Barbaralone was prepared by Michler ketone sensitized photoisomerization of bicyclo[4.2.1]nona-2,4,7-trien-9-one in benzene solution.[12]

9-Methylenebarbaralane, bp 71–73° (5 mm), was prepared by reduction of barbaralone with methylenetriphenylphosphorane in ether solution[10] and purified for the present study by preparative vpc isolation from a 5 ft × 0.25 in. column packed with 5% SE-30 on Chromosorb G.

(12) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 2155 (1972). See also T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *ibid.*, **94**, 5366 (1972); K. Kurabayashi, and T. Mukai, *Tetrahedron Lett.*, 1049 (1972).

Registry No.—**1** (X = CO), 6006-24-2; **1** (X = CCH_2), 37816-60-7.

Acknowledgments.—The authors are grateful for support of this work by the National Science Foundation (Grants GP-22942, GP-34259X, and GP-8678) and by the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-AC4).

Synthesis of 1-(2-Acetoxyethyl)bicyclo[4.3.0]non-5-en-4-one[1]

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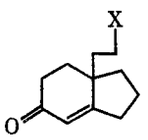
Received October 11, 1972

The synthesis of 1-(2-acetoxyethyl)bicyclo[4.3.0]non-5-en-4-one (**1a**), an intermediate in one synthetic route to the analogous enone bromide **1b** which was desired for intramolecular alkylation studies, is discussed. A novel method for determining the structure of the Michael adduct from ethyl 2-oxocyclopentaneacetate (**2**) and methyl vinyl ketone, using ^{13}C nmr spectroscopy, is described. An efficient method for ether fission of 9-oxatricyclo[4.3.3.0]dodecan-3-one (**8**) to yield the immediate precursor of **1a** is reported.

We are presently studying the intramolecular alkylation of 1-(2-bromoethyl)bicyclo[4.3.0]non-5-en-4-one (**1b**) and related compounds. The acetoxy analog **1a**,



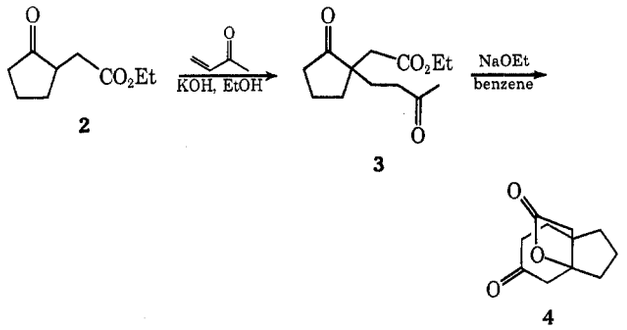
1a, X = OAc
b, X = Br

whose synthesis we report here, is an intermediate in one synthetic route to **1b**. Another synthetic route to **1b** and related compounds and a detailed analysis of their intramolecular alkylations will be reported shortly.[2]

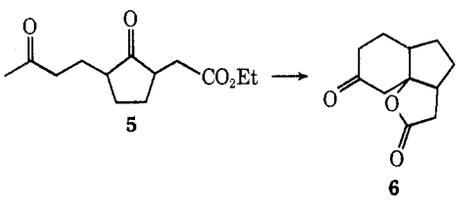
This synthesis began with ethyl 2-oxocyclopentaneacetate (**2**), which was condensed with methyl vinyl ketone to yield adduct **3**. Subsequent base-catalyzed condensation and lactonation gave keto lactone **4**,[3,4] as shown in Scheme I.

Although the structural assignments for compounds **3** and **4** have been made by Shchegolev and Kucherov,[3] and it is known that the Michael acceptor is usually introduced at the more highly substituted position of unsymmetrical ketones,[5] the possibility that **3** was

SCHEME I



actually the α,α'-substituted cyclopentanone **5** could not be eliminated. Spectral evidence did not distinguish between **3** and **5** (or **4** and **6**); the use of an



nmr shift reagent was not useful for differentiation (see Experimental Section). Moreover, all subsequent reactions performed on **4** by us (*vide infra*) and Shchegolev and Kucherov[3] yield products whose spectral data are compatible with isomeric materials, originating from **5**. It seemed important, therefore, to unequivocally establish the structure of the Michael adduct.

