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Preparation of Substituted Spiro[4.5]decan-7-ones. An Approach to the Synthesis of the Acorenones[1]

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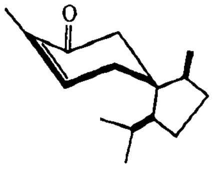
Uv irradiation of 2-acetoxy-2-cyclopentenone (**3**) and methylenecyclopentane (**8**) in benzene or acetonitrile yielded five products. By varying the irradiation conditions it was possible to favor the formation of certain products. Two of the photoproducts were shown to be α-acetoxy ketones formed by head-to-tail (**9**) and head-to-head (**13**) cycloaddition reactions of **3** and **8** while another two (**12** and **16**, respectively) were the type I cleavage products of these cycloadducts. The fifth product was 2-acetoxy-3-(1-cyclopentenylmethyl)cyclopentanone (**17**) and a mechanism for its formation is suggested. Rearrangement of adducts **9** and **13** under basic conditions followed by lead tetraacetate oxidation of the resultant ketols yielded spiro[4.5]decan-7-one-10-carboxylic acid (**11a**) and spiro[4.5]decan-6-one-9-carboxylic acid (**15a**), respectively. Application of this approach to the synthesis of the spiro sesquiterpenes, acorenone, and acorenone B, is discussed.

The sesquiterpene acorenone B was recently isolated from a hybrid grass of *Bothriochloa intermedia* and was shown by X-ray crystallographic studies to possess structure **1**.[2] The related sesquiterpene, acorenone (**2**) had previously been isolated from sweetflag oil[3] and presumably differs only in its configuration at the spiro carbon atom.[2] We wish to describe a versatile approach to the synthesis of substituted spiro[4.5]decan-7-ones with the ultimate objective being the synthesis of one or both of the acorenones.



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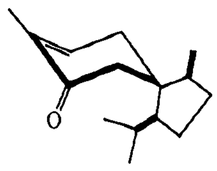

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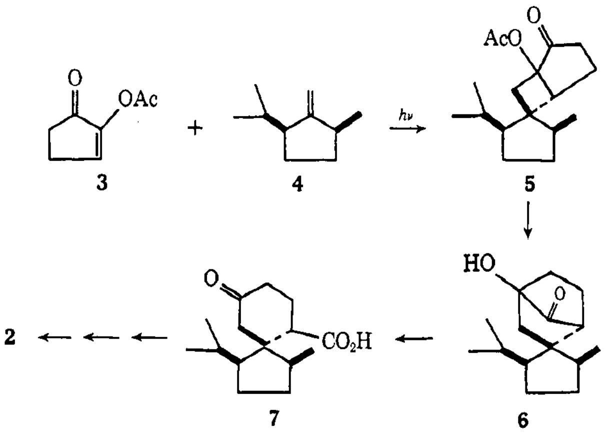
The proposed synthetic approach is outlined in Scheme I. Photochemical cycloaddition of 2-acetoxy-2-cyclopentenone (**3**) to the less hindered α face of the cis-disubstituted methylenecyclopentane **4** would be expected to yield adduct **5** as one of the major products. Photochemical cycloaddition of **3** to alkenes has previously been reported.[4] The rearrangement of **5** to **6** in basic solution followed by oxidative cleavage to give **7** is analogous to reported conversions.[4]

SCHEME I



The remaining steps to achieve the synthesis of acorenone (**2**) (esterification, alkylation, bromination, dehydrobromination, hydrolysis, and vinylogous decarboxylation) would not be expected to present any major obstacles. Cycloaddition of **3** to the more hindered β face of **4** would ultimately give acorenone B (**1**) as one of the possible products. The critical and potentially the most troublesome step in the scheme is the photochemical cycloaddition. Consequently, this step was studied in detail using the unsubstituted methylenecyclopentane (**8**) and the results are reported here.

Irradiation of benzene or acetonitrile solutions of **3** and **8** (tenfold excess) in a Pyrex vessel using a 350-nm source[5] resulted in the formation of five major prod-

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[1] This work was supported by the Research Advisory Board, University of Guelph, and the National Research Council of Canada.

