components in a ratio of 74:26, the latter having the same retention time as ketol **14**.

Photoproduct 17.—The compound was prepared by carrying out the irradiation in benzene as described in Table I, runs 1 or 5. Preparative glc collection of this last peak gave a pure sample of **17**: ir (CCl_4) 1762 (s), 1748 (s), 1234 cm^{-1} (s); nmr (CCl_4) τ 7.4–8.5 (13 H, m), 7.95 (3 H, s), 5.19 (1 H, d with additional fine splitting, J = 9 Hz), 4.57 (1 H, broad s); mass spectrum m/e (rel intensity) 222 (4, M^+), 120, (98), 80 (90), 43 (100).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.22; H, 8.37.

Degradation of 17.—To a solution of 130 mg (0.59 mmol) of **17** in 20 ml of AcOH was added 20 mg of 10% Pd on charcoal and the suspension was stirred under 1 atm of hydrogen until 1 equiv had been consumed. The catalyst was filtered, the solvent was removed, and the residue was examined by nmr, which showed that the resonance at τ 4.57 was no longer present.

This sample of dihydro **17** was dissolved in 15 ml of AcOH and heated to reflux for 24 hr with 4 g of Zn powder. The cooled reaction mixture was filtered, most of the AcOH was removed under reduced pressure, and 150 ml of Et_2O was added to this concentrate. The organic phase was extracted with saturated with Na_2CO_3 solution (three times) and dried. Removal of the solvent gave 80 mg (82%) of a brown oil which showed only one peak on glc analysis. Preparative glc yielded a pure sample of **18**: ir (CCl_4) 1743 (s), 1160 cm^{-1} (m); nmr (CCl_4) τ 7.5–9.0 (complex multiplet of all protons); mass spectrum m/e (rel intensity) 166 (5, M^+), 83 (80), 55 (56), 41 (100).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.45; H, 10.91. Found: C, 79.29; H, 10.77.

Preparation of 3-(Cyclopentylmethyl)cyclopentanone (18).—A solution of 3.75 g (23 mmol) of bromomethylcyclopentane[18] in 30 ml of dry tetrahydrofuran (THF) was added over 30 min to 0.486 g (0.020 g-atoms) of Mg turnings and the reaction was refluxed for an additional 30 min. The Grignard solution was added to a stirred suspension of 0.144 g (1 mmol) of freshly prepared CuBr[19,20] in 30 ml dry THF at 0° to give a yellowish-brown solution. A solution of 0.82 g (10 mmol) of 2-cyclopentenone in 30 ml of dry THF was added dropwise over 30 min to the Grignard–CuBr solution at 0°. The reaction mixture was allowed to warm to room temperature over 30 min then heated to reflux. The cooled reaction mixture was poured into 50 ml of NH_4Cl solution, the aqueous phase was separated and extracted with Et_2O (two times), and the combined organic phase was washed with saturated brine (two times) and dried. Removal of the solvent yielded 2.4 g of an oil which upon glc analysis showed two major components, the minor (21%) and more volatile compound being the coupling product, 1,2-dicyclopentylethane (mass spectrum m/e 166, M^+; ir indicated no carbonyl group), and the other being the desired ketone (68%). This residue was distilled to give 0.84 g (51%) of **18**, bp 93–96° (0.7 mm). The spectroscopic properties of this product were identical with those described above for the degradation product of **17**.

(18) E. E. Royals and A. H. Neal, *J. Org. Chem.*, **21**, 1448 (1956).

Registry No.—**3**, 28742-34-9; **8**, 1528-30-9; **9**, 39837-66-6; **10**, 39837-67-7; **11a**, 39837-68-8; **11b**, 39837-69-9; **11b** (tetradeuterio derivative), 39837-70-2; **12**, 39837-71-3; **13**, 39837-72-4; **14**, 39837-73-5; **15a**, 39837-74-6; **16**, 39837-75-7; **17**, 39837-76-8; **17** (dihydro derivative), 39837-77-9; **18**, 39837-78-0; 1,2-cyclopentanedione, 3008-40-0; ketene, 463-51-4; bromomethylcyclopentane, 3814-30-0; 2-cyclopentenone, 930-30-3.

(19) J. L. Hartwell, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 185.

(20) If the cuprous bromide is not freshly prepared the major product isolated from the reaction is 1,2-dicyclopentylethane, formed by coupling of the Grignard reagent.

