perborate dissociated to perhydroxyl depends on the reaction medium pH and the concentration of borate present: increasing pH and increasing borate concentration decrease the perhydroxyl ion concentration. Aqueous sodium perborate solutions afford substantial enhancements in organophosphorus ester decomposition rates relative to alkaline hydrolysis rates, the ratio $k_{HO_2^-}/k_{HO^-}$ is approximately 50 for neutral esters.

We can put the available rate enhancements into perspective as follows. At pH 9, 300 K, with 100 mM perborate present, estimated half-times for phosphorus ester degradation are 13, 0.4, and 0.13 min, respectively, for compounds **1**, **2**, and **3**. For any neutral organophosphorus ester whose reactivity toward alkaline hydrolysis is known, we can approximate the decomposition rate in aqueous perborate by using the ratio $k_{HO_2^-}/k_{HO^-} = 50$ and eq 14. A survey of the available literature reveals that a great variety of phosphorus esters will react extremely rapidly in moderately alkaline solutions of saturated sodium perborate. Because it has such high reactivity and commercial availability, we strongly recommend sodium perborate as a cleaning agent for removing hazardous organophosphorus ester residues.

Registry No. **1**, 311-45-5; **2**, 3735-98-6; **3**, 7531-39-7; **4**, 81349-02-2; **5**, 830-03-5; PB, 93184-29-3.

Halogenation and Rearrangement Reactions of Substituted Tricyclo[2.1.0.0^{2,5}]pentan-3-ones

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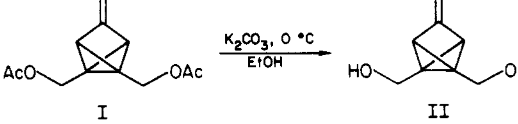
Hydrolysis of 1,5-bis(acetoxymethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (I) with potassium carbonate in methanol yielded 1,5-bis(hydroxymethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (II). Treatment of the latter with triphenylphosphine and carbon tetrabromide in acetonitrile yielded 1,5-bis(bromomethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (V). The analogous reaction with triphenylphosphine and carbon tetrachloride yielded little 1,5-bis(chloromethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (V). Instead, 3-oxabicyclo[3.3.0]octa-1,4-dien-7-one (VI) was found. An authentic sample of VI was synthesized by treating 3,4-bis(chloromethyl)furan (VII) with methyl (methylsulfinyl)methyl sulfide, yielding 3-oxa-7-(methylthio)-7-(methylsulfinyl)bicyclo[3.3.0]octa-1,4-diene (VIII). Treatment of VIII with acid yielded an authentic sample of the ketone VI. The dichloride V was prepared by the following alternative route. 1,4-Dichlorobut-2-yne was reacted with *tert*-butyl diazoacetate yielding *tert*-butyl 1,2-bis(chloromethyl)cyclopropene-3-carboxylate (XII). Deesterification with trifluoroacetic acid yielded 1,2-bis(chloromethyl)cyclopropene-3-carboxylic acid (XIII) that was converted with oxalyl bromide to 1,2-bis(chloromethyl)cyclopropene-3-carbonyl bromide (XIV). The latter was reacted with diazomethane and yielded 3-(diazoacetyl)-1,2-bis(chloromethyl)cyclopropene (XV) which was closed to V using dirhodium tetraacetate as catalyst. Rearrangement of the diol II upon treatment with triphenylphosphine and carbon tetrachloride may proceed by conversion to the [3.1.1]propellane IX followed by valence tautomerization to the cyclopentadienone X and prototopic rearrangement to the product VI. Likewise, treatment of 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one with iodine probably also results in the formation of 3,4-dimethylcyclopentadienone which dimerizes to XVIII. An authentic sample of XVIII was prepared by bromination of 3,4-dimethylcyclopent-2-en-1-one with *N*-bromosuccinimide, yielding 4-bromo-3,4-dimethylcyclopent-2-en-1-one (XX). Treatment of XX with triethylamine yielded an authentic sample of dimer XVIII. Reaction of XVIII with sodium methoxide in MeOD–D$_2$O resulted in the exchange of eight protons yielding XVIII-d_8. The high number of deuteriums incorporated is a consequence of a facile Cope rearrangement.