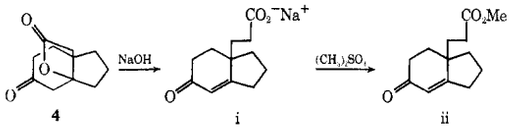
Since the chemical shift of a ^{13}C nucleus is increased in a downfield direction with increasing alkyl substitution,[6] we examined the proton-decoupled ^{13}C nmr spectrum of adduct **3**. Chemical shift assignments were made by comparing this spectrum with ^{13}C nmr spectra of model systems **2** and cyclopentanone.[7] The chem-

(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

(2) (a) T. E. Jackson and R. L. Cargill, to be published; (b) presented in part by T. E. Jackson at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, ORGN 139.

(3) A. A. Shchegolev and V. F. Kucherov, *Izv. Akad. Nauk SSSR Ser. Khim.*, No. 7, 1456 (1969).

(4) Although the authors[3] claim that lactone **4** could be opened to enone carboxylate i and methylated to enone ester ii, which could serve as an inter-

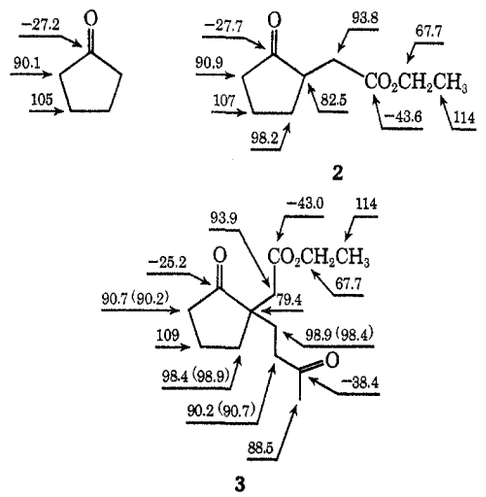


mediate in the synthesis of **1a**, they stated that ii was not stable and we chose not to pursue this route.

(5) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972.

(6) J. Mason, *J. Chem. Soc. A*, 1038 (1971).

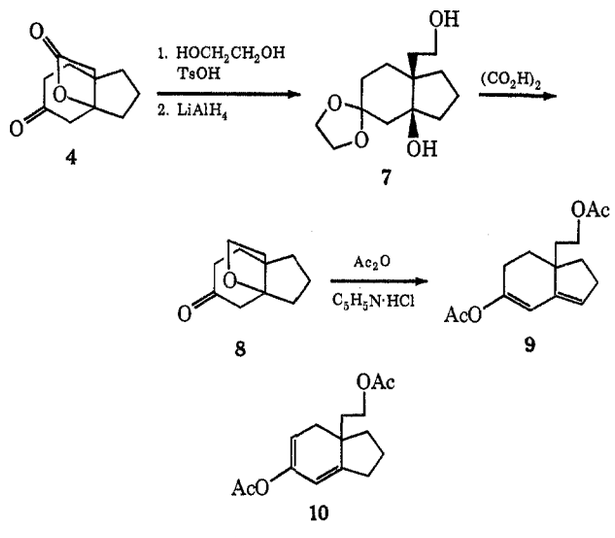
(7) These proton-decoupled nmr spectra were run in benzene-d_6 with a deuterium lock on a Varian XL-100 spectrometer.



ical shift values in the diagram represent parts per million from benzene-d_6. By examining the chemical shift values for the α- and α'-cyclopentanone positions in the three compounds, we see that the values for **3** (90.7 and 79.4 ppm) are clearly consistent with only the α,α-disubstituted cyclopentanone. Structure **5** would be expected to display two signals in an intermediate range (*ca.* 82.5 ppm) for its α- and α'-cyclopentanone carbons. This novel method for structural determination should prove to be extremely useful.