[2] R. J. McClure, K. S. Schorno, J. A. Bertrand, and L. H. Zalkow, *Chem. Commun.*, 1135 (1968).

[3] J. Vrkoc, V. Herout, and F. Sorm, *Collect. Czech. Chem. Commun.*, **26**, 3183 (1961).

[4] (a) D. Helmlinger, P. de Mayo, M. Nye, L. Westfelt, and R. B. Yeats, *Tetrahedron Lett.*, 349 (1970); (b) P. G. Bauslaugh, *Synthesis*, 287 (1970); (c) T. Matsumoto, H. Shirahama, A. Ichihara, S. Kagawa, and S. Matsumoto, *Tetrahedron Lett.*, 4103 (1969).

[5] The reaction proceeded at a much slower rate when a 300-nm source was used.

ucts (Scheme II) (but only four resolved peaks) as determined by gas–liquid chromatography (glc). The product distribution in the two solvents for normal and extended periods of irradiation is shown in Table I, runs 1–4. Comparison of runs 1 and 2 or 3 and 4 suggested that **9** was being converted to **12** during the course of the irradiation. Similarly, although products **13** and **16** could not be resolved by glc, it was noted that during the extended irradiations a shoulder appeared on the front side of this peak which gradually increased in size until it masked the original peak. Also, the combined percentages of **9** + **12** or **13** + **16** remained essentially constant in runs 1 and 2 or 3 and 4. These photochemical conversions will be of importance when discussing the structural elucidation of the products.

SCHEME II

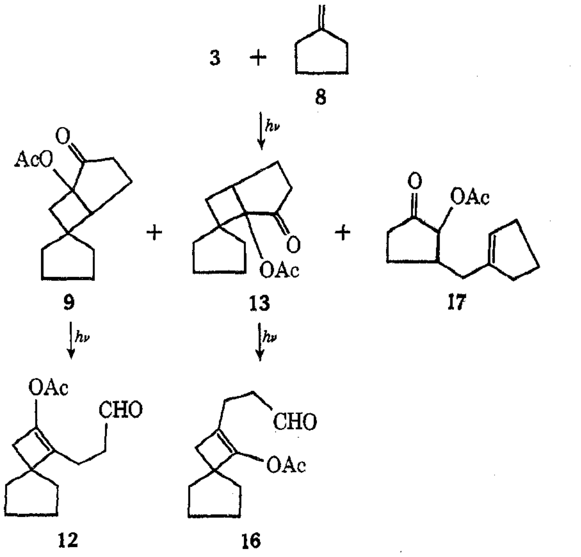


TABLE I

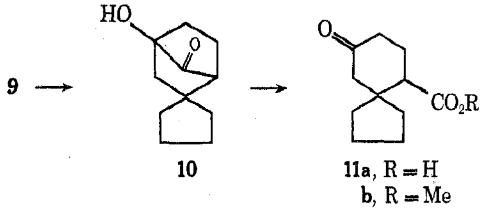
PRODUCT DISTRIBUTION FROM IRRADIATION OF **3** AND **8**

Run	Solvent	Irradiation time, hr	Unreacted **3**, %	Filter	Photoproducts, %[a] **13** + **16**[b]	**12**	**9**	**17**
1	Benzene	30	5	Pyrex	22	14	28	36
2	Benzene	75	0	Pyrex	20	35	8	30[c]
3	Acetonitrile	30	21	Pyrex	20	11	38	31
4	Acetonitrile	100	0	Pyrex	17	36	14	26[c]
5	Benzene	65	16	Uranium glass	21	6	36	37
6	Acetonitrile	67	20	Uranium glass	20	7	41	32

[a] Product distribution was determined by glc and the components are listed in order of elution from the column. The percentages are based on reacted **3** and are not corrected for differences in relative thermal response. [b] These two products were not resolved by glc. [c] In addition, 7% of a new product with a retention time slightly longer than that of **9** was detected.

The four major peaks were collected by preparative glc and the structures of the products were determined in the following manner.