Halogenation and Rearrangement

In the course of learning how to prepare functionalized derivatives of the tricyclo[2.1.0.0^{2,5}]pentan-3-one system,[2] several rearrangments were observed that provide insight into the strain and reactivity which are properties of this carbon skeleton. This is unexplored territory. Only the dimethyl, di-*n*-propyl, and diphenyl derivatives of the tricyclo[2.1.0.0^{2,5}]pentanone system were known before this work was begun.[2] Following the pioneering work of Doering[2a] and Masamune[2b] of 20 years ago, nothing had been added to this area until the very recent work of Maier.[2d]

The key substance in this research is the diol II, which



I

II

is prepared by mild hydrolysis of the diacetate I[1] using potassium carbonate in ethanol at 0 °C. The keto diol II was converted, in 45% yield, to the crystalline dibromide III, mp 68–69 °C, by treatment with triphenylphosphine and carbon tetrabromide at 50 °C in acetonitrile.[3] The

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(1) (a) H. Irngartinger, A. Goldman, R. Schappert, P. Garner, and P. Dowd *J. Chem. Soc., Chem. Commun.*, 455 (1981); (b) P. Dowd, P. Garner, R. Schappert, H. Irngartinger, and A. Goldmann, *J. Org. Chem.*, **47**, 4240 (1982). Part of this work has been published in preliminary form: P. Dowd, R. Schappert, and P. Garner, *Tetrahedron Lett.*, 3 (1982).

(2) The earliest tricyclo[2.1.0.0^{2,5}] systems were (a) the 1,3-dimethyl derivative of W. Doering and M. Pomerantz, *Tetrahedron Lett.*, 961 (1964); (b) the 1,5-diphenyl derivative of S. Masamune, *J. Am. Chem. Soc.*, **86**, 736 (1964); (c) see also G. Maier, H. P. Resenauer, and H. A. Freitag, *Tetrahedron Lett.*, 121 (1978); (d) G. Maier, M. Hoppe, and H. P. Reisenauer, *Angew. Chem., Int. Ed. Engl.*, **22**, 990 (1983).

(3) J Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968).

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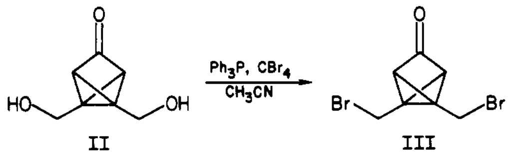
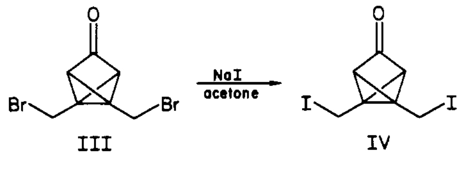
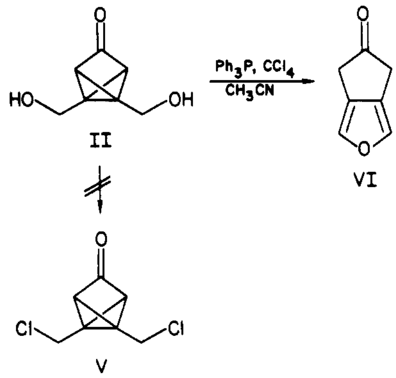


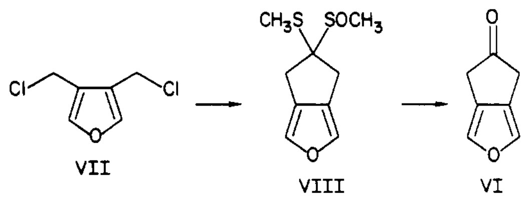
dibromide III was subjected to Finkelstein reaction at 0 °C using acetone saturated with sodium iodide. The diodide IV is quite sensitive and decomposes on standing at room temperature with evolution of molecular iodine. It has not yet been possible to identify the organic products resulting from the decomposition reaction of IV.



