[lit.¹³ bp 74° (10 mm)]; ir 1765 cm⁻¹ (γ -lactone C=O); nmr (neat) δ 1.43 [s, 6, (CH₂)₂], 2.37 (t, 2, CCH₂C), 4.48 (t, 2, CCH₂O).

Other lactones, commercial materials, were distilled and each stored in an ampoule.

Procedure for Irradiation.—A given amount of lactone or mixture with di-*tert*-butyl peroxide was degassed by three thawings and freezings at -190° in a glass tube or nmr sample tube, to which degassed trichlorosilane was transferred by a vacuum line. The tube, after being fused, was irradiated by γ rays from a ⁶⁰Co source or uv rays from a medium-pressure mercury lamp at room temperature.

Identification and estimation of cyclic ethers was performed by glpc, except for those described in footnote c in Table II. Commercial cyclic ethers purified by the conventional method were used as the standards, with the exception of 2-ethyl tetrahydrofuran and hexamethylene oxide. These were prepared by γ induced reduction of 25 g of γ - and ϵ -caprolactones with trichlorosilane, respectively. To the irradiated mixture was added water for decomposition of chlorosilanes and siloxanes. After neutralization with aqueous sodium hydroxide solution, the cyclic ethers produced were extracted with diethyl ether. Two distillations gave 2-ethyltetrahydrofuran and hexamethylene oxide, respectively, which were identified by the coincidence of physical constants cited in the literatures: 2-ethyltetrahydrofuran, bp 106-108° (lit.¹⁴ bp 108.5°), n^{20} D 1.4159 (lit.¹⁵ 1.4170); hexamethylene oxide, bp 117-118° [lit.¹⁶ bp 121° (741 mm)], n^{20} D 1.4369 [lit.¹⁷ 1.4361].

Identification and Estimation of Cyclic Ether by Nmr.—The cyclic ethers which were footnoted by c in Table II were identified by nmr. The nmr spectrum of α,α -dimethyl- γ -butyrolactone (5) in trichlorosilane follows: δ 1.54 [s, 6, (CH₃)₂], 2.42 (t, 2, >CCH₂C), 4.53 (t, 2, CCH₂O). The γ irradiation of the mixture in the same nmr tube as used for nmr determination of 5 in trichlorosilane gave the following spectrum: δ 1.45 [s, 6, (CH₃)₂],

(14) O. Riobe, Ann. Chim. (Rome), 4, 593 (1949); Chem. Abstr., 44, 2984b (1950).

(15) Yu. K. Yur'ev and I. P. Gragerov, Zh. Obshch. Khim., 19, 724 (1949);
 Chem. Abstr., 44, 1092f (1950).

(16) E. E. Schweizer and W. E. Parham, J. Amer. Chem. Soc., 82, 4085 (1960).

(17) J. Meinwald and H. Nozaki, ibid., 80, 3132 (1958).

CARGILL, et al.

1.57 (s, 0.7), 2.01 (t, 2, >CCH₂C), 3.72 (s, 2, >CCH₂O), 4.17 (t, 2, CH_2CH_2O). Among these, the singlet at δ 1.57 was regarded as the methyl signal of the unchanged lactone, and the others were assigned to protons of 3,3-dimethyltetrahydrofuran pro-duced. The amount of the ether produced was estimated by comparison of the intensity of the methyl signal which appeared newly at δ 3.72 with the sum of methyl absorptions of unchanged lactone (at δ 1.57) and the ether (at δ 1.45). The same procedure was applied for 2,2-dimethyl- and 3-methyltetrahydrofurans. In the case of 2,2-dimethyltetrahydrofuran, methyl absorption (δ 1.72) of the starting γ -isocaprolactone (3) was not observed among the absorptions of the irradiated mixture: δ 1.58 [s, 6, alloing the absorptions of the irradiated mixture. 0.103 [s, 6], $(CH_3)_2$], 2.11 (m, 4, CCH_2CH_2C), 4.15 (t, 2, CCH_2O). Nmr spectrum of the irradiated mixture of α -methyl- γ -butyrolactone (4) with trichlorosilane was δ 1.43 (d, 3, CH_3), 1.62 (d, 0.7), 1.70–3.00 (m, 3, CCH_2C and $>CH_3$), 3.60 (m, 1, one proton of $>CHCH_2O$), 4.12 (m, 3, CH_2CH_2O and one proton of $>CH-CH_2O$), 4.12 (m, 3, CH_2CH_2O and one proton of >CHCH₂O), where the doublet at δ 1.62 is regarded as the methyl signal of the unchanged 4. The >CHCH₂O group constitutes an ABX system; the multiplet at δ 3.60 is the B part; and the A and X parts may be contained in multiplets at δ 4.12 and 1.70-3.00, respectively. 3-Methyltetrahydrofuran produced was estimated by comparing the intensity of the methylene signal which appeared newly at δ 3.60 with the sum of methyl absorptions at δ 1.43 (ether) and 1.62 (4). 3-Chloropropoxytrimethylsilane.—The titled compound as

3-Chloropropoxytrimethylsilane.—The titled compound as standard was prepared by the procedure of Speier¹⁸ using pyridine as an acceptor for hydrogen chloride.

