benzaldehyde and 10^{-2} M KI in 10^{-2} M NaOH upon irradiation at 254 nm showed a rapid loss of aldehyde absorbance ($t_{1/2}$ = 30 sec). When 3,4,5-trimethoxybenzonitrile and KI solution are irradiated in 10^{-2} M NaOH, no 3,4,5-trimethoxybenzaldehyde was found, but 3,5-dimethoxybenzonitrile was isolated in 24% yield.

4-Nitrobenzonitrile. A 250-ml aqueous solution of 1.35×10^{-3} M 4-nitrobenzonitrile and 10^{-1} M KI was degassed and irradiated for 3 days. The reaction solution was basified and extracted with ether; the ethereal extract was dried and concentrated for preparative tlc using chloroform–benzene–ethyl acetate (65:15:15). 4-Aminobenzonitrile (~1% yield) and 4-aminobenzaldehyde (~1% yield) were eluted from the silica gel with ethanol and identified by comparison of uv spectra in acid and base, R_f values (three different solvent systems), and DNP color test (4-aminobenzaldehyde) with authentic samples.

The reaction solution was then acidified and extracted with ether; the ethereal extract was dried and concentrated for preparative tlc using chloroform–benzene–ethyl acetate (65:15:15). 4-Cyanophenol (<1% yield) and 4-hydroxybenzaldehyde (2% yield) were isolated by eluting from the silica gel with ethanol and were identified by comparison of uv spectra in acid and base, R_f values (three different solvent systems), and DNP color test (4-hydroxybenzaldehyde) with authentic samples. The low yields of products may be due in part to loss of product in the separation scheme and also the fact that a thermal hydrolysis of 4-nitrobenzonitrile to the amide occurs in neutral solution.

Trapping Experiments for the Solvated Electron. Trapping experiments were done using oxygen, NO_3^-, acetone, and protons, respectively, known electron scavengers. (a) Irradiation of 4-cyanophenol (10^{-4} M) in nondegassed aqueous NaOH (10^{-2} M) resulted in only a 20% yield of 4-hydroxybenzaldehyde. (b) 4-Cyanophenol (8.5×10^{-5} M) in 10^{-2} M NaOH and $NaNO_3$ (4.1×10^{-4} M) was degassed and irradiated at 254 nm for 100 min. Only a slight absorption for the aldehyde was noted at 330 nm. (c) 4-Cyanophenol (6.8×10^{-5} M) in 10^{-2} M NaOH and acetone (10^{-3} M) was degassed and irradiated at 254 nm for 40 min during which time most of the nitrile had reacted but no aldehyde absorption was noted. (d) 2-Cyanophenol (10^{-4} M) in 10^{-2} M HCl was irradiated at 254 nm with no salicylaldehyde absorption noted; only benzoxazole absorption.

Analysis for CNO^-, CN^-, and $NH_4^+Cl^-$ upon Irradiation of 4-Cyanophenol in Base. A convenient procedure was developed for the simultaneous detection of CN^-, CNO^-, and NH_4^+. 4-Cyanophenol (10^{-3} M) was irradiated for 31 hr at 254 nm in NaOH (10^{-2} M). The yellow aqueous solution was acidified and extracted with ether. The water layer was concentrated and paper chromatograms were run in three solvent systems with standards to check for the presence of CNO^-, CN^-, and NH_4Cl. NH_4Cl gives a pale yellow color with Bromocresol Green while cyanate and cyanide give bright blue colors. No cyanide was detected and only cyanate and ammonium chloride were observed. The observed R_f values are shown in Table III.

Table III. Simultaneous Analysis for Cyanate, Cyanide, and Ammonium Ions

Solvent system[a]	CN^-	R_f, CNO^-	NH_4^+
IEW	0.08	0.31	0.38
EAW	0.17	0.59	0.54
PA	0.16[b]	0.17[b]	0.33

[a] The solvent systems are described under General Procedures. [b] It is not possible to distinguish between CN^- and CNO^- in the PA system.

Acknowledgment. We thank Professor R. L. Strong for use of his flash photolysis apparatus and Professor D. A. Aikens for measuring the oxidation potential of 4-cyanophenol. We further acknowledge support of this work by the NIH in the form of a research grant (GM 15915) and a Research Career Development Award (to J. P. F., GM 6380).