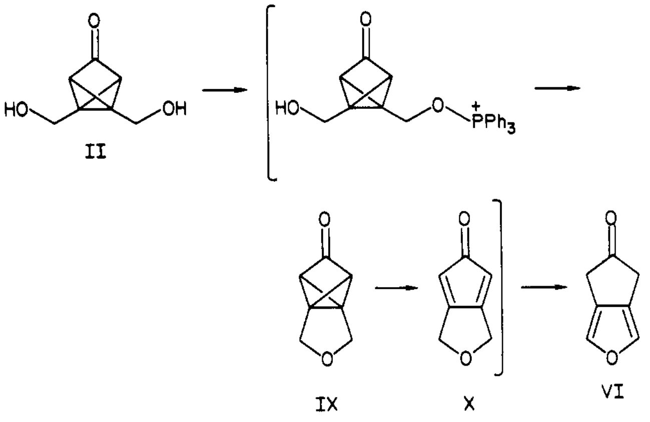
When the keto diol II was reacted with triphenylphosphine and carbon tetrachloride in acetonitrile, the principal product was not the desired dichloride V. Instead, the keto furan VI was formed in 37% yield. Only 8% of the dichloride V was isolated. Indeed, when 1.1 equiv of Hunig's base (ethyldiisopropylamine) was included in the reaction, no dichloride V was observed and keto furan VI was obtained in 60% yield.



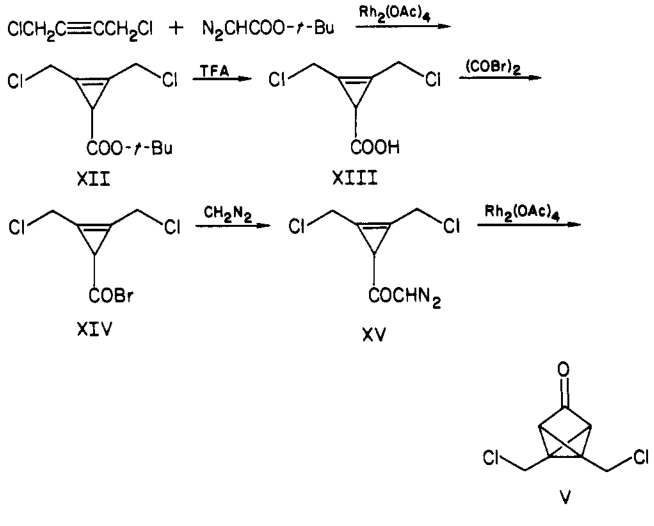
The structure of the keto furan VI was established on the basis of its spectral properties and by preparation of an authentic sample. The NMR spectrum showed a two-proton vinyl triplet ($J = 1$ Hz) at δ 7.29 and a four-proton methylene doublet ($J = 1$ Hz) at δ 3.33. The infrared spectrum showed a carbonyl band at 1761 cm^{-1}. An authentic sample of the keto furan VI was prepared by reaction of 3,4-bis(chloromethyl)furan[18] (VII) with methyl (methylsulfinyl)methyl sulfide in the presence of 2 mol of base.[4] Acid hydrolysis of the resulting sulfoxide VIII yielded the keto furan VI, which was identical in all respects with the product of rearrangement isolated from the triphenylphosphine–carbon tetrachloride reaction.



