*-1,4-methanonaphthalene-5,8-diol (**9**) in 75% yield.

As part of a continuing study of the synthesis[1] and chemistry[2–6] of substituted pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecanes, we have undertaken the synthesis and characterization of 1-methyl-, 2-methyl-, 3-methyl-, and 9-