The Reaction of Cyclopentanones with Methylsulfinyl Carbanion

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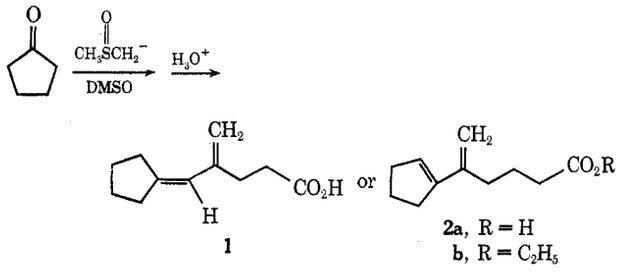
Methylsulfinyl carbanion reacts with cyclopentanone at ambient temperature to afford the unexpected δ-methylene-1-cyclopentene-1-pentanoic acid (**2a**) in good yield. This reaction appears limited to cyclopentanones, with only low yields isolated from 2- and 3-methylcyclopentanones. Mechanistic considerations and some reactions of the dienoic acid are discussed.

While investigating the reaction of methylsulfinyl carbanion with some enolizable ketones, we were surprised to observe that cyclopentanone does not react as does cyclohexanone. According to Corey and Chaykovsky,[1,2] the enolate anion and the β-hydroxy sulfoxide adduct are the major products from cyclohexanone and cycloheptanone. However, when cyclopentanone is added dropwise to dimsyl sodium in DMSO at 25°, the sodium salt of an 11-carbon dienoic acid was isolated from CH_2Cl_2–ether after a few hours. This observation prompted a study of the product structure and the reaction scope and mechanism.

Structure Proof.—Aqueous acidification of the isolated sodium salts yields (59% overall) a carboxylic acid as the sole organic product. The purified acid melts at 44.5–46.0°, analyzes for $C_{11}H_{16}O_2$, and shows a molecular ion of 180 mass units (31% relative abundance) and ions of 135 ($M\cdot^+ - CO_2H$, 4%) and 107 mass units ($M\cdot^+ - CH_2CH_2CO_2H$, 75%) in the mass spectrum. The uv spectrum has a single absorption at 237 nm (ε 16,300), suggestive of a trisubstituted, conjugated diene; ir peaks at 1580 and 1620 cm^{-1} are indicative of a conjugated diene; and the nmr spectrum has olefinic proton signals at 5.87 (s, 1, C=CH) and 4.98 ppm (s, 2, $C{=}CH_2$). The product reacts rapidly with maleic anhydride to form an adduct, mp 112.0–113.0°. The acid is converted to its ethyl ester with *N*,*N*′-carbonyldiimidazole and ethanol, and the ester is readily hydrogenated on 10% Pd/C in ethanol to an oil with a molecular ion of 212 mass units whose nmr spectrum shows a methyl signal at 0.90 ppm (broad singlet). From these data we considered structures **1** and **2a** for



1 **2a**, R = H; **b**, R = C_2H_5

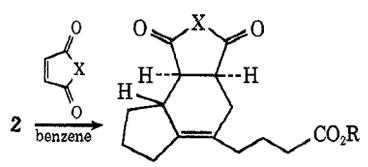
(1) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962).

(2) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

the initial acid product. The apparent lack of coupling for the methine signal at 5.87 ppm (line width at half height of 4 Hz) might favor **1**, whereas the ion of 107 mass units would favor **2** owing to predominance of allylic cleavage and stability of the allylic radical cation,[3] even though double-bond rearrangements are possible.

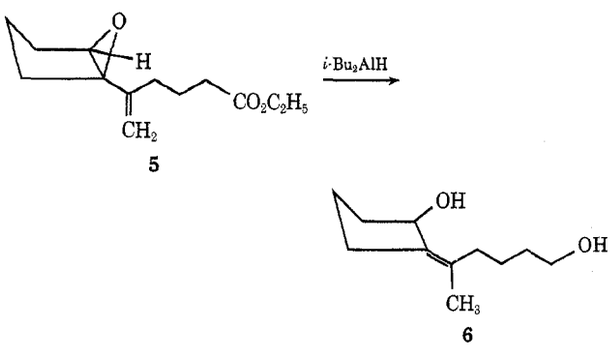
After oxidation of the acid by periodate–permanganate,[4] only glutaric acid was isolated (as diethyl ester) in 24% yield. This oxidative fragmentation establishes **2** as the correct structure, since **1** should yield succinic acid and cyclopentanone. In retrospect, the broadened singlet at 5.87 ppm can be rationalized for structure **2** by noting that similar vinyl protons from other cyclopentene systems are observed as broadened singlets.[5]

Additional support for structure **2** was obtained by examining some reactions of the dienoic acid. Adducts were obtained from maleic anhydride in fast, exothermic reactions, whereas the adduct from 4-cyclopentene-1,3-dione formed with a reaction half-life of 7.5 hr. None of these adducts show an olefinic proton signal in the nmr except **4**, which shows an exchangeable enol–olefinic proton at 4.88 ppm. The spiro adduct formed from structure **1** would contain an olefinic proton.