3-Chloropropoxydichlorosilane.—Degassed trichlorosilane was transferred by a vacuum line into a nmr tube, which in advance contained degassed trimethylene oxide. Nmr spectrum of the mixture after γ irradiation: δ 2.45 (m, 2, CCH₂C), 4.02 (t, 2, ClCH₂C or CCH₂O), 4.51 (t, 2, CCH₂O or ClCH₂C), 6.00 (s, 1, SiH).

Registry No.-Trichlorosilane, 10025-78-2.

Acknowledgment.—The authors wish to thank Dr. S. Kawamura for assistance in the interpretation of nmr spectra.

(18) J. L. Speier, ibid., 74, 1003 (1952).

Acid-Catalyzed Rearrangements and Additions of β , γ -Unsaturated Ketones¹

R. L. CARGILL,* M. E. BECKHAM, J. R. DAMEWOOD, D. M. POND, AND W. A. BUNDY

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

J. BORDNER

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607

Received June 9, 1971

The acid-catalyzed isomerization of 10,11-dimethyltricyclo[$4.3.2.0^{1.6}$]undec-10-en-7-one (1) to 7,8-dimethyltricyclo[$5.2.2.0^{1.6}$]undec-5-en-9-one (3) and 1,11-dimethyltricyclo[$6.2.1.0^{3.8}$]undec-3-en-2-one (4) is described. Chemical and X-ray diffraction analyses provided evidence for structures 3 and 4. The mechanism of the isomerization is discussed and a new interpretation of the addition of hydrogen halide to 7-ketonorbornene is presented.

We have previously described acid-catalyzed addition and isomerization reactions of β , γ -unsaturated ketones in which the double bond is contained in a four-membered ring.^{2,3} Similar studies have also been reported from other laboratories.³ We report here our study of the acid-catalyzed isomerizations of tricyclic ketones 1 and 2.

Ketones 1 and 2 have already been shown to undergo light-induced as well as acid-catalyzed interconversion.⁴

(1) We thank the National Science Foundation for generous support of this research.

(2) R. L. Cargill and J. W. Crawford, J. Org. Chem., 35, 356 (1970).
(3) R. L. Cargill, D. M. Pond, and S. O. LeGrand, *ibid.*, 35, 359 (1970),

and references cited therein. (4) R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, *ibid.*, **30**, 3647 (1965).



The equilibrium concentrations of 1 and 2 indicate that 1 is the more stable isomer by $ca. 1.5 \text{ kcal/mol.}^4$ In our investigation of the acid-catalyzed equilibration of 1 and 2 we found that vigorous or prolonged treatment of either 1 or 2 with *p*-toluenesulfonic acid in benzene led to disappearance of both 1 and 2 and formation of two new ketones which are assigned structures 3 and



Figure 1.—Stereoplot of compound 5.

4. These two new ketones are formed in approximately equal amounts and account for ca. 80% of the product mixture. The remainder is composed of two minor products⁵ which were not further investigated. Each of the new ketones, **3** and **4**, was recovered unchanged from boiling toluene containing *p*-toluenesulfonic acid, indicating that each is formed irreversibly from **1** or **2**.



Structures 3 and 4 for the two new ketones were first proposed on the basis of spectroscopic and mechanistic considerations. Subsequent chemical degradation and X-ray crystallographic analysis have confirmed these structures. We shall first discuss the evidence for the structural assignments, then we shall turn to the mechanisms of the isomerizations leading to ketones 3 and $4.^6$

Ketone 3 exhibits spectral characteristics⁷ typical

(5) Neither of these minor products is ketone 20 as evidenced by their separation from authentic 20 by glpc.
(6) (a) W. Parker, R. A. Raphael, and J. S. Roberts, *Tetrahedron Lett.*,

(6) (a) W. Parker, R. A. Raphael, and J. S. Roberts, Tetrahedron Lett., 2313 (1965); T. F. W. McKillop, J. Martin, R. A. Raphael, and J. S. Roberts, Chem. Commun., 162 (1967); (b) J. R. Prahlad, R. Ranganathan, U. R. Nayak, T. S. Santhanakrishnan, and S. Dev, Tetrahedron Lett., 417 (1964);
(c) W. G. Dauben and E. I. Aoyagi, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, No. ORGN 74; (d) G. Brieger, J. Amer. Chem. Soc., 35, 3783 (1963); see also E. J. Corey and R. S. Glass, *ibid.*, 89, 2600 (1967).

of a cyclopentanone, a strained double bond, a β , γ unsaturated ketone, a methyl on tertiary carbon, a methyl on quaternary carbon, and a single vinyl hydrogen. Ketone **3** undergoes base-catalyzed hydrogen-deuterium exchange, whereupon the methyl doublet at δ 1.02 collapses to a singlet, with no further change in the nmr spectrum, indicating that the corresponding methyl is attached to the carbon α to the carbonyl, and further that the configuration at this α carbon is the thermodynamically favored one. Oxidation of **3** with osmium tetroxide gave the crystalline diol **5** in high yield. This diol was converted into 4-(3,4-dimethylphenyl)butyric acid (6) by the sequence outlined in Scheme I, with only spectroscopic characterization⁷ of the indicated intermediates.