An explanation accounting for this unusual rearrangement may lie with the difference in nucleophilicity of the halide ions. Both the carbon tetrabromide–triphenylphosphine and carbon tetrachloride–triphenylphosphine reagents can react with the hydroxyl group forming the corresponding oxaphosphonium salts. Displacement occurs normally when bromide ion is the nucleophile. When, however, the displacing agent is the less nucleophilic chloride ion, internal displacement by the proximate hydroxyl group can compete in the displacement reaction resulting in ring closure to the propellane IX, which is expected to be a highly strained and reactive substance.[6] Outlet is provided through opening to the valence tautomer X. The escape route almost proves illusory because it generates a cyclopentadienone intermediate. However, final release is provided by tautomerization to the keto furan VI. This is, of course, a tentative rationale. However, the bicyclobutane to butadiene isomerization is well-known to occur in other instances.[7] The observation that the dichloride V is suppressed and the yield of keto furan VI is enhanced in the presence of Hunig's base is consistent with this mechanism.



Dichloro ketone V was prepared by a route analogous to that leading to the corresponding diacetate.[1] Reaction of 1,4-dichloro-2-butyne (XI) with *tert*-butyl diazoacetate[8] in the presence of a catalytic amount (0.013 molar equiv) of dirhodium tetraacetate[9] yielded the bis(chloro-



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[4] K. Ogura, M. Yamashita, M. Suzuki, and G. Tsuchinhashi, *Tetrahedron Lett.* 3653 (1974); K. Ogura, M. Yamashita, S. Furukawa, M. Suzuki, and G. Tsuchinhashi, *Tetrahedron Lett.*, 2767 (1975).

[5] Cf. G. W. Barry and J. L. Fry, *J. Org. Chem.*, **45**, 970 (1980); C. N. Barry and S. A. Evans, Jr., *ibid.*, **46**, 3361 (1981).

[6] Cf. P. G. Gassman and G. S. Proehl, *J. Am. Chem. Soc.*, **102**, 6682 (1980); K. Minaric-Majerski, *ibid.*, **102**, 1418 (1980). Reviews: D. Ginsburg, "Propellanes", Verlag-Chemie Weinheim, West Germany, 1975. A. Greenberg and J. F. Liebman, "Strained Organic Molecules", Academic Press, New York, 1978, pp 344–365.

[7] K. B. Wiberg and G. Sziemies, *Tetrahedron Lett.*, 1235 (1968); G. L. Closs and P. E. Pfeffer, *J. Am. Chem. Soc.*, **90**, 2452 (1968).

[8] M. Regitz, J. Hocker, and A. Liedhegener, "Organic Syntheses", Coll. Vol. V, Wiley, New York, 1973, p 179.

methyl)cyclopropene ester XII. This experiment testifies to the versatility of the rhodium acetate catalyst[9] and its tolerance of diverse functional groups.

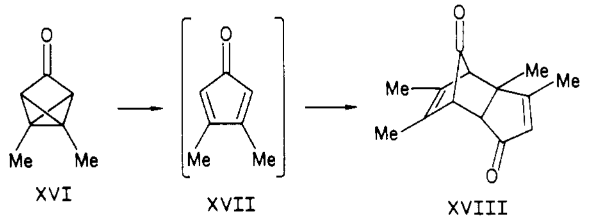
The cyclopropene ester XII was converted to the corresponding carboxylic acid XIII with trifluoroacetic acid. For the diazo ketone XV, the same regimen used to prepare the corresponding diacetate was followed.[1] Conversion to the acid bromide XIV followed by treatment at -78 °C with ethereal diazomethane resulted in formation of diazo ketone XV.

The diazo ketone XV was closed to the dichloride V in 37% yield by slow addition of a chloroform solution of XV to a second chloroform solution containing 0.013 molar equiv of dirhodium tetraacetate at 60 °C. With an authentic sample of V in hand, it was easy to ascertain the presence or absence of the dichloride V in the reactions leading to the rearranged keto furan VI.