Photoproduct 9.—This component, the third to be eluted from the glc column, exhibited strong ir absorption bands at 1755 and 1740 cm^{-1} which were attributed to cyclopentanone and acetate carbonyl groups. In the nmr spectrum, a three-proton singlet at τ 8.00 also supported the presence of the acetate group. The mass spectrum of the compound showed a molecular ion at *m/e* 222 as expected for the union of **3** and **8**. Further structural information was obtained by conversion of **9** to **10** (95%) in dilute base. The ir spectrum of the product indicated the presence of a hydroxyl group and a strained cycloalkanone (1782 cm^{-1}), which suggested that the desired acyloin rearrangement[4] had occurred. Oxidation of ketol **10** with lead tetraacetate gave keto acid **11a** (74%), which upon esterification with diazomethane gave keto ester **11b**. Treatment of **11b** with deuterium oxide and potassium carbonate gave the tetradeuterio derivative, as determined by nmr and mass spectrometry. This result requires that four hydrogen atoms be placed α to the ketone group in **11a** and supports the structure as depicted rather than the isomer in which the ketone group is adjacent to the spiro carbon atom. Further evidence to support this assignment will be presented when discussing compound **13**. Having proven the structure of the keto acid **11a** it was then possible to assign structures to **9** and **10** on the basis of their interconversions.



The formation of the head-to-tail cycloadduct **9** (41%, see Table I, run 6) and its subsequent conversion in high yield to the desired **11a** confirms that this is a practical approach to the synthesis of substituted spiro[4.5]decan-7-ones. In order to gain a better understanding of the photochemical step, the structures of the other products were also elucidated.

Photoproduct 12.—The ir spectrum of **12** indicated the presence of an aldehyde function (2820, 2720, 1730 cm^{-1})[6] and an enol acetate moiety (1755, 1710, 1210 cm^{-1}).[6] This assignment was supported by the nmr spectrum, which showed an aldehyde proton at τ 0.22 and a three-proton singlet for the acetate methyl group at τ 7.94. The mass spectrum had a molecular ion at *m/e* 222 as expected for **3** + **8**. The ir spectrum of the hydrolysis product of **12** showed absorptions at 1775 and 1730 cm^{-1} for the cyclobutanone and aldehyde carbonyl groups, respectively. As mentioned above, the precursor of **12** appeared to be cycloadduct **9** and thus the structure of the aldehyde must be as depicted (Scheme II). To prove this conversion, a pure sample of **9** was irradiated in benzene in a Pyrex tube and was converted cleanly to **12**. This photochemical transformation is an example of the well-known type I cleavage.[7] Examination of Table I, runs 5 and 6, indicates that this cleavage reaction could be suppressed by the use of a uranium glass

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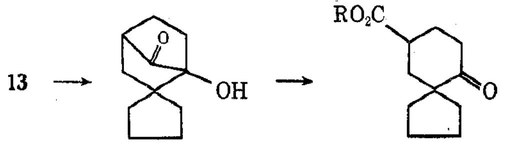
(6) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, pp 43–44.

(7) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *J. Amer. Chem. Soc.*, **93**, 7213 (1971), and references cited therein.

filter ($\lambda > 330$ nm),[8] which protected the saturated ketone **9** while allowing absorption of irradiation by the enone **3**.

Photoproducts 13 and 16.—The first product peak (**13**) eluted from glc separation of the irradiation mixtures described in Table I, runs 5 and 6 ($\lambda > 330$), was collected. The ir spectrum (strong absorptions at 1740 and 1250 cm^{-1}), the nmr spectrum (three-proton singlet at τ 8.00), and the mass spectrum (parent peak at *m/e* 222) suggested that this component was an acetoxycyclopentanone isomeric to **9**. Rearrangement of **13** in dilute base gave a strained hydroxy ketone (1775 cm^{-1}) which upon oxidation with lead tetraacetate yielded keto acid **15a**, which in turn gave keto ester **15b** upon treatment with diazomethane. Both **15a** and **15b** were identical with authentic samples.[9] Thus the hydroxy ketone must have structure **14** and the acetoxy ketone must be the head-to-head cycloadduct **13** by virtue of the reactions which they undergo and the known products to which they are converted.