Cleavage of the glycol **5** with lead tetraacetate gave an oily aldehyde in which the β -dicarbonyl function evidently remains intact. Conversion of the aldehyde function into the corresponding carboxylic acid with bromine-water was apparently accompanied by some, but not complete, hydrolysis of the β -dicarbonyl system. Complete hydrolysis was effected with methanolic potassium hydroxide. Reduction of the remaining ketone with sodium borohydride followed by eliminative decarboxylation and dehydrogenation gave 4-(3,4-dimethylphenyl)butyric acid (6).⁸ These data indicate structure **3** for one of the new ketones.

Unambiguous confirmation of structure **3** was obtained by single-crystal X-ray diffraction analysis of glycol **5**. (See Figure 1.)

Spectroscopic analysis' of ketone 4 indicated the presence of a cisoid α,β -unsaturated ketone bearing a β -vinyl proton, a methyl on quaternary carbon, and a methyl on tertiary carbon. Catalytic hydrogenation of 4 gave a cyclopentanone 7. Periodate-permanganate oxidation of 4 gave a triacid **8a** without loss of carbon. Heating the triacid at 120° for 20 min gave an anhydride (1860, 1765 cm⁻¹) presumably 9. The

⁽⁷⁾ Spectroscopic data are presented in the Experimental Section.

⁽⁸⁾ E. Barnett and F. G. Sanders, J. Chem. Soc., 434 (1933).

CARGILL, et al.







mass spectrum of triester **8b** is easily interpreted in terms of the assigned structure.⁷



Removal of the butyric acid side chain of 8 by Barbier-Wieland degradation to provide santenic acid would establish completely the structure and stereochemistry of ketone 4. Reaction of 8b with phenylmagnesium bromide followed by dehydration of the crude alcohol gave diphenyl diester 10a. Attempts to introduce the required second double bond by allylic bromination-dehydrobromination were frustrated in that invariably a mixture of products apparently containing the geometrical isomers of bromodiene thought to be 12 (ratio ca. 2:1) was obtained. The structure of the bromodiene 12a is assigned on the basis of the mass spectrum (M⁺ 496, 498) and the 100-MHz nmr spectrum (AB quartet δ 6.62, $\Delta_{AB} = 51.0$ Hz, $J_{AB} = 10$ Hz) (AB quartet δ 6.35, $\Delta_{AB} = 58.7$ Hz, $J_{AB} = 9$ Hz).⁹ This product probably arises from the desired 11 via an addition-elimination sequence.¹⁰



When a mixture of 1 and 2 was stirred with 6 N hydrochloric acid a new crystalline hydroxy ketone was obtained in 54% yield. On the basis of spectroscopic evidence and our previous experience³ with this reaction we proposed structure 13 for the hydration product. Conversion of 13 into ketone 4 by dehydration with thionyl chloride in pyridine confirmed the relation of ketones 4 and 13. Final proof of the structure of 13, and therefore of 4, was obtained by single-crystal Xray diffraction analysis (see Figure 2).

We now turn to the mechanism by which the new ketones 3 and 4 are formed. Although either 1 or 2 could serve as the immediate precursor of the new

(9) We thank Dr. P. D. Ellis for this nmr spectrum and the National Science Foundation for a Department Development Grant which provided funds for the purchase of the Varian XL-100-15 nmr spectrometer.
(10) J. H. Incremona and J. C. Martin, J. Amer. Chem. Soc., 92, 627

(10) J. H. Incremona and J. C. Martin, J. Amer. Chem. Soc., 92, 624 (1970).



isomers, both 3 and 4 must arise from 1, as will be Net migration of the etheno bridge in the seen. protonated ketone leads to ion 15 with relief of considerable strain. Loss of a proton provides the undetected alcohol 16. Protonation of the tetrasubstituted double bond in 16 from the top side (path a) followed by a Wagner-Meerwein shift leads directly to ketone 4. The santenone-type stereochemistry of 4 is determined by the exo protonation of 16³ (Scheme II).



Ketone 3 is considered to arise from alcohol 16 via protonation (path b) and Wagner-Meerwein shift giving 18. Isomerization of ion 18 to 19 followed by a second carbon shift provides 3.

An alternate path for production of 3 from 1 is shown in Scheme III. In order to test this hypothesis we synthesized the supposed intermediate ketone 20 and subjected it to treatment with p-toluenesulfonic acid in boiling benzene and in boiling o-dichlorobenzene. In each case only unchanged 20 was recovered.¹¹

The synthesis of ketone 20 is of some interest. Condensation of cyclohexene and crotonic acid with poly-



phosphoric acid gave the bicyclic enone 22.¹² Conversion of 22 into 23 was accomplished by methods already described¹³ in 53% yield. Condensation of 23 with ethyl formate gave the hydroxymethylene compound 24 which was then converted into the methylene ketone 25.¹⁴ Although 25 was recovered unchanged from attempted acid-catalyzed isomerization,¹⁵ the desired 20 was obtained in 83% yield when an ethanolic solution of 25 was refluxed with a trace of palladium on charcoal (Scheme IV).¹⁶