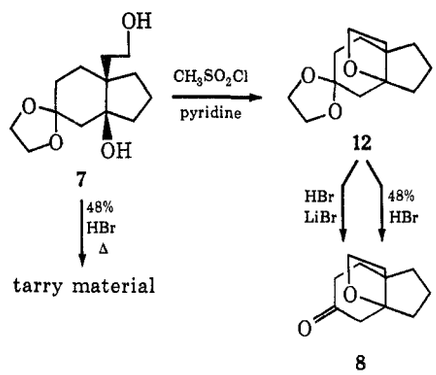
Preparation of enone acetate **1a** was accomplished from diacetate **9**, whose synthesis is outlined in Scheme II. The ethylene ketal of keto lactone **4** was prepared

SCHEME II



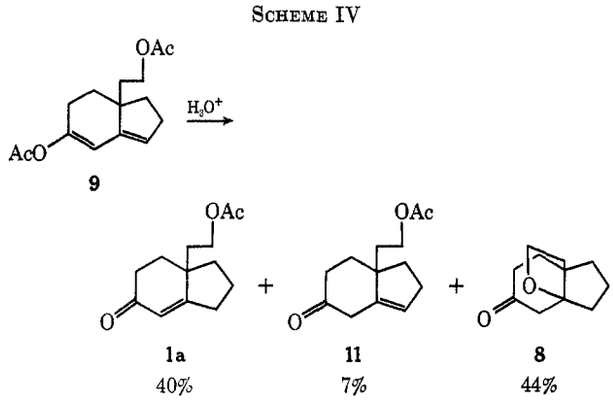
and reduced with $LiAlH_4$ to ketal diol **7**. It was not possible, in our hands (using a variety of mild acidic, conditions), to remove the ketal block from **7** without cyclizing the diol to the tetrahydrofuran, nor were we able to convert the primary alcohol functionality in **7** into a good leaving group, because of facile ether formation. Thus, treatment of ketal diol **7** under conditions which would remove the ketal group produced keto ether **8** (Scheme III). These results are not surprising in view of literature reports of the instability of a 1,4 diol monomesylate[8] with respect to the tetrahydrofuran, and of a 1,4 diol[9] which cyclizes under very mild, acidic conditions. Treatment of keto ether **8** with acetic anhydride and pyridine hydrochloride yielded diacetate **9**, which was distinguished from the homoannular diene isomer **10** by its uv spectrum (λ_{max} 242 nm). This experimental procedure is similar to that employed by Ireland and Mander[10] to open a tetrahydrofuran to a 1-chloro-4-acetoxybutane. This efficient (93%) method of ether cleavage to a useful intermediate is significant, since other standard methods of ether cleavage failed.

SCHEME III



Diacetate **9** was treated with aqueous acid to produce a mixture of enone acetate **1a** (40%), the β,γ-unsaturated enone acetate **11** (7%), and keto ether **8** (44%) (Scheme IV). Hydrolysis was monitored by ir

SCHEME IV



and discontinued when the enol acetate carbonyl band at 1760 cm^{-1} had disappeared. Enone acetate **1a** was easily separated from the mixture by glpc; other separation techniques would presumably work as well. It should be pointed out that this preparation of **1a** is very efficient, since coproducts **11** and **8** can be recycled to produce **1a**.

An attempt to monomesylate ketal diol **7** with methanesulfonyl chloride and pyridine resulted in the production of ketal ether **12** (Scheme III), whose ether linkage could not be opened with ether 48% HBr or a mixture of HBr–LiBr. Vigorous treatment of ketal diol **7** with HBr led to tarry material.

An alternate route to enone acetate **1a** involved the successful monoacetylation of ketal diol **7**, followed by

(8) H. W. Whitlock, Jr., *J. Amer. Chem. Soc.*, **84**, 3412 (1962).

(9) D. Becker and J. Kalo, *Tetrahedron Lett.*, 3725 (1971).

(10) R. E. Ireland and L. N. Mander, *J. Org. Chem.*, **34**, 142 (1969).

hydrolysis of the ethylene ketal with aqueous acid and dehydration of the resulting ketol with *p*-toluenesulfonic acid.