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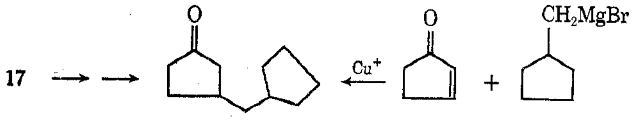
15a, R = H
b, R = Me

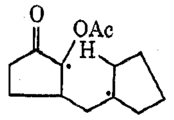
Upon prolonged irradiation of **3** and **8** in a Pyrex vessel (Table I, runs 2 and 4), cycloadduct **13** was converted to a compound (**16**) (Scheme II) which had almost the same glc retention time as **13** (discussed above) but which had completely different spectral properties. The ir spectrum indicated the presence of an aldehyde group (2810, 2710, 1730 cm^{-1})[6] and an enol acetate moiety (1755, 1700, 1205 cm^{-1})[6] and these assignments were supported by the nmr spectrum (one proton at τ 0.26 and a three-proton singlet at τ 7.90). The ir spectrum of the hydrolysis product of **16** showed absorptions at 1770 and 1725 cm^{-1} for the cyclobutanone and aldehyde carbonyl groups, respectively. Thus the structure of the acetoxy aldehyde must be **16**, the type I cleavage product of **13**. It was not possible to obtain analytical samples of **13** and **16** because of their very similar glc retention times on several different columns, and in all the irradiations described there was always a small amount of one of the components as an impurity in the other. Cleavage reactions of α-acetoxycyclopentanones related to **9** and **13** may have some synthetic utility, as these compounds appear to be converted rather cleanly to products with unusual structural features.[10]

Photoproduct 17.—The ir spectrum of the fourth product (**17**) to be eluted from the glc column indicated two carbonyl bands (1748 and 1762 cm^{-1}), the former attributed to an acetate group (1230 cm^{-1}) and the latter to a cyclopentanone ring. The nmr spectrum exhibited a one-proton vinyl resonance at τ 4.57 and a one-proton doublet ($J = 9$ Hz) at τ 5.19 assigned to the methine proton on the carbon atom bearing the acetoxy group (methyl at τ 7.95). Upon hydrogenation of this photoproduct the resonance at τ 4.57 disappeared and upon treatment of this dihydro product with zinc in refluxing acetic acid the acetoxy group was removed to give the substituted cyclopentanone **18** (1743 cm^{-1}). The latter experiment suggests that the acetoxy group is on a carbon atom α to the ketone group.[11] The structure of degradation product **18** was proven by an unambiguous synthesis. Conjugate addition of the Grignard reagent of cyclopentylmethyl bromide to 2-cyclopentenone in the presence of cuprous bromide gave 3-(cyclopentylmethyl)cyclopentanone, which was identical with the product derived from **17**. Thus, the most reasonable structure for **17** is 2-acetoxy-3-(1-cyclopentenylmethyl)cyclopentanone (Scheme II).



18

The formation of **17** upon irradiation of **3** and **8** is analogous to the formation of 2-(β-methallyl)cyclohexanone upon irradiation of 2-cyclohexenone and isobutylene as reported by Corey.[12] A plausible mechanism would involve the conversion of the initially formed diradical **19** to **17** *via* a hydrogen atom transfer in a six-membered transition state.



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Compounds **9** and **12** may be characterized as being products of a head-to-tail union of **3** and **8**, while **13**, **16**, and **17** are the result of a head-to-head union. Table I shows that in benzene the head-to-tail products comprised ~42% of the irradiation mixture while in acetonitrile this percentage increased to ~49%. Similar changes in product ratios upon varying the dielectric constant of the solvent have been noted.[13]

Preparation of the optically active alkene **4** is presently underway. In the irradiation of **3** and **4** it is hoped that the steric hindrance of the added alkyl substituents will enhance further the proportion of the desired head-to-tail adduct **5**.