Alternatively, hydrogenolysis of the benzoate of 24 provided 20 as a minor product along with the corresponding saturated ketone.¹⁷

At this point a brief discussion of the addition of hydrogen halides to the β,γ -unsaturated ketone, 7ketonorbornene (26), is appropriate. Caple¹⁸ has shown that addition of deuterium bromide to 26 yields 27 and 28. The suggested mechanisms for the formation of these products involves exo, cis addition of DBr to yield 27 and exo protonation, rearrangement to an α -keto carbonium ion, and trapping of the latter from the exo side by bromide ion to yield 28. Initial interaction of acid with the carbonyl group is discounted. We suggest that 27 and 28 more likely arise

(12) S. Dev, J. Indian Chem. Soc., 33, 703 (1956); 34, 169 (1957). See (12) S. Ber, S. Institut Chem. Soc., 33, 105 (1950); 34, 109 (1951). See also J.-M. Conia and M.-L. Leriverend, Tetrahedron Lett., 2101 (1968); Bull. Soc. Chim. Fr., 2981, 2991 (1970).
 (13) (a) R. L. Cargill, A. C. Miller, D. M. Pond, P. de Mayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, Mol. Photochem., 1, 301 (1969);

(b) R. L. Cargill, W. A. Bundy, D. M. Pond, A. B. Sears, J. Saltiel, and J. Winterle, ibid., in press.

(14) A. J. Manson and D. Wood, J. Org. Chem., 32, 3434 (1967)

(15) J.-M. Conia and P. Anice, Bull. Soc. Chim. Fr., 2972 (1970)
(16) The synthesis of 20 is described in detail in ref 13b.

(17) B. D. Astill and V. Boekelheide, J. Amer. Chem. Soc., 77, 4079

(1955)(18) R. Caple, H. W. Tan, and F. M. Hsu, J. Org. Chem., 33, 1542 (1968).

⁽¹¹⁾ The corresponding unsubstituted tricyclic enone was likewise recovered from treatment with acid.



via the more complex series of changes in Scheme V.¹⁹ The absence of the endo bromo ketones 31 and 32 in the reaction mixture is more likely the result of their reversion to the precursors 29 and 30 (a stereoelectronically favorable process) than their not being formed.²⁰ The depicted mechanism by which 27 and 28 may arise is consistent with a great body of known carbonium ion chemistry²¹ and has the advantages that the first step is protonation of 26 at its most basic site, the carbonyl oxygen, and the acid-catalyzed opening of the cyclopropanol systems is consistent with the findings of DePuy²² and Nickon.^{23,23a}

Experimental Section

All boiling and melting points are uncorrected. Microanalyses were performed by Bernhardt Microanalytisches Laboratorium,

(20) J. J. Tufariello and R. J. Lorence, J. Amer. Chem. Soc., 91, 1546

(1969); J. Lhomme, A. Diaz, and S. Winstein, *ibid.*, 91, 1548 (1969).
(21) (a) P. D. Bartlett, Ed., "Nonclassical Ions: Reprints and Commentary," (b) J. A. Berson in "Molecular Rearrangements," Part 1, P.

de Mayo, Ed., Interscience, New York, N. Y., 1963, p 111.
(22) C. H. DePuy, Accounts Chem. Res., 1, 33 (1968).
(23) A. Nickon, J. L. Lambert, S. J., R. O. Williams, and N. H. Werstuick, J. Amer. Chem. Soc., 88, 3354 (1966).

(23a) NOTE ADDED IN PROOF. -- Dr. T. E. Jackson of this laboratory has pointed out that products 27 and 28 are those expected from the addition of bromide ion to ion i, which is the nonclassical equivalent of 30.



Acid-Catalyzed Rearrangement of 10,11-Dimethyltricyclo-[4.3.2.0^{1,6}] undec-10-en-7-one (1) and 7,8-Dimethyltricyclo[6.3.-0.0^{1,6}]undec-6-en-9-one (2).—To a solution of 4.43 g (23.2 mmol) of a mixture of 1 and 2^4 in benzene was added 1.5 g of *p*-toluenesulfonic acid and the mixture was refluxed for 5 hr. The solution was washed with 5% sodium hydroxide, then with water, dried (MgSO₄), and concentrated to yield 4.18 g of crude product. Distillation (bath temperature 100°, 0.5 Torr) gave 3.42 g (77.4%) of a colorless liquid containing four new compounds, two of which, ketones 3 and 4, constituted ca. 80% and were present in approximately equal amounts (glpc). Pure samples of 3 and 4 were obtained by preparative glpc (20% DEGS). 7,8-Dimethyltricyclo[5.2.2.0^{1,6}] undec-5-en-9-one (3) gave uv

max (95% ethanol) 298 nm (ϵ 221); uv max (isooctane) 305 nm (ϵ 200); ir (CCl₄) 3010, 1745, 1700, and 955 cm⁻¹; nmr (CCl₄) δ 1.02 (d, 3, J = 7.0 Hz), 1.20 (s, 3), and 5.47 (m, 1).