3a, X = O; R = H
3b, X = O; R = C_2H_5
4, X = CH_2; R = H

The ester **2b** reacted with *m*-chloroperbenzoic acid to give a single epoxide, **5**. The nmr spectrum of **5** contains a doublet at 5.00 ppm and one at 5.25 ppm for the methylene protons with geminal coupling constants $J \cong 1$ Hz, and a singlet for the epoxide OCH at 3.38 ppm with a line width at half height of 1.7 Hz. The lack of AB_2 coupling may be attributed to the probable boat conformation for epoxycyclopentanes,[6] which would minimize J_{cis}. Similar observations have been made for steroidal ring D epoxides.[7] The mass spectrum of **5** shows a molecular ion of 224 mass units and



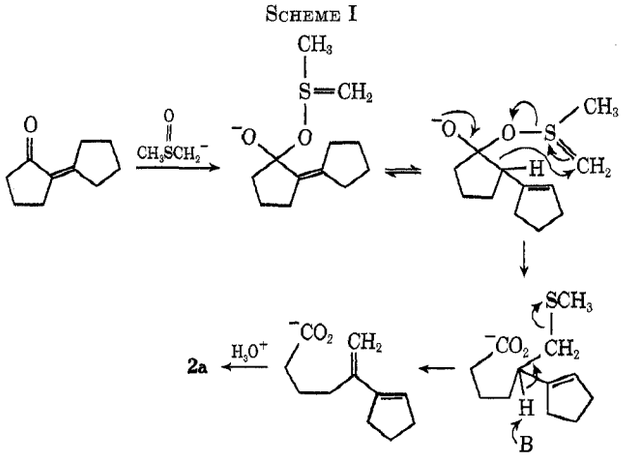
5 **6**

an allylic ion of 123 mass units ($M \cdot^+ - CH_2CH_2CO_2C_2H_5$, 67% relative abundance). Reduction of the epoxide **5** with $LiAlH_4$ yielded a mixture of two diols, both containing a C=CH_2 group according to their nmr spectra. However, a selective reduction of **5** with diisobutylaluminum hydride in benzene[8] afforded **6** in good yield. In addition to a broad one-proton singlet for the alcohol methine at 4.68 ppm, a methyl resonance near 1.80 ppm is observed in the nmr spectrum of **6**. These spectral properties of **6** support the epoxide being derived from **2** rather than **1**.

Reaction Mechanism.—The structure **2a** for the product of this unusual reaction suggests that the reaction may proceed *via* base-catalyzed dimerization of cyclopentanone followed by a one-carbon alkylation and oxidation. An aldol condensation of cyclopentanone to form 2-cyclopentylidenecyclopentanone could be expected in the basic DMSO medium, although self-condensation of enolate anions from cyclohexanone and cycloheptanone was not observed under similar conditions.[1,2] A sample of cyclopentylidenecyclopentanone was prepared[9] and added to 1 equiv of methylsulfinyl carbanion in DMSO. The same carboxylic acid product **2a** was isolated in 26% yield, which strongly implicates self-condensation as the initial step.

Although we presently have no direct mechanistic evidence for the subsequent alkylation and oxidation, we offer a feasible pathway in Scheme I. The oxidation

SCHEME I



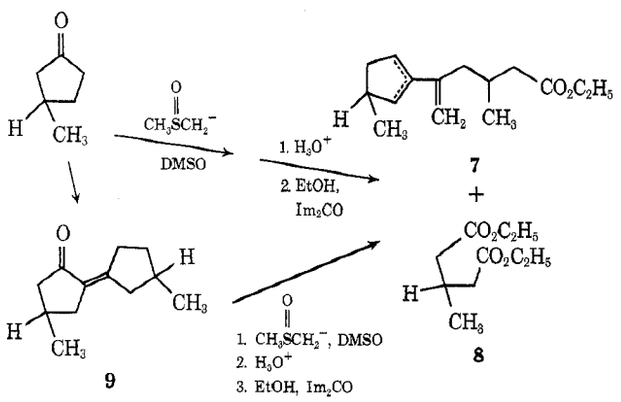
may be explained by nucleophilic attack at the carbonyl carbon by sulfoxide oxygen rather than attack by carbon as with larger cycloalkanones.[1] Gassman and coworkers suggest a similar mechanism for the oxidative cleavage of nonenolizable ketones.[10] The endocyclic double bond shift is reasonable with loss of the conjugated enone; then an allowed [2,3]-sigmatropic shift[11] would form the product following loss of methylmercaptan.[12] The nmr spectrum of the salts as isolated from the reaction mixture is essentially identical with the spectrum of purified acid **2a**; hence the carboxylate product is formed under the reaction conditions and aqueous acid merely converts the carboxylate anion to free acid.