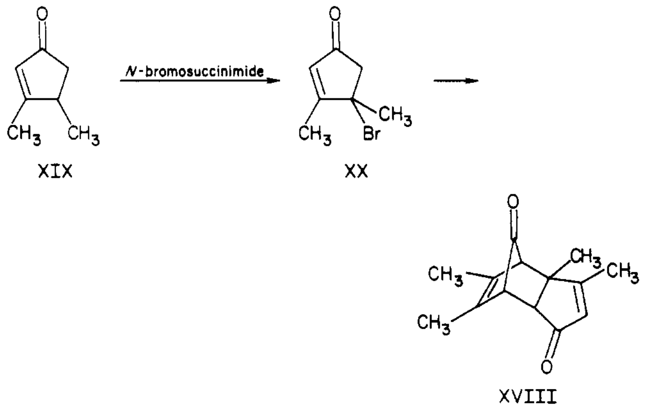
Rearrangement of Doering's Tricyclic Ketone XVI upon Treatment with Iodine

The tricyclo[2.1.0.0^{2,5}]pentan-3-one skeleton is itself susceptible to electrophilic attack. There is good precedent in the literature for the addition of halogen across the zero-carbon bridge of bicyclobutane. Thus, an adduct, whose structure was established by X-ray crystallography,[10] is formed between iodine and tricyclo[4.1.0.0^{2,7}]heptane. Masamune[11] reported the addition of bromine across the zero-carbon bridge of 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pentan-3-one. The structure of the adduct was inferred from the low-temperature NMR spectrum of the reaction mixture and the in situ conversion to the closed alcohol following treatment with lithium aluminum hydride.

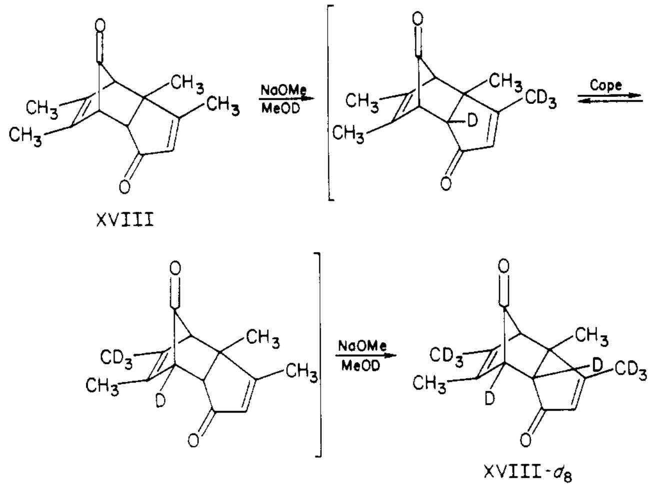
When the ketone XVI was treated with molecular iodine under a variety of experimental conditions: I_2/CCl_4/50–55 °C, I_2/CH_3I/reflux,[12] and $I_2/NaI/CH_3OCH_3$/ambient temperature; a white crystalline solid was isolated and identified as dimer XVIII. The latter is presumably formed by the dimerization of 3,4-dimethylcyclopentadienone (XVII). Dimer XVIII was identified by its spectral properties, which are quite definitive, and by synthesis of an authentic sample prepared as shown.



Thus, 3,4-dimethylcyclopent-2-enone (XIX), prepared according to Conia,[15] was brominated with *N*-bromosuccinimide, yielding the bromide XX. Treatment of the latter with triethylamine then gave the dimer XVIII identical with the product of rearrangement.



Dimer XVIII undergoes an interesting degenerate Cope rearrangement[16] which only becomes apparent as a consequence of an unusual incorporation of deuterium upon heating with sodium methoxide in methanol-*d*. The NMR spectrum of the deuterated product XVIII-d_8 showed only four singlets at δ 6.02, 2.65, 1.71, and 1.36 in the ratio 1:1:3:3. The starting undeuterated material XVIII shows: a one-proton vinyl quartet (^4J = 1.2 Hz) at δ 6.02, a one-proton bridgehead methine doublet of doublets (^3J = 5.0 Hz and ^4J = 1.4 Hz) at δ 3.11, a one-proton bridgehead methine doublet (^4J = 1.4 Hz) at δ 2.66, a one-proton methine doublet (^3J = 5.5 Hz) at δ 2.45, a three-proton vinyl methyl doublet (^4J = 1.2 Hz) at δ 2.05, a three-proton vinyl methyl quartet[14] (^5J = 1.0 Hz) at δ 1.71, a three-proton vinyl methyl quartet[17] (^5J = 1.0 Hz) at δ 1.66, and a three-proton methyl singlet at δ 1.36.