Anal. Calcd for C13H18O (190.25): C, 82.06; H, 9.54. Found: C, 81.91; H, 9.73.

1,11-Dimethyltricyclo[6.2.1.0^{3,8}] undec-3-en-2-one (4) gave uv max (95% ethanol) 332 (\$ 55) and 238 nm (\$ 13,000); uv max (isooctane) 340 (\$\epsilon 46\$) and 238 nm (\$\epsilon\$, 14,000); ir (CCl₄) 3015, (1500 ctalle) bits ($t \neq 0$) and 250 mm ($t \neq 1$, 500); if ($t \neq 0$) bits, 1730, 1670, and 865 cm⁻¹; nmr (CCl₄) δ 0.87 (d, 3, J = 7.0 Hz), 0.98 (s, 3), and 6.33 (t, 1, J = 3.0 Hz). Anal. Calcd for C₁₈H₁₈O (190.25): C, 82.06; H, 9.54.

Found: C, 81.87; H, 9.73.

The semicarbazone had mp 186-188°, from ethanol.

Anal. Calcd for C₁₄H₂₁N₈O(259.28): C, 67.98; H, 8.56; N, 16.99. Found: C, 67.87; H, 8.29; N. 17.03.

The 2,4-dinitrophenylhydrazone had mp 170-171°, from ethanol

Anal. Calcd for $C_{19}H_{22}N_4O_4$ (370.40): C, 61.61; H, 5.99; N, 15.12. Found: C, 61.75; H, 6.20; N, 15.20.

Hydrogenation of 4 in ethanol over platinum oxide provided the dihydro derivative 7: mass spectrum (70 eV) m/e (molecular ion) 192; ir (CCl₄) 1740 cm⁻¹; nmr (CCl₄) δ (d, 3, J = 6.5Hz) and 0.97 (s, 3)

 $5,6-Dihydroxy-7,8-dimethyltricyclo [5.2.2.0^{1,6}] undecan-9-one$ (5).—A solution of 358 mg (1.88 mmol) of 3, 511 mg (2.02 mmol) of osmium tetroxide, and 15 ml of pyridine was stirred in the dark at room temperature for 26 hr. To this solution was added a mixture of 1.80 g of sodium bisulfite, 30 ml of water, and 200 ml of pyridine. The resulting solution was stirred for 6 hr (until it became orange) and extracted with chloroform (four 50-ml por-The organic phase was washed with several portions of tions). water, dried (K₂CO₃), and concentrated in vacuo to yield 407 mg (96.5%) of light brown solid. Recrystallization from benzene gave white plates: mp 183.5-184.5°; ir (CCl₄) 3610, 3560, and 1745 cm^{-1}

Calcd for C₁₃H₂₀O₈ (224.29): C, 69.61; H, 8.99. Anal. Found: C, 69.51; H, 8.77.

Degradation of 5. 4-(3,4-Dimethylphenyl)butyric Acid (6).-To a rapidly stirred solution of 110 mg (0.49 mmol) of 5 in 10 ml of benzene was added 270 mg (0.56 mmol) of lead tetraacetate in 10 ml of benzene. The solution was stirred for 1 hr, filtered, dried (K_2CO_3) , and concentrated at reduced pressure to yield a milky oil. Chromatography over 10 g of Merck acid-washed alumina gave 90 mg of an oily aldehyde: ir (CCl₄) 2715, 1790, and 1740 cm⁻¹; nmr (CCl₄) δ 1.10 (s, 3), 1.19 (d, 3, J = 7.0 Hz), and 9.7 (t, 1, J = 1.5 Hz)

To 300 mg (1.35 mmol) of the above aldehyde was added saturated bromine water until the rapid uptake of bromine ceased Water (20 ml) and 3 ml of saturated sodium bisulfite (3.0 ml).were added and the mixture was extracted with ether (two 50-ml portions). The organic phase was dried (Na₂SO₄) and concentrated to yield 260 mg of an oily keto acid, ir (CCl₄) 3450 (broad), 1770, and 1740 cm⁻¹.

A solution of 260 mg (1.05 mmol) of the keto acid, 520 mg of potassium hydroxide, and 10 ml of methanol was refluxed for 3 hr. The resulting solution was acidified with 20% sulfuric acid and continuously extracted for 12 hr. The ether extract was dried (Na₂SO₄) and concentrated to yield 240 mg of a keto diacid, ir (CCl₄) 3500 (broad) and 1710 cm⁻¹.