Experimental Section

The infrared spectra were determined with a Beckman Model IR-5A or IR-12 infrared spectrophotometer. Ultraviolet spectra were recorded on a Unicam SP 800 spectrophotometer and the mass spectra were obtained with a Varian Mat CH7 spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian A-60A spectrometer using the internal standard tetramethylsilane (TMS, τ 10.0). Gas chromatographic separations and collections were carried out on an Aerograph Autoprep

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[8] (a) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964); (b) W. C. Agosta and Amos B. Smith, III, *ibid.*, **93**, 5513 (1971).

[9] We thank Professor Lawton for generously supplying us with samples of **15a** and **15b**. See D. J. Dunham and R. G. Lawton, *J. Amer. Chem. Soc.*, **93**, 2074 (1971).

[10] The cycloadduct of enone **3** and cyclopentene was found to undergo the same cleavage reaction.

[11] H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 158.

[12] E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

[13] B. D. Challand and P. de Mayo, *Chem. Commun.*, 982 (1968).

Model A-700 using a column of 20% Carbowax 20M on Chromosorb W, 60–80 mesh, 6 ft × 0.25 in. The peak areas were determined by triangulation and were not corrected for differences in thermal response. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were performed by H. S. McKinnon, Chemistry Department, University of Guelph, and A. B. Gygli, Toronto.

Photochemical irradiations were performed in a Rayonet Model RPR 208 preparative reactor equipped with 350-nm lamps. Spectrograde benzene and acetonitrile were distilled before use in the irradiations. Methylenecyclopentane was prepared using Corey's general procedure.[14]

Preparation of 2-Acetoxy-2-cyclopentenone (3).—A solution of 4.0 g (41 mmol) of 1,2-cyclopentanedione[15] in 250 ml of dry Et_2O was placed in a two-neck 500-ml round-bottomed flask equipped with a gas dispersion tube and a Dry Ice–acetone condenser with a drying tube at the top. An excess of ketene, prepared by pyrolysis at 550° of 30 ml of freshly distilled diketene,[16] was passed into the solution for 5–6 hr at 0° with stirring. The mixture was stirred for an additional 5–6 hr to complete the reaction and the excess ketene was swept out with dry nitrogen. Removal of the solvent left a pale yellow solid, which was recrystallized from petroleum ether (bp 60–90°) to give 4.7 g (82%) of **3** as white crystals: mp 57–58°; ir (CCl_4) 1775 (s), 1735 (s), 1370 (m), 1200 (vs), 1085 cm^{-1} (m); uv max (EtOH) 228 nm (ϵ 9250), 308 (51); nmr (CCl_4) τ 7.79 (3 H, s), 7.64 (2 H, m), 7.35 (2 H, m), 2.73 (1 H, t, J = 3 Hz).

Anal. Calcd for $C_7H_8O_3$: C, 59.99; H, 5.74. Found: C, 60.18; H, 5.89.

Irradiations of 3 and 8.—In each of the irradiations listed in Table I, a solution of 0.25 g (1.78 mmol) of **3** and 1.46 g (17.8 mmol, tenfold excess) of **8** in 4 ml of solvent (either benzene or acetonitrile) was placed in a Pyrex or uranium glass (Corning no. 3320)[8] tube and degassed with purified dry nitrogen. The tube was sealed with a serum cap, placed in a water-cooled jacket (~15°) inside the reactor, and irradiated for the indicated period of time. The reaction was followed by glc analysis of aliquots removed at various times. At the end of the irradiation period the solvent was removed and the product composition was determined by glc to give the results recorded in Table I. At a column temperature of 183° the starting enone and products were eluted in the following order (retention time in minutes): **3** (6.8), **13** and **16** (13.7), **12** (17.5), **9** (20.0), and **17** (32.2). Each fraction was collected by preparative glc to give the five photoproducts described below.

Photoproduct 9.—This product was most effectively prepared using the irradiation conditions described in Table I, run 6. Pure **9** exhibited the following properties: ir (CCl_4) 1755 (s), 1740 (s), 1255 (s) cm^{-1}; nmr (CCl_4) τ 8.05–8.52 (8 H, m), 8.00 (3 H, s), 6.87–7.93 (7 H, m); mass spectrum m/e (rel intensity) 222 (3, M^+), 162 (40), 137 (29), 80 (31), 67 (66), 43 (100).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.31; H, 8.35.