(3) H. A. Bondarovich and S. K. Freeman, "Interpretive Spectroscopy," S. K. Freeman, Ed., Reinhold, New York, N. Y., 1965, p 193.
(4) R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710, 1714 (1955).
(5) A. D. Ketley and J. L. McClanahan, *J. Org. Chem.*, **30**, 940 (1965).
(6) J. J. McCullough, H. B. Henbest, R. J. Bishop, G. M. Glover, and L. E. Sutton, *J. Chem. Soc.*, 5496 (1965).
(7) K. Tori, T. Komeno, and T. Nakagawa, *J. Org. Chem.*, **29**, 1136 (1964).
(8) L. I. Zakharkin and I. M. Khorlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **65**, 862 (1965); *Chem. Abstr.*, **63**, 5574*f* (1965).
(9) H. S. French and L. Wiley, *J. Amer. Chem. Soc.*, **71**, 3702 (1949).
(10) P. G. Gassman, J. T. Lumb, and F. V. Zalar, *J. Amer. Chem. Soc.*, **89**, 946 (1967).
(11) J. E. Baldwin and C. N. Armstrong, *Chem. Commun.*, 631 (1970).
(12) T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *J. Amer. Chem. Soc.*, **85**, 2739 (1963).

Further support for these mechanistic considerations was obtained by adding cyclopentanone to deuterated dimsyl sodium, generated from DMSO-d_6 (99.5% isotope purity). The dienoic acid isolated was partially deuterated at the methylene group (40%) and the ring vinyl proton (75%). Although exchange undoubtedly occurs, we feel that deuteration of the ring vinyl proton is consistent with the endocyclic double bond rearrangement, and deuteration of the methylene group establishes that it derives from DMSO. Mass spectral analysis of the deuterated sample showed 3% containing no D, 5% one D, 18% two D's, 38% three D's, 24% four D's, and 12% five D's. The presence of material containing up to five deuterium atoms is consistent with Scheme I and the nmr data.

Reaction Scope.—When cyclobutanone was added to dimsyl sodium in DMSO at room temperature, a complex mixture of carboxylic acid salts was isolated with no evidence supporting a dienoic acid analogous to **2**. Substituted cyclopentanones were then investigated under the same reaction conditions. The least hindered ketone, 3-methylcyclopentanone, gave a mixture of acids in low yield (Scheme II). The oily acids

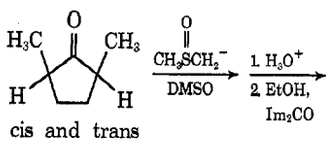
SCHEME II

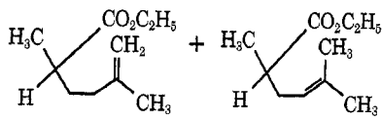


were esterified with *N,N'*-carbonyldiimidazole in EtOH, and the esters were fractionated at reduced pressure. A material analogous to **2b** was isolated in 5.3% yield, and vpc analysis shows **7** to be a mixture of two compounds which are isomeric with respect to the ring methyl and double bond; a molecular ion of 236 mass units was observed in the mass spectrum. Compound **7** reacted with maleic anhydride to give an adduct, which was purified by column chromatography. The adduct is analogous to **3a**, but its nmr spectrum indicates a mixture of methyl positional isomers. The self-condensation product **9** was also prepared[9] and added to dimsyl sodium; from this reaction **7** was obtained in low yield. Since the enone **9** is readily formed, the low yield of **7** compared to **2** may be due to steric hindrance by the 3-methyl group in the sigmatropic rearrangement.

A more volatile ester was also recovered from the reaction mixture in 2% yield and assigned structure **8**. 3-Methyl glutarate is presumably derived from 3-methylcyclopentanone *via* a semidione intermediate formed in the presence of some oxygen.[13]

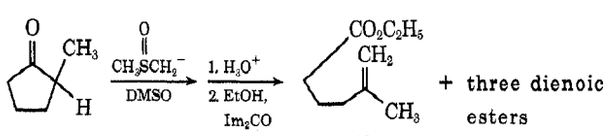
When 2,5-dimethylcyclopentanone was added to dimsyl sodium, and the crude acids esterified as for **2b**, a mixture of monomeric carboxylates was obtained; **10** and **11** were each formed in 1% yield. An nmr spec-





trum of the ester mixture showed olefinic signals at 5.25 (m, 1, C=CH) and 4.70 ppm (m, 2, C=CH_2), with a molecular ion of 170 mass units. A moderate yield of the sodium enolate of 2,5-dimethylcyclopentanone was also present in the initial reaction product. Since the methyl groups of this ketone prevent self-condensation, it is not surprising that only monomeric products were isolated. Nevertheless, the structures **10** and **11** substantiate the mechanistic considerations of Scheme I and the ambident character of the DMSO anion.