Experimental Section

1,5-Bis(hydroxymethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (II). To a solution of 0.314 g (1.4 mmol) of diacetoxy ketone[1a,b] I in 10 mL of absolute ethanol was added 0.774 g (5.6 mmol) of anhydrous potassium carbonate at 0 °C. The suspension was stirred for 14 h at 25 °C and then filtered and the solvent removed. The resulting oil was chromatographed on 20 g of silica gel using 10:1 ethyl acetate–methanol as eluant. This yielded 0.134 g (68%) of the keto diol II as a white solid, mp 38–39 °C, with R_f 0.45 (10:1 ethyl acetate–methanol). Recrystallization from ether yielded colorless needles, mp 39–40 °C.

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[9] N. Petiniot, A. J. Auciaux, A. F. Noels, A. J. Hubert, and Ph. Teyssie, *Tetrahedron Lett.*, 1239 (1978); A. J. Hubert, A. F. Noels, A. J. Auciaux, and Ph. Teyssie, *Synthesis*, 600 (1976); A. J. Auciaux, A. J. Hubert, A. F. Noels, N. Petiniot, and Ph. Teyssie, *J. Org. Chem.*, **45**, 695 (1980), and references cited therein.

[10] S. Mazur, A. H. Schroder, and M. C. Weiss, *J. Chem. Soc., Chem. Commun.*, 2623 (1977).

[11] S. Masamune, *Tetrahedron Lett.*, 945 (1965).

[12] K. B. Wiberg, W. E. Pratt, and W. F. Bailey, *J. Am. Chem. Soc.*, **99**, 2297 (1977).

[13] For an iodine-promoted bicyclobutane to butadiene isomerization, see C. R. Watson, Jr., R. M. Pagni, J. R. Dodds, and J. E. Bloor, *J. Am. Chem. Soc.*, **98**, 2551 (1976).

[14] E. W. Garbisch, Jr., and R. F. Sprecher, *J. Am. Chem. Soc.*, **97**, 6785 (1969).

[15] J. M. Conia and M. L. Leriverend, *Bull. Soc. Chim. Fr.*, 2981 (1970).

[16] Cf. D. W. Jones and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 417 (1980).

[17] The methyl groups at δ 2.05 and 1.71 appear as doublets, but double-resonance experiments show that the two vinyl methyl groups are coupled to one another.

[18] The 3,4-bis(chloromethyl)furan, bp 104–105 °C (16 mm), was obtained by thionyl chloride/pyridine treatment of furan-3,4-dimethanol (Aldrich).

The proton NMR spectrum ($CDCl_3$) of II showed: a four-proton hydroxymethyl singlet at δ 4.75, a two-proton hydroxyl singlet at δ 3.20, and a two-proton methine singlet at δ 2.32. The infrared spectrum in CCl_4 showed bands at 3600 (m, OH), 3500–3350 (m, OH), and 1780 cm^{1} (s, C=O). The mass spectrum (15 eV) showed *m/e* (relative intensity) 140 (6, M^+), 110 (10), 94 (12, $M^+ - CO - H_2O$), 66 (100).

The partially coupled ^{13}C NMR ($CDCl_3$) showed: a ketone carbonyl singlet at δ 185.05, a hydroxymethyl carbon triplet at δ 54.32, a methine carbon doublet of doublets at δ 41.32, and a quarternary carbon singlet at δ 18.19.