A mixture containing 240 mg (0.93 mmol) of the keto diacid, 48 mg of sodium borohydride, and 20 ml of methanol was stirred at room temperature for 3 hr. The resulting mixture was acidi-

⁽¹⁹⁾ For clarity, ions are drawn as equilibrating classical ions.

fied with 20% sulfuric acid and continuously extracted for 12 hr. The ether extract was dried (Na₂SO₄) and concentrated to yield 210 mg of a hydroxy diacid. A solution of 200 mg of *o*-chloranil, 100 mg of *p*-toluenesulfonic acid, 136 mg (0.53 mmol) of the hydroxy diacid, and 25 ml of xylene was refluxed for 4 hr. The resulting mixture was filtered, washed with water, and extracted with 10% sodium bicarbonate. The basic extract was acidified and continuously extracted with pentane for 24 hr. The organic extract was dried (Na₂SO₄) and concentrated to yield 22 mg of a milky oil. The organic extract was dried (Na₂SO₄) and concentrated to yield 22 mg of a milky oil. Crystallization from pentane gave a white solid, mp 48-51°, which showed no melting point depression upon admixture with an authentic sample of 4-(3,4dimethylphenyl)butyric acid (6).⁸

4-(1,3-Dicarboxy-2,3-dimethylcyclopentyl)butyric Acid (8a).— A solution containing 1.24 g (6.51 mmol) of 4, 2.5 g of potassium carbonate, 12 g of sodium metaperiodate, and 0.05 g of potassium permanganate in 1500 ml of water was stirred for 72 hr. A small amount of sodium metaperiodate was added after 24 hr to restore the original color of the mixture. The solution was made basic with *ca*. 1 g of potassium hydroxide and the neutral material was extracted with pentane (200 ml). The aqueous solution was acidified, saturated with sodium chloride, and extracted with ether (three 500-ml portions). The combined organic layers were dried (Na₂SO₄) and concentrated to yield a white solid. Subsequent recrystallization from ether yielded 1.63 g (91.8%) of white solid 8a: mp 199-200° dec; ir (KBr) 3410 and 1720 cm⁻¹.

Anal. Calcd for $C_{13}H_{20}O_6$ (272.29): C, 57.34; H, 7.40. Found: C, 57.26; H, 7.32.

When the melt was cooled, the infrared spectrum of the resulting material exhibited absorptions of 1820 and 1765 cm⁻¹.

Dimethyl 1-(4,4-Diphenylbut-3-enyl)-2,3-dimethylcyclopentan-1,3-dicarboxylate (10a).--A solution of phenylmagnesium bromide, prepared from 1.25 ml of bromobenzene and 290 mg (12.1 mg-atoms) of magnesium turnings, in 10 ml of anhydrous ether was added dropwise to a stirred solution of 1.25 g (4.0 mmol) of triester 8b in 100 ml of anhydrous ether in a dry nitrogen atmosphere. After 6 hr ice was added, followed by saturated aqueous ammonium chloride solution until the ether layer was clarified. The layers were separated, and the aqueous layer was extracted with ether (three 50-ml portions). The combined organic phase was concentrated, the residue was dissolved in 100 ml of glacial acetic acid and 10 ml of water, and the resulting solution was refluxed for 4 hr. The acetic acid was removed at aspirator pressure and the residue was dissolved in ether. The ethereal solution was washed with aqueous sodium bicarbonate, water, and brine, dried (MgSQ₄), and concentrated to yield 10a as a crude oil: ir (CCl₄) 3070, 3050, 3015, 1720, 1200, and 1115 cm⁻¹; nmr (CCl₄) δ 0.95 (d, 3, J = 7.0 Hz), 1.08 (s, 3), 3.48 (s, 3), 3.57 (s, 3), 5.94 (t, 1, J = 7.0 Hz), and 7.18 (m, 10).

The crude diester 10a was added to a solution of 1 g of potassium hydroxide in 100 ml of water containing 1 ml of methanol and refluxed for 48 hr. The reaction mixture was cooled, extracted with pentane (100 ml), acidified (3 *M* HCl), and extracted with ether (3 100-ml portions). The ethereal solution was dried (MgSO₄) and concentrated. Crystallization of the residue from ether yielded 810 mg (51.6%) of white solid 10b: mp 131-132°; uv max (95% ethanol) 252 nm (ϵ 15,800); ir (KBr) 3400, 3075, 3050, 3010, 1710, 765, and 700 cm⁻¹; nmr (CCl₄) δ 5.97 (m, 1), 7.08 (m, 10), and 12.38 (s broad, 1); mass spectrum (70 eV) *m/e* 392 (M⁺).

Anal. Calcd for $C_{25}H_{28}O_4$ (392.47): C, 76.50; H, 7.19. Found: C, 76.22; H, 7.06. Attempted Synthesis of Dimethyl 1-(4,4-Diphenylbuta-1,3-