Spiroketal Reductive Ring Opening[1]

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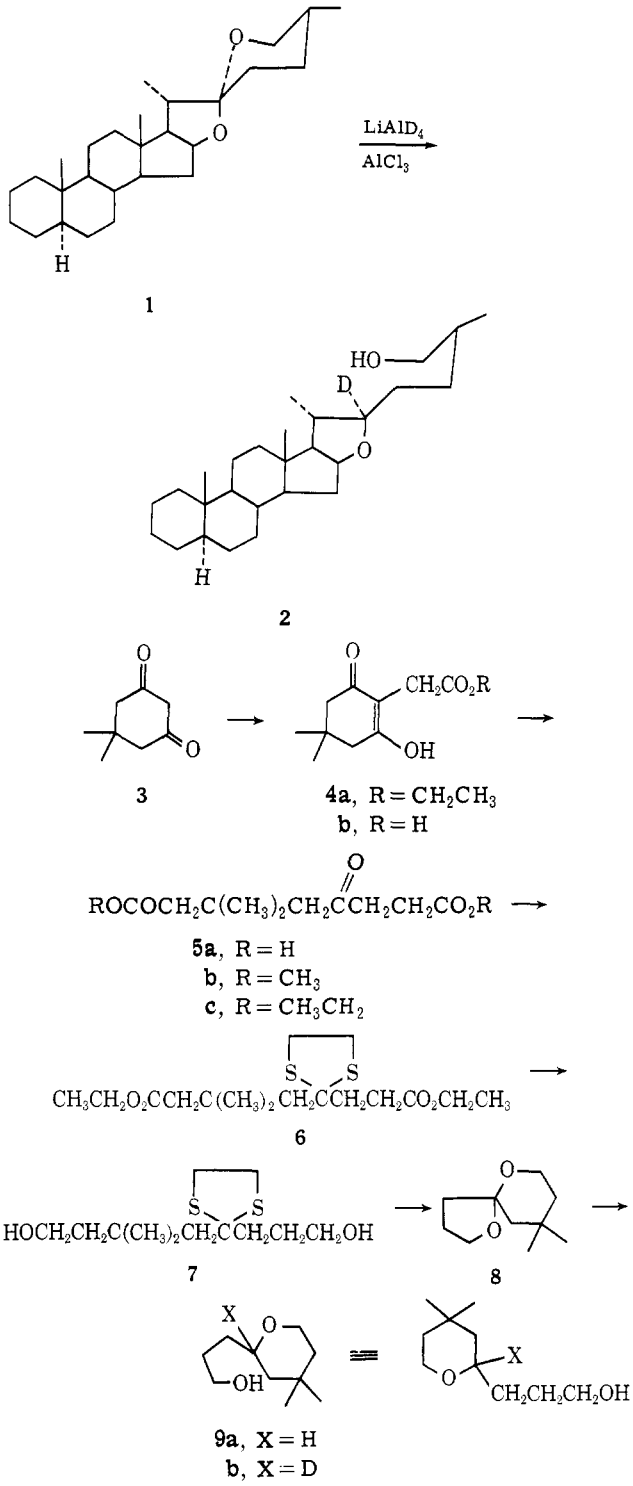
Abstract: Both the direction and mechanism of reductive ring opening with the spiroketal 9,9-dimethyl-1,6-dioxaspiro[4.5]decane (**8**) have been explored. With dimedone (**3**) as precursor, synthesis of spiroketal **8** was realized by way of intermediates **4**, **5**, **6**, and **7**. Lithium aluminum hydride–aluminum chloride catalyzed reduction of spiroketal **8** was found to yield tetrahydropyran **9** in contrast to the steroidal sapogenins which undergo reductive cleavage of the tetrahydropyran ring. The mechanism of ring opening was examined using deuterium labeling (**8** → **9b**) combined with mass and proton magnetic resonance spectral measurements. Reductive ring opening of spiroketal **8** was thereby found to proceed by transfer of reagent hydride directly to the spirocarbon. The experimental results also suggested that reductive ring opening of relatively nonhindered spiroketals related to **8** may offer a new synthetic route to certain substituted tetrahydropyrans.

The spiroketal system of steroidal sapogenins will undergo lithium aluminum hydride–aluminum chloride catalyzed opening of the tetrahydropyran ring to afford the corresponding dihydrosapogenin (**1** → **2**).[2a] Subsequent to our initial observation of this convenient route to dihydrosapogenins, several attractive mechanistic pathways were evaluated using deuterium labeling and the stereochemical consequences of this reduction reaction were considered.[2b,c] Direct transfer of hydride from a metal hydride intermediate to the spirocarbon was found to occur and the single epimer produced seemed best represented by structure **2** (see Chart I). Exclusive opening of the tetrahydropyran ring was found in all such reactions viewed. That the steric compression around ring D may present a specialized situation in this reduction reaction was uncovered by extending the study to an analogous but

(1) This investigation was supported by Public Health Service Research Grants CA-10612-03, CA-10612-04, and CA-11451-03 from the National Cancer Institute. The Atlas mass spectrometers were purchased with funds from National Science Foundation Grants GB-4939 and GP-6979. We are also pleased to acknowledge financial assistance from Merck and Co. The present contribution was abstracted in part from the doctoral dissertation submitted by A. A. to the graduate school, Arizona State University, Feb 1971.