Preparation of Ketol 10.—A solution of 2 ml of 1% methanolic NaOH (0.50 mmol) and 109 mg (0.49 mmol) of **9** was allowed to stand in a nitrogen atmosphere for 1 hr. After addition of 20 ml of H_2O, the solution was extracted with Et_2O (five times), and the combined extracts were washed with saturated brine and dried ($MgSO_4$). Removal of the solvent gave 84 mg (95%) of an oil which was >95% pure by glc analysis. An analytical sample of **10** was obtained by glc: ir (CCl_4) 3550 (w), 3460 (w), 1782 cm^{-1} (s); nmr (CCl_4) τ 8.18–8.72 (9 H, m), 8.02–8.18 (3 H, m), 7.00–8.02 (3 H, m), 6.56 (1 H, s, exchanges with D_2O); mass spectrum m/e (rel intensity) 180 (9, M^+), 134 (34), 95 (66), 94 (100), 79 (31), 67 (35).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.28; H, 8.95. Found: C, 73.40; H, 9.00.

Preparation of 11a and 11b.—To a solution of 125 mg (0.69 mmol) of ketol **10** in 2.3 ml of dry benzene was added 0.34 g (0.77 mmol) of $Pb(OAc)_4$ and the suspension was stirred for 4 hr at room temperature. The reaction mixture was filtered, the solid was washed with 20 ml of benzene, and the combined organic phase was extracted with 25 ml of saturated $NaHCO_3$ solution (four times). The combined aqueous phase was acidified to Congo red with HCl and extracted with Et_2O (five times). The combined Et_2O extract was washed with saturated brine and dried. Removal of the solvent gave 101 mg (74%) of **11a** which crystallized on cooling. Recrystallization of this product from Et_2O–petroleum ether gave an analytical sample of keto acid **11a**: mp 86–87°; ir (CCl_4) 3000–2500 (s), 1712 cm^{-1} (vs, broad); nmr (CCl_4) τ 8.0–8.6 (8 H, m), 7.4–8.0 (4 H, m), 7.0–7.4 (3 H, m), −1.50 (1 H, broad s); mass spectrum m/e (rel intensity) 196 (53, M^+), 109 (100).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.42; H, 8.28.

Treatment of an Et_2O solution of **11a** with diazomethane gave a quantitative yield of the methyl ester **11b**, which exhibited only one peak on glc analysis: ir (CCl_4) 1738 (s), 1716 (s), 1166 cm^{-1} (s); nmr (CCl_4) τ 8.1–8.6 (8 H, m), 7.5–8.1 (4 H, m), 7.1–7.5 (3 H, m), 6.30 (3 H, s); mass spectrum m/e (rel intensity) 210 (32, M^+), 150 (55), 109 (100), 100 (72).

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.58; H, 8.66.

Preparation of Tetradeuterio 11b.—A mixture of 54 mg (0.26 mmol) of keto ester **11b**, 1.14 ml of D_2O, and 0.11 g of K_2CO_3[17] was refluxed with stirring for 5.5 hr. The product was extracted with Et_2O and examination of the residue showed that exchange was not complete. The procedure was repeated to give 24 mg of an acid fraction and 26 mg of tetradeuterio **11b**: ir (CCl_4) 1738 (s), 1714 cm^{-1} (s); nmr (CCl_4) τ 8.1–8.6 (8 H, m), 7.93 (2 H, d, J = 5 Hz), 7.42 (1 H, t, J = 5 Hz), 6.30 (3 H, s); mass spectrum m/e (rel intensity) 214 (79, M^+), 154 (73), 110 (73), 102 (100).

Photoproduct 12.—This product was prepared most effectively using the irradiation conditions described in Table I, runs 2 or 4. Preparative glc yielded a pure sample of **12**: ir (CCl_4) 2820 (w), 2720 (w), 1755 (s), 1730 (s), 1710 (m) 1210 cm^{-1} (vs); nmr (CCl_4) τ 8.3–8.4 (8 H, broad s), 7.94 (3 H, s), 6.9–7.9 (6 H, m), 0.22 (1 H, s); mass spectrum m/e (rel intensity) 222 (3, M^+), 67 (37), 43 (100).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.13; H, 8.30.