Experimental Section[11]

Ethyl 2-Oxocyclopentaneacetate (2).—The potassium salt of 2-carbethoxycyclopentanone was prepared and alkylated with ethyl bromoacetate in dimethyl sulfoxide.[12] Saponification and decarboxylation[13] yielded 2-oxocyclopentaneacetic acid, which was esterified[14] to yield **2** (33% overall). Alternate synthetic routes to **2** are available.[15]

9-Oxa[4.3.3.0]dodecane-3,8-dione (4).—Keto lactone **4** was prepared in two steps from **2** using the method of Shchegolev and Kucherov.[3] A 25.5-g (150 mmol) quantity of **2** and 12.1 g (172 mmol) of methyl vinyl ketone were condensed to give 19.8 g (55%) of ethyl 2-oxo-1-(3-oxobutyl)cyclopentaneacetate (**3**): bp 131° (0.45 mm); n^{28}D 1.4687 [lit.[3] bp 145–150° (2.5 mm), n^{20}D 1.4748]; ir (CCl_4) 1720 (C=O) and 1735 cm^{-1} (ester C=O); nmr (CCl_4) δ 4.00 (q, J = 7.2 Hz, 2, OCH_2CH_3), 2.55–1.35 (m, 13, all protons except OCH_2CH_3, with $COCH_3$ s at 2.04), 1.22 (t, J = 7.2 Hz, 3, OCH_2CH_3); nmr [CCl_4 + Eu(DPM)$_3$] δ 4.38 (t, J 7.2 Hz, 2, OCH_2CH_3), 3.45–3.00 (m, 6, $COCH_2$ groups), 2.90–1.97 (m, 9, CH_2 groups not adjacent to C=O and $COCH_3$ s at 2.57), 1.36 (t, J = 7.2 Hz, 3, OCH_2CH_3).

A 13.3-g (55.2 mmol) quantity of **3** was treated with excess sodium methoxide to yield 4.76 g (44%) of keto lactone **4**: mp 99–102° (lit.[3] mp 100–102°); ir (CCl_4) 1720 (C=O) and 1765 cm^{-1} (ester C=O); nmr ($CDCl_3$) δ 2.77 (m, 2, $COCH_2$), 2.68 (s, 2, CO_2CH_2), 2.56–1.50 (m, 10, remaining protons).

1-Hydroxy-6-(2-hydroxyethyl)bicyclo[4.3.0]nonan-3-one Ethylene Ketal (7).—A 4.65-g (23.9 mmol) quantity of keto lactone **4** was heated at reflux in benzene (175 ml) with 2.98 g (48.0 mmol) of ethylene glycol (Baker) and 0.2 g of *p*-toluenesulfonic acid monohydrate (Matheson, $TsOH \cdot H_2O$). The reaction mixture was cooled, washed with 10% K_2CO_3 (20 ml), dried ($MgSO_4$), and concentrated to leave 5.70 g (theory) of ketal lactone: ir (CCl_4) 1775 cm^{-1} (lactone C=O); nmr ($CDCl_3$) δ 4.2–3.0 (m, 4, OCH_2CH_2O), 3.0–1.5 (m, 14, remaining protons).

The 5.70-g quantity of the ketal lactone was added, in ether (75 ml) over a 30-min period, to a slurry of 2.28 g (60.0 mmol) of $LiAlH_4$ (Foote) in ether (75 ml). After 16 hr, excess hydride was destroyed by the slow addition of ethyl acetate. The reaction mixture was diluted with 15% $(NH_4)_2SO_4$ (100 ml) and filtered (Celite), and the layers were separated. The aqueous phase was extracted with ether (3 × 40 ml) and the combined ether phases were dried ($MgSO_4$) and concentrated to leave 5.49 g (96% from keto lactone **4**) of ketal diol **7**: ir ($CHCl_3$) 3700–3050 (OH) and 3580 cm^{-1} (OH); nmr ($CDCl_3$) δ 4.12–3.36 (m, 8, OCH_2CH_2O, CH_2OH, and OH), 2.10–1.05 (m, 14, remaining protons).