(2) (a) G. R. Pettit and W. J. Bowyer, *J. Org. Chem.*, **25**, 84 (1960); (b) A. H. Albert, G. R. Pettit, and P. Brown, *ibid.*, in press; (c) P. Brown A. H. Albert, and G. R. Pettit, *J. Amer. Chem. Soc.*, **92**, 3212 (1970).

Chart I



relatively unhindered spiroketal as reported in the sequel.

Synthesis and reductive ring opening of the new spiroketal **8** were selected for investigation.[3] Dimedone (**3**) was selected as starting material and alkylated with ethyl bromoacetate essentially as described by Rosenmund[4] and Stetter.[5] The product, ethyl ester **4a**, upon hydrolysis in concentrated hydrochloric acid yielded acetic acid derivative **4b** and diacid **5a**. The yield of diacid **5a** was improved by subjecting acid **4b** to further reaction with hydrochloric acid. Methyl (**5b**) and ethyl (**5c**) ester derivatives of the diacid were easily prepared, but many attempts to prepare an ethylene ketal[6] or simple methyl or ethyl ketal derivative were unsuccessful and suggested steric interference by the geminal dimethyl group. However, necessary protection of the ketone was achieved employing ethanedithiol in boron trifluoride etherate. The resulting thioketal **6** upon careful reduction with lithium aluminum hydride afforded diol **7**. The diol **7** according to infrared, pmr, and mass spectral data was obtained in good yield (81%) but did not give satisfactory elemental analytical data. Soon, it was found that diol **7** undergoes extensive change on standing. Consequently, diol **7** was promptly desulfurized with the mercuric chloride–cadmium carbonate reagent. The liquid spiroketal **8** formed immediately and following distillation was obtained in 36% yield. An infrared spectrum of spiroketal **8** showed no hydroxyl or carbonyl absorption bands but did show the four characteristic bands associated with a ketal group.[7] The proton magnetic resonance spectrum, mass spectrum, and elemental analytical data also unequivocally supported structure **8**. The electron impact induced fragmentation (Chart II) of spiroketal **8** was analogous to that observed with the steroidal sapogenins.[8]

Reduction of spiroketal **8** with lithium aluminum hydride–aluminum chloride[2] led to an alcohol which analyzed correctly for the "dihydro" derivative **9a**. However, the appearance of two discrete methyl signals in its pmr spectrum indicated that in contrast to the steroidal sapogenins the five- and not the six-membered ring had opened. The mass spectral fragmentation and, in particular, the facile loss of the side chain (*m/e* 113) gave definite evidence that the product corresponded to structure **9a**. As expected, the electron impact fragments (Table I) of alcohol **9** and the possible modes of formation (Chart III) are quite different from those experienced with the steroidal sapogenins.

The deuterium-labeled alcohol **9b** was prepared by reducing spiroketal **8** with lithium aluminum deuteride–aluminum chloride. Electron impact induced cleavage of the labeled derivative **9b** gave both labeled (*m/e* 114) and unlabeled (*m/e* 113) cyclic oxonium ion fragments (Table I). As with the steroidal sapogenins,[2c] this indicated that the deuterium had been introduced directly (position 2 of the tetrahydropyran ring), without intramolecular hydride migration, and that H–D exchange had taken place in the molecular ion. The extent of exchange could not be precisely determined, however, since the parent ion peak groups for the labeled (**9b**) and unlabeled (**9a**) alcohols could not be compared due to weak molecular and strong M + 1 ions. Hence, it was not possible to determine the extent to which deuterium had been incorporated into labeled tetrahydropyran **9b** and to calculate the per cent of the M − 60 ion due to exchange. If it is

(3) Similar spiroketals have been prepared by H. Stetter and H. Rauhut, *Chem. Ber.*, **91**, 2543 (1958).

(4) K. W. Rosenmund, H. Herzberg, and H. Schütt, *ibid.*, **87**, 1264 (1954).

(5) H. Stetter, H. Kesseler, and H. Meisel, *ibid.*, **87**, 1619 (1954).