Finally, 2-methylcyclopentanone was added to dimsyl sodium. The mixture of carboxylate salts thus obtained was acidified and then esterified to give a mixture of five esters (vpc, 10% SE-30 on Chromosorb W, 120–180°). The most abundant component had the shortest retention time, and was isolated by fractional distillation, bp 84° (1.5 mm). This volatile component represents the product obtained from oxidation and alkylation of 2-methylcyclopentanone itself rather than the dimeric enone, presumably *via* a mechanism similar to Scheme I, and is assigned structure **12**; it had char-



acteristic nmr peaks at 4.70 (s, 2, C=CH_2) and 1.75 ppm (s, 3, C=CCH_3), with a molecular ion of 156 mass units. Three of the remaining four esters distilled as a mixture, and demonstrated similar vpc retention times. An nmr spectrum of the mixture resembled that of structures **2b** and **7**; olefinic proton signals were seen at 4.80 (s, 2, C=CH_2) and 5.75 ppm (s, 1, C=CH). The mass spectrum showed *m/e* 236 ($M\cdot^+$, 1.7%), 148 ($M\cdot^+ - CO_2C_2H_5$ and CH_3, 25%), 135 ($M\cdot^+ - CH_3CHCO_2C_2H_5$), and 121 ($M\cdot^+ - CH_2CH_3CHCO_2C_2H_5$). The mixture gave a single adduct with maleic anhydride which was separated from unreacted esters on a silica gel column, but the exact identity of these three dimeric esters is still being investigated.

Although the aldol condensation of 2-methylcyclopentanone has not been reported, we find that it does occur under rigorous conditions to give a mixture of enones which is being further investigated.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary apparatus according to USP Class 1, and are corrected. Elemental analyses were determined with an F & M Model 185

(13) G. A. Russell, E. R. Talaty, and R. H. Horrocks, *J. Org. Chem.*, **32**, 353 (1967).

analyzer. Gas chromatographic (vpc) separations were obtained with a Perkin-Elmer F11 gas chromatograph using 0.125 × 36 in. columns with 10% SE-30 on Chromosorb W. Infrared spectra were recorded on a Beckman IR-18A using KBr pellets for solids. Uv spectra were obtained on absolute ethanol solutions and recorded with a Cary Model 14 spectrophotometer. Nmr spectra were obtained with $CDCl_3$ solutions and recorded by a Varian XL-100 spectrometer using TMS as an internal standard. Mass spectral data were obtained with a CEC Model 21-104 spectrometer.

δ-Methylene-1-cyclopentene-1-pentanoic Acid (2a).—A suspension of NaH (54.0 g of 57% mineral oil dispersion, 1.28 mol) in 250 ml of dry DMSO was vigorously stirred under a dry nitrogen atmosphere and heated gradually (oil bath) to 71°, then maintained at that temperature until solution resulted and hydrogen evolution was no longer observed.[1,14] The gray mixture was immediately cooled to 25°[15,16] and maintained at <25° while cyclopentanone (100 g, 1.19 mol) was added dropwise. The mixture was stirred for 30 min with cooling to moderate the exothermic reaction, then at 25° for 5 hr. The reaction mixture was poured into 2 l. of chilled methylene chloride–ether (1:1), and the resulting suspension was refrigerated overnight. The fine solid was filtered on a sintered-glass filter, washed with ether–methylene chloride (9:1), and then thoroughly dried. The crude salts were dissolved in water and the solution was neutralized with 6 *N* HCl. The odorous mixture was extracted with ether, and the extract was dried ($MgSO_4$), filtered from Darco G-60, and evaporated to give 62.8 g (59%) of orange oil which crystallized on standing. Purification was achieved by dissolving the crude acid in aqueous alkali followed by acidification to yield white crystals: mp 44.5–46.0; tlc on silica gel ($CHCl_3$–CH_3OH, 9:1), R_f 0.60.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.20; H, 8.83.

Ethyl δ-Methylene-1-cyclopentene-1-pentanoate (2b).—To the acid **2a** (11.6 g, 0.065 mol) in 50 ml of dry THF was added *N*,*N*′-carbonyldiimidazole (11.3 g, 0.070 mol) in small portions. When CO_2 evolution had ceased, 50 ml of dry ethanol with a catalytic amount of sodium ethoxide was added and the mixture was stirred at room temperature for 2 hr. The solvent was evaporated and the residue was dissolved in ether, then washed with water, cold 1 *N* NaOH, and cold 1 *N* HCl. The ether extract was dried ($MgSO_4$), evaporated, and distilled to give 13.5 g (100%) of the ethyl ester: bp 70–71° (0.2 mm); $n^{26}D$ 1.484; ir (film) 1740 cm^{-1} (ester C=O).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.88; H, 9.77.