9-Oxatricyclo[4.3.3.0]dodecan-3-one (8).—A solution of 1.48 g (6.11 mmol) of ketal diol **7** and 1.5 g of oxalic acid (Baker) in methanol (22 ml) and water (16 ml) was heated at reflux for 1 hr. Dilution of the cool reaction mixture with 10% K_2CO_3 (50 ml) and ether extraction (4 × 30 ml) followed by drying ($MgSO_4$) and concentration of the ether extracts left 0.979 g (89%) of pure keto ether **8**, which displayed a single peak on glpc (3% SE-30, 8 ft × 0.125 in., 150°, 30 cc/min of He): bp 89° (0.40 mm); n^{28}D 1.4945; uv[16] (95% EtOH) 239 nm (ϵ 75) and 288 (26); ir (CCl_4) 1725 cm^{-1} (C=O); nmr (CCl_4) δ 3.92–3.56 (overlapping triplets, 2, OCH_2), 2.54 (m, 2, $COCH_2$), 2.42–1.23 (m, 12, remaining protons); nmr [CCl_4 + Eu(DPM)$_3$] δ 4.72 (t, J = 7.2 Hz, 2, OCH_2), 4.36–3.65 [m, 2, $COCH_2$ (4 position)], 3.47 [t, J = 7.2 Hz, 2, $COCH_2$ (2 position)], 2.72–1.83 (m, 10, remaining protons); mass spectrum (70 eV) m/e 180 (molecular ion).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.13; H, 8.81.

4-Acetoxy-1-(2-acetoxyethyl)bicyclo[4.3.0]nona-4,6-diene (9).—A solution of 0.340 g (1.88 mmol) of keto ether **8** and pyridine hydrochloride (1 g) in acetic anhydride (20 ml) was heated at reflux for 5.5 hr, poured onto crushed ice (50 g), and extracted with 1:1 pentane–ether (4 × 30 ml). The combined ether extracts were washed with 10% KOH until the washings were basic, dried (Na_2SO_4), and concentrated to leave 0.461 g (93%) of pure diacetate **9**, which displayed a single peak on glpc (3% SE-30, 8 ft × 0.125 in., 175°, 30 cc/min of He): uv max (95% EtOH) 245 nm (ϵ 11,000); ir (CCl_4) 1760 (C=O) and 1740 cm^{-1} (C=O); nmr (CCl_4) δ 5.87 (m, 1, vinyl), 5.40 (m, 1, vinyl), 4.05 (t, J = 7 Hz, 2, OCH_2), 2.7–1.2 (m, 16, remaining protons, with $COCH_3$ singlets at 2.06 and 1.96, and OCH_2CH_2 t, J = 7 Hz, at 1.70); mass spectrum m/e (rel intensity) 264 (3), 43 (100). Diacetate **9** appeared to decompose slowly upon standing, and was therefore not submitted for analysis.

1-(2-Acetoxyethyl)bicyclo[4.3.0]non-5-en-4-one (1a).—A solution of 0.659 g (2.49 mmol) of diacetate **9** in methanol (10 ml), water (10 ml), and concentrated HCl (1 ml) was stirred for 2.2 hr. Disappearance of the acetate C=O band at 1760 cm^{-1} was monitored by ir. The reaction solution was diluted with 10% K_2CO_3 (30 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined extracts were dried ($MgSO_4$) and concentrated to afford 0.518 g of material which by glpc analysis (20% SE-30, 5 ft × 0.25 in., 175°, 85 cc/min of He) was 40% enone acetate **1a**, 7% β,γ-unsaturated isomer **11**, and 44% keto ether **8**. Enone acetate **1a** was collected from glpc for spectral analysis: uv max (95% EtOH) 242 nm (ϵ 11,200); ir (CCl_4) 3020 (vinyl CH), 1740 (ester C=O), and 1670 cm^{-1} (C=O); nmr (CCl_4) δ 5.64 (m, 1, vinyl), 4.07 (t, J = 7.2 Hz, 2, CH_2OAc), 2.8–1.2 (m, 15, remaining protons, with $COCH_3$ s at 1.98); mass spectrum (70 eV) m/e (rel intensity) 222 (19), 180 (5), 162 (16), 134 (100), and 43 (96). All spectral data for **1a** compared favorably with that for enone bromide **1b**.[2] Since enone acetate **1a** slowly converted, upon standing, to keto ether **8**, a satisfactory analysis was not obtained.