1,5-Bis(bromomethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (III). To a solution of 0.029 g (0.21 mmol) of dihydroxy ketone II and 0.151 g (0.46 mmol) of carbon tetrabromide in 4 mL of acetonitrile was added 0.136 g (0.519 mmol) of triphenylphosphine at 25 °C under a nitrogen atmosphere. The temperature was raised to 50 °C, and the reaction was heated for 8 h. The reaction was cooled, and solvent was removed, leaving a black oil. Chromatography of this oil on 3 g of silica gel using chloroform as eluant yielded 0.025 g (45%) of the dibromo ketone III as white crystals, mp 68–69 °C, with R_f 0.60 in chloroform.

The proton NMR spectrum ($CDCl_3$) showed: a four-proton bromomethyl singlet at δ 4.36 and a two-proton methine singlet at δ 2.37. The infrared spectrum (CCl_4) showed bands at 1854, 1881, and 1795 cm^{-1} (s, C=O). The mass spectrum (15 eV) showed *m/e* (relative intensity) 268, 266, 264 (11, 18, 8, M^+), 159, 157 (76, 84, $M^+ - CO - Br$), 78 (100, $M^+ - CO - 2Br$). Exact mass: calcd for $C_7H_6O^{79}Br^{81}Br$, 265.8765; found, 265.8761.

The fully coupled ^{13}C NMR spectrum ($CDCl_3$) showed a carbonyl carbon singlet at δ 180.41, a bridgehead methine doublet of doublets at δ 45.69 (^1J = 192.46 Hz, ^3J = 14.66 Hz), a quarternary carbon singlet at δ 31.11, and a bromomethyl carbon triplet at δ 21.36 (J = 158.19 Hz).

1,5-Bis(iodomethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (IV). An acetone solution (4.0 mL) saturated with sodium iodide was added to 0.024 g (0.09 mmol) of dibromide III at 0 °C under a nitrogen atmosphere. After the solution had stirred at 0 °C for 30 min the solvent was removed. The residue was taken up in 5 mL of ethyl ether and extracted with 5 mL of water. The ether layer was dried over sodium sulfate and filtered, and the solvent was removed yielding 0.029 g (90%) of a clear oil.

The spectral properties were those expected of the pure diiodide IV. The proton NMR spectrum ($CDCl_3$) showed a four-proton iodomethyl singlet at δ 4.18 and a two-proton methine singlet at δ 2.34. The infrared spectrum (Cl_4) showed bands at 1840 (m), 1805 (s, C=O), and 1788 cm^{-1} (s, C=O). The mass spectrum (15 eV) showed *m/e* (relative intensity) 360 (0.4, M^+), 233 (5, $M^+ - I$), 205 (49, $M^+ - I - CO$), 106 (15, $M^+ - 2I$), 78 (100, $C_6H_6^+$). Exact mass: calcd for C_7H_6OI, 232.9463; found, 232.9465. This compound should be used immediately, because it decomposes rapidly at room temperature.

3-Oxabicyclo[3.3.0]octa-1,4-dien-7-one (VI). To a solution of 0.026 g (0.21 mmol) of keto diol II, 0.074 g (0.49 mmol) of carbon tetrachloride, and 10 μL of ethyldiisopropylamine in 4 mL of acetonitrile was added 0.141 g (0.39 mmol) of triphenylphosphine at 25 °C under a nitrogen atmosphere. The mixture was stirred for 13 h at 47 °C, and then the solvent was removed. Chromatography of the resulting dark oil on 5 g of silica gel, eluting with chloroform, yielded 0.014 g (62%) of the crystalline keto furan VI, mp 89–93 °C. Recrystallization from ether–hexane yielded keto furan VI, mp 92–94 °C.

The proton NMR spectrum ($CDCl_3$) of VI showed a two-proton vinyl triplet at δ 7.29 (J = 1 Hz) and a four-proton methylene doublet at δ 3.33 (J = 1 Hz). The infrared spectrum (CCl_4) showed bands at 1761 (s, C=O) and 1725 cm^{-1} (m, C=C). The mass spectrum (15 eV) showed *m/e* (relative intensity) 122 (70, M^+), 94 (100, $M^+ - CO$), 83 (17). Exact mass: calcd for $C_7H_6O_2$, 122.0368; found, 122.0375.