Ethyl 5-Cyclopentylhexanoate.—The ester **2b** (6.65 g, 0.032 mol) in 50 ml of dry ethanol was hydrogenated with 0.1 g of 10% Pd/C at 60 psi and ambient temperature in a Parr apparatus. The theoretical amount of hydrogen was absorbed in 1 hr, the catalyst was filtered, and the solution was evaporated and then distilled to give a colorless oil: 6.6 g (98%); bp 75–76° (0.2 mm); $n^{26}D$ 1.455; ir (film) 1730 cm^{-1} (ester C=O).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.40. Found: C, 73.84; H, 11.29.

7-(3-Carboxypropyl)-2,3,3a,4,5,6-hexahydroindene-4,5-*cis*-dicarboxylic Acid Anhydride (3a).—To the acid **2a** (5.00 g, 0.0277 mol) in 25 ml of dry benzene, maleic anhydride (2.74 g, 0.028 mol) was added slowly. The exothermic reaction was moderated with an ice bath, and then the mixture was stirred at room temperature for 1 hr. Ether (100 ml) was added and the brown solution was filtered from Darco G-60, then evaporated to give an oil which crystallized on standing, 7.7 g (99%). The solid recrystallized from ether to give white crystals: mp 100.0–106.0°; ir (KBr) 1710 (acid C=O), 1780, 1840 cm^{-1} (anhydride C=O).

Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 64.60; H, 6.49.

7-[3-(Ethoxycarbonyl)propyl]-2,3,3a,4,5,6-hexahydroindene-4,5-*cis*-dicarboxylic Acid Anhydride (3b).—This ester adduct was prepared as described for the acid adduct **3a**, and the oily orange crystals (87%) were recrystallized from ether–petroleum ether (bp 30–60°) to give off-white crystals: mp 85.5–87.0°; ir (KBr) 1720 (ester C=O), 1770, 1840 cm^{-1} (anhydride C=O).

Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.70; H, 7.49.

1,2,3,5,5aα,6,7,8,8aα,8b-Decahydro-6,8-dioxo-*cis*-indacene-4-butyric Acid (4).—To the acid **2a** (1.00 g, 5.56 mmol) in 1.0 ml of dry benzene, 4-cyclopentene-1,3-dione (0.534 g, 5.56 mmol) was added and the mixture was stirred at room temperature for 24 hr. The reaction mixture was filtered to give a white solid, 0.80 g (52%), which recrystallized from acetone to yield white crystals: mp 154–157°; ir (KBr) 1715 (acid C=O), 1590 cm^{-1} (β diketone); nmr ($CDCl_3$) δ 4.88 (s, 1, COCH=CO), 2.75 (s, broad, 2, cis CHCO).

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.74; H, 7.06.

5-(2-Hydroxycyclohexylidene)-1-hexanol (6).—To a solution of the ester **2b** (27.10 g, 0.130 mol) in 150 ml of dry CH_2Cl_2 was added dropwise 85% *m*-chloroperbenzoic acid (29.4 g, 0.144 mol) in 300 ml of dry CH_2Cl_2 with stirring at 0°. After the addition was complete, the mixture was stirred at 25° for 2 hr, and then the *m*-chlorobenzoic acid was filtered. The filtrate was twice washed with 100 ml of Na_2SO_3 solution followed by 100 ml of cold 1 *N* NaOH. The organic layer was dried ($MgSO_4$) and evaporated to give 28.10 g (97%) of a yellow oil. The product was purified by chromatography (silica gel, ether) to yield the colorless, thermally unstable epoxide **5**: nmr ($CDCl_3$) δ 5.00 (d, 1, $J_{gem} \cong 1$ Hz, C=CH_2), 5.25 (d, 1, $J_{gem} \cong 1$ Hz, C=CH_2), 3.38 (s, 1, OCH); mass spectrum *m*/*e* (rel intensity) 224 (3.3), 123 (67).

The epoxide **5** (4.67 g, 0.0208 mol) in 5 ml of dry benzene was directly added dropwise to diisobutylaluminum hydride (46.7 ml of 24.8% in benzene, 0.0686 mol, Texas Alkyls Inc.) with stirring at 0°. The mixture was stirred at 0° for 16 hr; then 1 ml of methanol was added, followed by 2 ml of water. The solids were filtered and rinsed with ether. The filtrates were evaporated to an oil which was chromatographed (silica gel, ether) to give a colorless, viscous oil, **6**: nmr ($CDCl_3$) δ 4.68 (s, 1, OCH), 1.80 (s, 3, C=CCH_3); ir (KBr) 3370 cm^{-1} (OH); mass spectrum *m*/*e* (rel intensity) 184 (1.1), 166 (18), 149 (36).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.68; H, 10.75.