A sample of β,γ-unsaturated enone acetate **11** was also collected for spectral analysis: ir (CCl_4) 1755 (ester C=O) and 1715 cm^{-1} (C=O); nmr (CCl_4) δ 5.29 (m, 1, vinyl), 3.63 (t, J = 7.2 Hz, 2, CH_2OAc), 2.7–1.3 (m, remaining protons, with $COCH_3$ s at 2.05); mass spectrum (70 eV) m/e (rel intensity) 222 (2), 180 (18), 138 (100), and 43 (29).

9-Oxatricyclo[4.3.3.0]dodecan-3-one Ethylene Ketal (12).—A 0.907-g (3.74 mmol) quantity of ketal diol **7** was stirred with 0.593 g (5.18 mmol) of methanesulfonyl chloride (Matheson) and pyridine (4 ml) for 2 hr under an inert atmosphere. The reaction mixture was cooled, diluted with a cold mixture of water (5 ml) and pyridine (10 ml), and extracted with ether (3 × 30 ml). The combined extracts were dried ($MgSO_4$) and concentrated to leave 0.853 g (theory) of ketal ether **12**, which displayed a single peak on glpc (3% SE-30, 8 ft × 0.125 in., 170°, 30 cc/min of He): ir (CCl_4) showed no C=O; nmr ($CDCl_3$) δ 4.45–3.25 (m, 6, OCH_2CH_2O and CH_2OH), 3.02 (d, J = 6 Hz, 1, CH_2OH), 2.5–1.2 (m, 15, remaining protons).

A solution of 0.711 g (3.17 mmol) of ketal ether **12** in methanol (5 ml), water (5 ml), and concentrated HCl (0.2 ml) was stirred for 45 min, diluted with water (20 ml), and extracted with ether (3 × 25 ml). The combined extracts were dried ($MgSO_4$) and concentrated to leave 0.554 g (98.5%) of keto ether **8**.

Attempted Cleavage of Ketal Ether 12 with HBr.—A 0.305-g (1.36 mmol) quantity of ketal ether **12** was stirred with 6 ml of 48% HBr (Baker) for 1 hr, diluted with water (25 ml), and extracted with ether (3 × 25 ml). The extracts were dried (K_2CO_3) and concentrated to leave 0.177 g (72%) of keto ether **8**. When ketal ether **12** was treated in a similar manner with 48% HBr and an equal volume of saturated LiBr, work-up afforded keto ether **8** quantitatively. Treatment of ketal diol **7** with 48% HBr at reflux for 2 hr afforded tarry materials.

Alternate Route to Enone Acetate 1a.—A 0.291-g (1.20 mmol) quantity of ketal diol **7** was stirred with acetic anhydride (2 ml) for 3 hr, diluted with cold 10% K_2CO_3 (50 ml), and extracted with ether (2 × 25 ml). The extracts were dried ($MgSO_4$) and concentrated to leave 0.201 g (59%) of 6-(2-acetoxyethyl)-1-hy-

(11) All boiling points and melting points are uncorrected. Microanalyses were performed by Bernhardt Microanalytisches Laboratorium, Elbach uber Engelskirchen, West Germany. Infrared spectra were recorded using a Perkin-Elmer Model 257 grating spectrophotometer. All nmr spectra were determined using tetramethylsilane as an internal standard, with a Varian A-60 spectrometer. Ultraviolet spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer. Analytical gas–liquid partition chromatograms were determined using a Varian Aerograph 1200 flame ionization chromatograph, and preparative glpc separations were conducted using a Varian Aerograph 90-P-3 chromatograph.