The partially coupled ^{13}C NMR ($CDCl_3$) showed a carbonyl carbon singlet at δ 215.84, a vinyl carbon doublet at δ 135.02, a vinyl carbon singlet at δ 123.84, and a methylene carbon triplet at δ 36.90.

3-Oxa-7-(methylthio)-7-(methylsulfinyl)bicyclo[3.3.0]octa-1,4-diene (VIII). In a dry 50-mL side-arm flask 0.854 g (6.89 mmol) of methyl (methylsulfinyl)methyl sulfide was dissolved in 25 mL of tetrahydrofuran (distilled from sodium–benzophenone solution), and the solution was cooled to −10 °C. To this solution was added 4.24 mL (6.3 mmol) of 1.50 M *n*-butyllithium. After being stirred 1 h at −10 °C the solution was cooled to −78 °C and 0.458 g (2.67 mmol) of 3,4-bis(chloromethyl)furan[18] was added. After being warmed slowly to room temperature, the mixture was stirred for 17 h. The resulting suspension was filtered and the solvent removed, leaving a yellow oil. Chromatography of this oil on 100 g of silica gel using 3:1 ethyl acetate–hexane as eluant yielded 0.474 g (79%) of a white crystalline solid, VIII, R_f 0.24 in 3:1 ethyl acetate–hexane. The proton NMR spectrum ($CDCl_3$) of the furan VIII showed a methyl singlet at δ 2.24, a methyl singlet at δ 2.59, a two-proton apparent AB quartet at δ 2.83 (J = 9 Hz, J = 17 Hz), a one-proton doublet at δ 3.31 (J = 5.5 Hz), a one-proton doublet at δ 3.50 (J = 6 Hz), and a two-proton vinyl proton singlet at δ 7.14. The infrared spectrum ($CDCl_3$) showed sulfoxide absorption at 1072 cm^{-1} (vs). The mass spectrum at 15 eV showed *m/e* (relative intensity) 201 (2, $M^+ - CH_3$), 153 (90, $M^+ - SOCH_3$), 106 (100, $M^+ - S_2O(CH_3)_2$), 77 (10), 137 (12).

3-Oxabicyclo[3.3.0]octa-1,4-dien-7-one (VI) from Furan VIII. In a 10-mL flask 0.024 g of the furan VIII was dissolved in 2 mL of anhydrous ether and cooled to 0 °C. Two milliliters of 70% perchloric acid was added, and the reaction mixture was stirred 1 h at 0 °C. Evaporation of the solvent yielded a thick brown oil that was chromatographed on 25 g of silica gel. Elution with chloroform gave 0.008 g (60%) of white crystals, mp 92–94 °C, identical in all respects with the keto furan VI from the rearrangement of the diol II.

Acknowledgment. This research was generously supported by the National Science Foundation.

Registry No. I, 78998-58-0; II, 81710-08-9; III, 81715-26-6; IV, 93530-80-4; V, 81710-12-5; VI, 81715-27-7; VII, 6372-18-5; VIII, 81715-28-8; XI, 821-10-3; XII, 93564-58-0; XIII, 93530-81-5; XIV, 93530-82-6; XV, 93530-83-7; XVI, 3350-02-5; XVII, 40430-97-5; XVIII, 40430-98-6; XVIII-d_8, 93564-59-1; XIX, 30434-64-1; XX, 81715-29-9; $(Me_2CH)_2NEt$, 7087-68-5; $MeSCH_2S(O)Me$, 33577-16-1; $N_2CHC(O)OBu$-*t*, 35059-50-8; $Rh_2(OAc)_4$, 15956-28-2; $(BrCO)_2$, 15219-34-8; furan-3,4-dimethanol, 14496-24-3.

Supplementary Material Available: Full experimental details for the preparation of 1,5-bis(chloromethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (V) and for the 3,4-dimethylcyclopentadienone dimer XVIII preparation and deuterium exchange (6 pages). Ordering information is given on any current masthead page.