Attempted Synthesis of Dimethyl 1-(4,4-Diphenylbuta-1,3dienyl)-2,3-dimethylcyclopentan-1,3-dicarboxylate (11).—A solution of 390 mg (0.099 mmol) of $10a^{24}$ and 200 mg of N-bromosuccinimide in 25 ml of carbon tetrachloride was refluxed under irradiation from a sunlamp for 30 min. The solution was cooled, filtered, and the carbon tetrachloride removed by distillation with 8 ml of s-collidine as a cosolvent. The residual solution was diluted with 50 ml of 5% s-collidine in xylene and refluxed for 4 hr. The solution was cooled and washed successively with 3 *M* hydrochloric acid (two 75-ml portions), water (two 75-ml portions), and sodium bicarbonate solution (two 75-ml portions). The organic phase was dried (MgSO₄) and concentrated to yield 434 mg of crude material. Chromatography over 10 g of Woelm neutral alumina gave 216 mg of an oily mixture of geometric isomers of 12 (ratio 2:1): uv max (95% ethanol) 307 nm (ϵ 26,000); ir (neat) 3070, 3050, 3020, 1750, 1670, 1220, and 700 cm⁻¹; nmr (100 MHz) (CCl₄), major isomer, δ 0.94 (d, 3, J = 8.0 Hz), 1.12 (s, 3), 3.60 (s, 3), 3.64 (s, 3), 6.62 (AB q, 2, $\Delta_{AB} = 51.0$ Hz, $J_{AB} = 10.0$ Hz), and 7.30 (m, 10); minor isomer, 1.02 (d, 3, J = 7.0 Hz), 1.10 (s, 3), 3.60 (s, 3), 3.56 (s, 3), 6.35 (AB q, 2, $\Delta_{AB} = 58.7$ Hz, $J_{AB} = 9.0$ Hz), and 7.30 (m, 10); mass spectrum (70 eV) m/e 496, 498 (M⁺). 1,11-Dimethyl-endo-3-hydroxytricyclo[6.2.1.0^{3,8}] undecan-2-one

1,11-Dimethyl-endo-3-hydroxytricyclo[$6.2.1.0^{3,8}$] undecan-2-one (13).—A solution containing 842 mg (4.42 mmol) of a mixture of 1 and 2 (ratio ca. $3:7)^4$ in 50 ml of ether was stirred with 20 ml of 6 *M* hydrochloric acid for 75 hr. The reaction mixture was poured into 100 ml of water and extracted with ether (three 100ml portions). The combined extracts were dried (MgSO₄) and concentrated to give a thick brown oil which crystallized upon standing. The crystalline mass was dissolved in 5 ml of ether and passed through activated charcoal. Removal of the ether gave white crystals which were dried ($25-30^\circ$) at reduced pressure (0.4 Torr) for 24 hr to yield 500 mg (54.3%) of 13: mp 96–97°; ir (CCl₄) 3560, 3445, and 1745 cm⁻¹; nmr (CCl₄) δ 0.84 (d, 3, J = 6.5 Hz), 0.98 (s, 3), 2.67 (s, 1), and 1.55 (m, 13); nmr (DMSO) δ 5.10 (s, 1).

Anal. Calcd for $C_{13}H_{20}O_2$ (208.30): C, 74.96; H, 9.68. Found: C, 74.75; H, 9.64.

Dehydration of 1,11-Dimethyl-endo-3-hydroxytricyclo[6.2.-1.0^{3,3}]tricycloundecan-2-one (13).—To a stirred solution of 137 mg (0.63 mmol) of 13 in 25 ml of pyridine maintained at 0° was added 2 ml of thionyl chloride. The solution was allowed to warm to room temperature and was stirred for 10 hr at 25°. The solution was poured onto ice and extracted with pentane (three 75-ml portions). The combined organic phase was washed several times with 3 M hydrochloric acid to remove pyridine, dried (MgSO₄), and concentrated to yield 90 mg (65%) of 4, which was identified by comparison of glpc retention time (coinjection), ir spectra, and nmr spectra with those of 4 obtained as described above.

Attempted Rearrangement of 8,9-Dimethyltricyclo[4.3.2.0^{1,6}]undec-8-en-7-one (20).—A mixture of 23 mg (0.012 mmol) of 20, 40 mg of *p*-toluenesulfonic acid, and 15 ml of benzene was refluxed for 4 days. Analysis by glpc showed that the only change was slight decomposition of 20. A similar experiment using *o*-dichlorobenzene as solvent gave the same result. Attempts to rearrange tricyclo[4.3.2.0^{1,6}] undec-8-en-7-one in the manner also led only to recovered starting material.

X-Ray Analysis of 5 and 13.—The crystal structure of compounds 5 and 13 were concluded in a routine manner. Since both analyses were similar, they will be reported together. Suitable crystals of both compounds were grown from suitable solvents (see Table I) by slow evaporation. The resulting platelike

TABLE	Ι
-------	---

DETAILS OF CRYSTAL SURVEYS

Compound	5	13	
Crystallization media	Benzene	Pentane	
Crystal size, mm	0.3 imes 0.4 imes 0.3	0.2 imes 0.3 imes 0.4	
Cell dimensions, Å	$a = 8.45 \pm 0.01$ $b = 9.89 \pm 0.01$	$a = 9.56 \pm 0.01$ $b = 11.91 \pm 0.01$	
0	$c = 15.17 \pm 0.01$ $\beta = 103.32 \pm 0.03^{\circ}$	$c = 13.89 \pm 0.01$ $\beta = 132.13 \pm 0.04^{\circ}$	
Space group	$P2_1/c$	$P2_{1}/c$	
Molecules/unit cell	4	4	
Density observed, g/cm ³	1.19	1.17	
Density calculated, g/cm ³	1.208	1.179	
Number of reflec- tions	1263	1215	
Nonzero reflections	1136	1119	

crystals were cut to a suitable size and surveyed on a precession camera. Both the survey and data collection were performed at ambient room temperature. Compound 13 was observed to slowly sublime at room temperature and was therefore enclosed in a 0.3-mm capillary tube. Compound 5 was stable at room