(12) D. M. Pond and R. L. Cargill, *J. Org. Chem.*, **32**, 4064 (1967).

(13) R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934).

(14) R. Granger and P. F. G. Nau, *Bull. Soc. Chim. Fr.*, 1807 (1959).

(15) A. W. Noltes and F. Kogl, *Recl. Trav. Chim. Pays-Bas*, **80**, 1334 (1961).

(16) When 0.2 ml of 3 *N* NaOMe was added to the 0.0099 *M* uv sample and the spectrum was rerun at timed intervals, the absorption band at 239 nm steadily intensified. The addition of 0.1 ml of concentrated HCl to another sample had little effect on the spectrum.

droxybicyclo[4.3.0]nonan-3-one ethylene ketal: ir (CCl_4) 3600–3400 (OH) and 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.25–3.45 (m, 6, OCH_2CH_2O and CH_2OAc), 3.25 (broad s, 1, OH), 2.5–1.5 (m, 14, remaining protons).

A solution of 0.111 g (0.390 mmol) of the above acetate in methanol (10 ml), water (10 ml), and concentrated HCl (1 ml) was stirred for 30 min and worked up as above to yield 0.0771 g (82.3%) of 6-(2-acetoxyethyl)-1-hydroxybicyclo[4.3.0]nonan-3-one: ir (CCl_4) 3600–3300 (OH), 1735 (ester C=O), and 1720 cm^{-1} (C=O).

A solution of 0.0771 g (0.321 mmol) of the ketol acetate and 50 mg of $TsOH \cdot H_2O$ in benzene (60 ml) was heated at reflux for 2 hr with azeotropic removal of water. The benzene solution was cooled, washed with 10% K_2CO_3 (30 ml), dried ($MgSO_4$), and concentrated to leave 0.0713 g (theory) of crude (80% pure by glpc) enone acetate **1a**.

Registry No.—**1a**, 38312-34-4; **2**, 20826-94-2; **3**, 24054-04-4; **4**, 24109-44-2; **7**, 38312-38-8; **8**, 38312-39-9; **9**, 38312-40-2; **11**, 38312-41-3; **12**, 38312-42-4; 9-oxatricyclo[4.3.3.0]dodecane-3,8-dione ethylene ketal, 38312-43-5; 6-(2-acetoxyethyl)-1-hydroxybicyclo[4.3.0]non-3-one ethylene ketal, 38312-44-6; 6-(2-acetoxyethyl)-1-hydroxybicyclo[4.3.0]nonan-3-one, 38312-45-7.

Acknowledgment.—The authors are grateful to Dr. P. D. Ellis for determining the ^{13}C nmr spectra.

Synthesis and Acid-Catalyzed Rearrangements of Tricyclo[4.3.2.0]undecanones[1]

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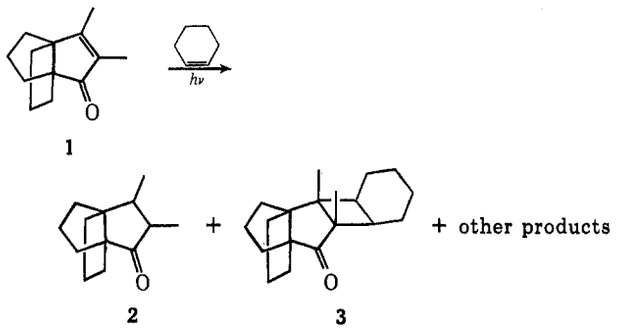
Received October 12, 1972