Ethyl β-Methyl-δ-methylene-(3- or 4-methyl-1-cyclopentene)-1-pentanoate (7).—3-Methylcyclopentanone reacted with methylsulfinyl carbanion as described for the preparation of **2a**, and then the reaction products were esterified as for **2b**, giving a yellow oil which was distilled to yield diethyl 3-methylglutarate, (**8**), bp 89° (0.3 mm), mass spectrum *m*/*e* (rel intensity) 157 (21, $M^{\cdot+} - OC_2H_5$), followed by **7**: bp 116° (0.3 mm); $n^{23}D$ 1.3074; nmr ($CDCl_3$) δ 5.75 (s, 1, C=CH), 4.80 (s, 2, C=CH_2); mass spectrum *m*/*e* (rel intensity) 236 (35), 191 (20).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.20; H, 10.20.

7-[2-(Ethoxycarbonyl)-2-methylpropyl]-2- or -3-methyl-2,3,3a,-4,5,6-hexahydro-4,5-indene-*cis*-dicarboxylic Acid Anhydride.—This adduct was prepared from **7** and maleic anhydride as described for **3a**. The crude adduct (100%) was purified by elution chromatography (silica gel, ether–petroleum ether), giving a yellow oil: $n^{23}D$ 1.5007; ir (KBr) 1720 (ester C=O), 1770, 1840 cm^{-1} (anhydride C=O).

Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 68.05; H, 8.11.

Registry No.—**2a**, 39495-68-6; **2b**, 39495-69-7; **3a**, 39495-70-0; **3b**, 39495-71-1; **4**, 39495-72-2; **5**, 39495-78-8; **6**, 39495-79-9; **7** (3-methyl), 39495-80-2; **7** (4-methyl), 39495-81-3; **12**, 39495-82-4; methylsulfinyl carbanion, 13810-16-7; cyclopentanone, 120-92-3; ethyl 5-cyclopentylhexanoate, 39495-83-5; maleic anhydride, 108-31-6; 4-cyclopentene-1,3-dione, 930-60-9; 3-methylcyclopentanone, 1757-42-2; 7-[2-(ethoxycarbonyl)-2-methylpropyl]-2-methyl-2,3,3a,4,5,6-hexahydro-4,5-indene-*cis*-dicarboxylic acid anhydride, 39495-84-6; 7-[2-(ethoxycarbonyl)-2-methylpropyl]-3-methyl-2,3,-3a,4,5,6-hexahydro-4,5-indene-*cis*-dicarboxylic acid anhydride, 39495-85-7.

(14) The same acid **2a** was formed in comparable yield by using fresh KO-*t*-Bu in dry DMSO at room temperature instead of NaH.

(15) Prolonged standing of this reagent above 25° resulted in explosive decomposition on one occasion.

(16) Hazards of generating dimsylsodium are cited in *Chem. Eng. News*, June 13, 1966, p 7.

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Intramolecular Alkylations of Bicyclic α,β-Unsaturated Ketones[1]

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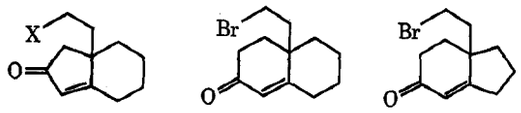
Bicyclic α,β-unsaturated ketones **1**, **2**, and **3**, having 2-bromoethyl groups as angular substituents, were prepared and their cyclizations by intramolecular alkylation investigated. High selectivities for α′-alkylation were found; tricyclic ketones **10**, **15**, and **17** were the major or sole products of cyclization.

Intramolecular alkylation of ketones is an attractive and popular synthetic route to polycyclic ketones. In most cases the synthetic scheme is designed such that only one mode of cyclization is possible. We here describe the intramolecular alkylations of a series of bicyclic α,β-unsaturated ketones (**1**, **2**, and **3**) in

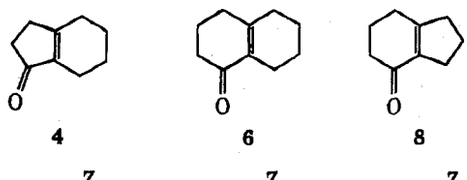


1a, X = Br
b, X = OMs

2 **3**

which, *a priori*, three possibilities for cyclization exist, *i. e.*, alkylation at the α position, at the γ position, or at the α′ position. Several examples of intramolecular alkylations of α,β-unsaturated ketones have been reported.[2-7] In some cases, the stereochemistry of the compound to be cyclized was such that only γ-alkylation was feasible;[2,3] however, in other cases in which competition among the several sites for alkylation seemed possible, selectivities for cyclization to the γ position[4,5] and to the α position[6,7] were observed.