⁽²⁴⁾ Prepared from a pure sample of 10b with ethereal diazomethane.

temperature. Final cell dimensions were obtained on the Syntex P₁ diffractometer using a least-squares fit of six high angle (2 θ >55°) axial reflections (the three positive and the three negative directions). Both surveys are summarized in Table I. A 1-Å data set (maximum $2\theta = 100.0^{\circ}$) was collected on a Syntex P₁ diffractometer using copper radiation which had been passed through a graphite monochromator. A θ -2 θ scan technique was employed, the scan rate was 2°/min, and the background was counted for half the scan time at each end of the scan. A single check reflection was monitored every 30 reflections; this reflection indicated no crystal damage and was reproducible well within counting statistics.

The diffractometer output was processed using subprograms of the CRYM crystallographic computer system.²⁵ The processing included corrections for background and for Lorentz and polarization effects. The effect of the graphite monochromator was included in these corrections. No correction for absorption was made. The data processing also included calculation of the F^2 value and its standard deviation for each reflection (reflections with observed intensities less than or equal to zero were assigned a value of zero intensity). The standard deviations were assigned on the basis of the following equation

$$\sigma^{2}(I) = S + (B_{1} + B_{2})\alpha^{2} + (dS)^{2}$$

where S is the scan count, B_1 and B_2 are the background counts, d is an empirical constant equal to 0.02, and $\alpha = n/2mt$ where n = scan range, m = scanning speed, and t = time for background count in seconds. Finally, the data set was placed on an absolute scale by means of Wilson statistics.²⁶

Determination of Structure and Refinement.—A trial set of phases was obtained through the reiterative application of Sayre's equation.^{27,28} In both compounds, a trial structure was obtained with the first E map and refined smoothly to an acceptable R index. The refinement procedure included a full matrix least-squares treatment of coordinates, anisotropic temperature factors, and scale factor. Hydrogen positions were located by difference Fourier techniques and were added to the structure factor calculation in the latter stages of refinement. Hydrogen parameters were not refined. The quantity minimized by the least-squares procedure is $\Sigma w (F_o^2 - F_o^2)^2$, where $w = 1/\sigma^2 (F_o^2)$.

(25) D. J. Duchamp, Annual Meeting of the American Association of Crystallographers, Bozeman, Mont., 1964, Abstracts, Paper B-14, p 29.
(26) A. J. C. Wilson, Nature, 150, 152 (1942).

(27) D. Savre, Acta Crystallogr., 5, 60 (1952).

(28) The phasing process was facilitated by the use of a computer program written by R. E. Long, U.C.L.A. Of the 16 possible solutions generated by the program, in each case, the solution which converged in the fewest cycles and had the highest internal consistency index proved to be the correct solution. Compound **5** converged in 7 cycles and has a consistency index of 0.74805. Compound **13** converged in 7 cycles and had a consistency index of 0.83394.

TABLE II

DATA	FIT	AND	DEVIATIONS	
			_	

Compound	5	13
Final R index $(\Sigma F_o - F_c / \Sigma F_o)$	0.064	0.091
Std deviations ^a of coordinates, Å		
C	0.005	0,008
0	0.003	0.006
Uncertainties in C, O bond lengths, Å	0.007	0.01
Uncertainties in C, O bond angles, deg	0.4	0.8
Range in C-C single bond lengths,	1.51 - 1.56	1.52 - 1.56

Å ^a Standard deviations in the coordinates were derived from the residuals and the diagonalized elements of the inverse matrix of the final least-squares cycle.

The final R values are given in Table II. A final difference Fourier revealed no missing or misplaced atoms.

Results of the X-Ray Analyses.—The structures obtained in this were stereographically plotted (Figures 1 and 2) using the ORTEP computer program of Johnson.²⁹ An estimate of errors in positional parameters, bond lengths, and bond angles is summarized in Table II. The data fit for compound 5 is slightly superior to that of compound 13. This is to be expected, since data for compound 13 was collected on a crystal enclosed in a capillary. Bond distances and angles for both compounds were as expected. Therefore, due to limitations in space they will not be reported here. Full crystallographic data may be obtained by writing the author.³⁰

Registry No.—3, 32298-47-8; 4, 32298-48-9; 4 semicarbazone, 32298-49-0; 4 DNPH, 32298-50-3; 5, 32298-51-4; 6, 5465-18-9; 7, 32298-53-6; 8a, 32298-54-7; 10a, 32298-55-8; 10b, 32367-55-8; 12 (one isomer), 32298-56-9; 12 (second isomer), 32298-57-0; 13, 32298-58-1.

Acknowledgment.—It is a pleasure to thank Professor G. Büchi for his interest in and his stimulating discussions of this work. It was he who first brought structures 3 and 4 to our attention.

 (29) C. K. Johnson, ORTEP, ORNL-3794, Oak Ridge National Laboratories, Oak Ridge, Tenn.
 (30) J. Bordner.