To definitely establish the origin of **12**, a solution of 71 mg of pure **9** and 2.5 ml of benzene in a Pyrex tube was degassed and irradiated under the usual conditions for 42 hr. Glc analysis of the solution indicated an 80% conversion to **12** and no other products were observed.

A sample of 116 mg (0.52 mmol) of **12** was hydrolyzed using the conditions described for the preparation of ketol **10** to give 76 mg (66%) of a yellow oil which glc analysis showed to contain one major peak (>90%) plus minor impurities. The ir spectrum of the sample exhibited strong bands at 1775 and 1730 cm^{-1}.

Photoproduct 13.—The irradiation conditions that produced this compound most effectively are recorded in Table I, runs 5 and 6. Preparative glc of this first product peak gave a fraction which was >90% **13**: ir (CCl_4) 1740 (s), 1250 cm^{-1} (s); nmr (CCl_4) τ 8.1–8.7 (10 H, m), 8.00 (3 H, s), 6.9–7.9 (5 H, m), a minor peak at 0.26 indicated **16** was the impurity in this fraction; mass spectrum m/e (rel intensity) 222 (9, M^+), 141 (100), 99 (100), 43 (95).

Preparation of 15a and 15b *via* Ketol 14.—A sample of 38 mg (0.17 mmol) of **13** (>90% in purity) was treated with methanolic NaOH as described in the preparation of ketol **10**. The residue (27 mg, 87%) was shown by glc to be a 94:6 mixture of two components. The ir spectrum of the mixture showed an hydroxyl band at 3440 cm^{-1} and a strong carbonyl band at 1775 cm^{-1}.

This crude ketol fraction was oxidized with $Pb(OAc)_4$ as described for the preparation of **11a** to give 19 mg (66%) of keto acid **15a** which crystallized on cooling. This sample was shown to be identical with spiro[4.5]decan-6-one-9-carboxylic acid synthesized independently by Lawton.[9] The methyl ester **15b** was prepared by treatment of **15a** with diazomethane and was similarly found to be identical with an authentic sample.[9]

Photoproduct 16.—This product was prepared by prolonged irradiation of **3** and **8** as described in Table I, runs 2 and 4. Preparative glc of the first product peak eluted gave a fraction which was rich in **16** (~75%): ir (CCl_4) 2810 (w), 2710 (w), 1755 (s), 1730 (s), 1700 (w), 1205 cm^{-1} (vs); nmr (CCl_4) τ 0.26 (~1 H, s), 7.90 (~3 H, s), a much smaller singlet at 8.00 for **13** also observed. Hydrolysis of **16** using conditions previously described gave a fraction which exhibited ir bands at 1770 and 1725 cm^{-1} and which showed by glc analysis the presence of two

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[14] R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

[15] H. Herloffinhoffen and H. Kramer, *Chem. Ber.*, **87**, 488 (1954).

[16] S. Andreades and H. D. Carlson, *Org. Syn.*, **45**, 50 (1965).

[17] M. St-Jacques and C. Vaziri, *Can. J. Chem.*, **49**, 1256 (1971).

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**.

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.

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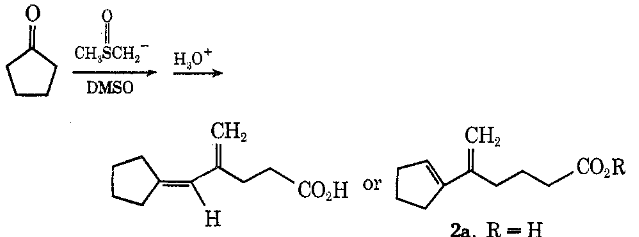
Methylsulfinyl carbanion reacts with cyclopentanone at ambient temperature to afford the unexpected δ-methylene-1-cyclopentene-1-pentanoic acid (**2a**) in good yield. This reaction appears limited to cyclopentanones, with only low yields isolated from 2- and 3-methylcyclopentanones. Mechanistic considerations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

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[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).