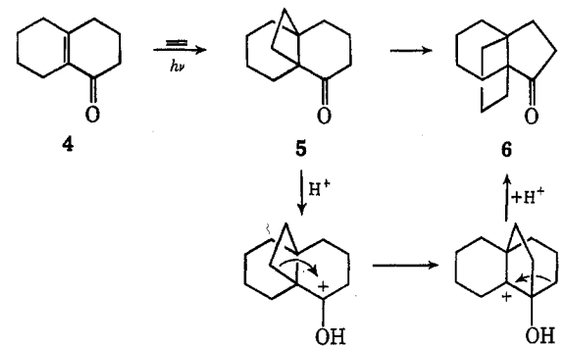
A novel synthesis of 3,4-dimethyltricyclo[3.3.3.0]undecan-2-one (**2**) from bicyclo[4.3.0]non-1(6)-en-2-one (**7**) is reported. A mechanistic interpretation for the different ratio of the three cycloadducts (**8a–c**) obtained from irradiation of **4** with *cis*- and *trans*-2-butene is presented. Cycloadducts **8a** and **8b** were found to undergo rearrangement to **2** at different rates. A synthesis of tricyclo[4.3.3.0]dodecan-7-one (**6**) is also reported.

In our recent investigation of cycloaddition reactions of crowded enones and olefins,[2] we irradiated 3,4-dimethyltricyclo[3.3.3.0]undec-3-en-2-one (**1**) in cyclohexene. In addition to the [2 + 2] cycloadduct **3** (and other products isomeric with **3**) was formed a product suspected to be 3,4-dimethyltricyclo[3.3.3.0]undecan-2-one (**2**), derived from photoreduction. In order to confirm this suspicion we chose to synthesize **2** independently. Although the saturated ketone **2** could undoubtedly be generated from enone **1** by reduction with lithium in ammonia,[3] we chose to use a less obvious approach which was suggested by some other work which will be described shortly. This decision led not only to a novel synthesis of **2**, but also yielded some mechanistic information on enone photoannulation (an area of study where information is sparse[4]) as well as interesting relative rate differences of Wagner–Meerwein shifts in isomeric systems.



The earlier results which suggested this alternate approach to **2** are shown in Scheme I. Although bicyclo[4.3.0]non-1(6)-en-2-one (**7**) undergoes photocycloaddition with 1,2-dichloroethylene readily,[5] preliminary results from our laboratory indicated that cycloaddition reactions of bicyclo[4.4.0]dec-1(6)-en-2-one (**4**) with olefins (other than ethylene) were not successful.[6] Enone **4**, however, does undergo sluggish photoannulation with ethylene to yield tricyclo[4.4.2.0]-dodecan-2-one (**5**). Ketone **5**, when treated with *p*-toluenesulfonic acid (TsOH) in benzene at reflux, undergoes two Wagner–Meerwein shifts to yield tricyclo[4.3.3.0]dodecan-7-one (**6**), quantitatively.

SCHEME I



The efficiency of the acid-catalyzed rearrangement of **5** to **6** suggested that the photoannulation of enone **7** with 2-butene, followed by acid-catalyzed rearrangement of the resulting isomers **8**, should comprise a good synthesis of ketone **2** (Scheme II). Execution of this reaction sequence (using *cis*-2-butene) resulted in the production of ketone **2** from a mixture of isomers **8**, in an overall yield of 82%. This product was identical with the photoreduced product obtained from the irradiation of enone **1** in cyclohexene. The trans relationship of the methyl groups in **2** was ascertained

(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

(2) R. L. Cargill, N. P. Peet, D. M. Pond, A. B. Sears, W. A. Bundy, and M. G. Rosenblum, to be published.

(3) (a) T. G. Halsall, D. W. Theobald, and K. B. Walshaw, *J. Chem. Soc.*, 1029 (1964); (b) H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 360 (1963).

(4) (a) R. M. Bowman, C. Calvo, J. J. McCullough, P. W. Rasmussen, and F. F. Snyder, *J. Org. Chem.*, **37**, 2084 (1972); (b) P. de Mayo, *Accounts Chem. Res.*, **4**, 41 (1971).

(5) R. L. Cargill and J. W. Crawford, *J. Org. Chem.*, **35**, 356 (1970).

(6) One explanation for this difference holds that the excited state of **4** is not as long-lived as the excited state of **7**, owing to rigidity differences, which would make decay of excited **4** to ground state a more favorable process than decay of **7** to ground state.