The preparative route to ketones **1**, **2**, and **3** was based on Burgstahler's procedure for angular substitution[8] and the allylic oxidation method introduced by Dauben.[9] Thus, improvement[10] of the previously reported procedures for the conversion of **4** into **5a**[11] and **6** into **7a**[9] and extension to **8** to provide **9a** gave good yields of the angularly substituted bicyclic olefins.[12] Reduction of the aldehydes **5a**, **7a**, and **9a** gave the corresponding alcohols **5b**, **7b**, and **9b**, which were converted to the mesylates **5c**, **7c**, and **9c** and



4 **6** **8**

5 **7** **9**

a, Z = CHO
b, Z = CH_2OH
c, Z = CH_2OMs
d, Z = CH_2Br

treated with lithium bromide[13] to afford the bromo olefins **5d**, **7d**, and **9d**.[14] Oxidation[9] of the olefins with chromium trioxide–dipyridine complex, formed *in situ*,[15] provided the desired α,β-unsaturated ketones **1a**, **2**, and **3** (and **1b** from **5c**).

When cyclopentenone **1a** (or **1b**) was treated with potassium *tert*-butoxide in *tert*-butyl alcohol,[3] a mixture of ketones was obtained in which α,β-unsaturated ketone **10**, the product of α′-alkylation, and β,γ-unsaturated ketone **11**, the product of α-alkylation, were present in the ratio of 95:5. That the α,β-unsaturated ketone produced was **10** rather than **12**, the product of γ-alkylation, was demonstrated by catalytic reduction of the double bond to saturated ketone **13** followed by mild basic exchange of the active methylene hydrogens in methanol-*O*-*D*. The presence of only two exchangeable hydrogens confirmed the assignment of structures **13** and **10**; the saturated ketone **14**, derivable from **12**, would have had four exchangeable hydrogens.

(1) Presented in part at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, Abstracts, ORGN140.

(2) R. B. Bates, G. Büchi, T. Matsura, and R. R. Shaffer, *J. Amer. Chem. Soc.*, **82**, 2327 (1960). See also G. Büchi, W. Hofheinz, and J. V. Paukstelis *ibid.*, **91**, 6473 (1969).

(3) Intramolecular cyclization to the 4 position of the phenol can be considered γ-alkylation of an α,β-unsaturated ketone. For example, see S. Masamune, *ibid.*, **83**, 1009 (1961).

(4) (a) J. J. Bonet, H. Wehrli, and K. Schaffner, *Helv. Chim. Acta.*, **45**, 2615 (1962); (b) O. Halpern, P. Crabbe, A. D. Cross, I. Delfin, L. Cervantes, and A. Bowers, *Steroids*, **4**, 1 (1964).

(5) P. C. Mukharji and A. N. Ganguly, *Tetrahedron*, **25**, 5281 (1969).

(6) P. Grafen, H. J. Kabbe, O. Roos, G. D. Diana, Tsung-tee Li, and R. B. Turner, *J. Amer. Chem. Soc.*, **90**, 6131 (1968).

(7) C. Mercier, A. R. Addas, and P. Deslongshamps, *Can. J. Chem.*, **50**, 1882 (1972).

(8) A. W. Burgstahler and I. C. Nordin, *J. Amer. Chem. Soc.*, **83**, 198 (1961).

(9) W. G. Dauben, M. Lorber, and D. S. Fullerton, *J. Org. Chem.*, **34**, 3587 (1969).

(10) Longer reaction times in formation of the vinyl ethers of the allylic alcohols obtained upon reduction of **4**, **6**, and **8** resulted in much improved yields.

(11) (a) R. L. Cargill and A. M. Foster, *J. Org. Chem.*, **35**, 1971 (1970); (b) A. M. Foster, Ph.D. Thesis, University of South Carolina, Columbia, S. C., 1970.

(12) Attempts to convert the alcohol obtained from **4** into the methyl ester corresponding to **5a** by the orthoacetate method [W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, Tsung-tee Li, D. J. Faulkner, and M. R. Petersen, *J. Amer. Chem. Soc.*, **92**, 741 (1970)] failed owing to elimination from the allylic alcohol, which is unstable to storage.

(13) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 2539 (1959).

(14) The bromides were preferred to the mesylates owing to easier purification of the bromo olefins and bromo enones.

(15) R. Ratcliffe and R. Rodehurst, *J. Org. Chem.*, **35**, 4000 (1970).