(6) For example, see R. J. Stedman, L. D. Davis, and L. S. Miller, *J. Org. Chem.*, **33**, 1280 (1968).

(7) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966.

(8) H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *Monatsh. Chem.*, **93**, 1033 (1962); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 2, Holden-Day, San Francisco, Calif., 1964; C. Djerassi, personal communication, 1969, and W. H. Faul and C. Djerassi, *Org. Mass. Spectrom.*, **3**, 1187 (1970).

Chart II. Mass Spectral Fragmentation of 9,9-Dimethyl-1,6-dioxaspiro[4.5]decane (**8**)

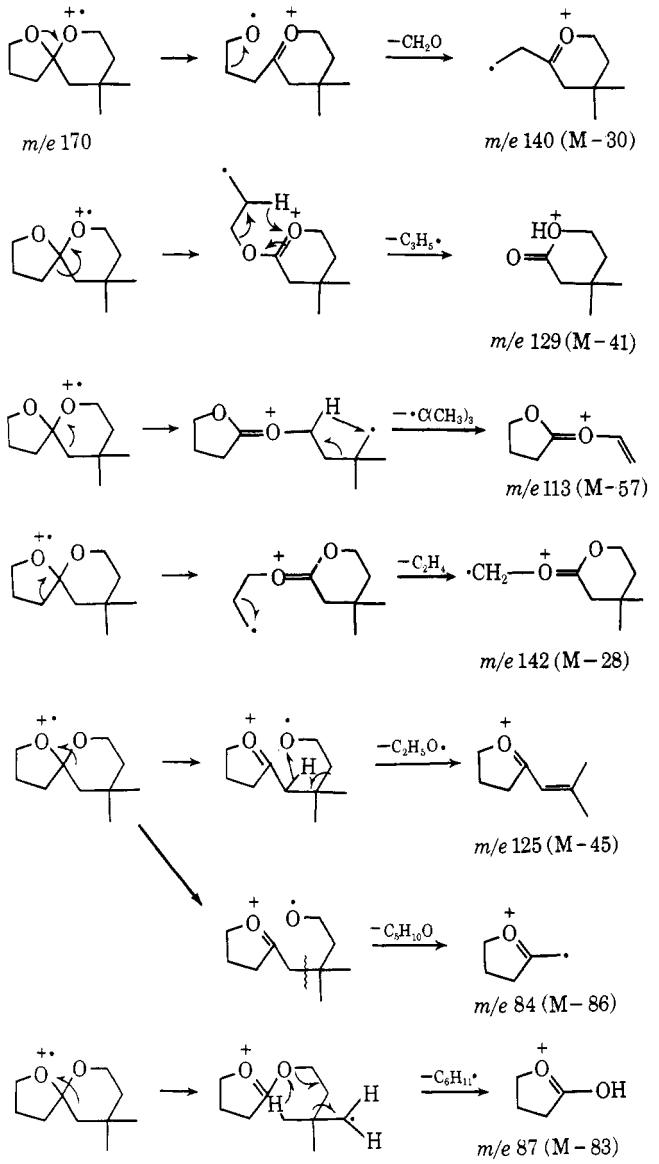


Table I. Mass Spectral Fragmentation of the Unlabeled (**9a**) and Labeled (**9b**) Reduction Products of Spiroketal **8**

9a *m/e* (rel intensity)	Fragment[a]	**9b** *m/e* (rel intensity)
173 (1)	M + 1	174 (3)
157 (0)	M − 15	158 (1)
155 (1)	(M + 1) − 18	156 (2)
143 (3)	M − CHO	144 (12)
	M − CDO	143 (7)
141 (2)		142 (6)
		141 (6)
139 (3)	M − CH_3 − H_2O	140 (5)
	M − CH_3 − HDO	139 (7)
129 (1)		130 (3)
126 (4)		126 (11)
125 (3)		125 (8)
121 (1)	M − CH_3 − $2H_2O$	122 (2)
115 (7)	M − C_4H_9	116 (15)
113 (100)		114 (100)
		113 (18)

[a] See Chart III.

assumed that 100% deuterium incorporation had taken place,[9] it can be estimated from Table II that the *maximum* amount of exchange possible is about 15%. This percentage is remarkably low considering the fact that H–D exchange in this system would proceed through a six-centered transition state **10**, compared with the seven-centered transition state required in the sapogenin system which gave about 25% exchange.[2b,2c]

Chart III. Mass Spectral Fragmentation of 2-(3′-Hydroxypropyl)-4,4-dimethyltetrahydropyran (**9a**)

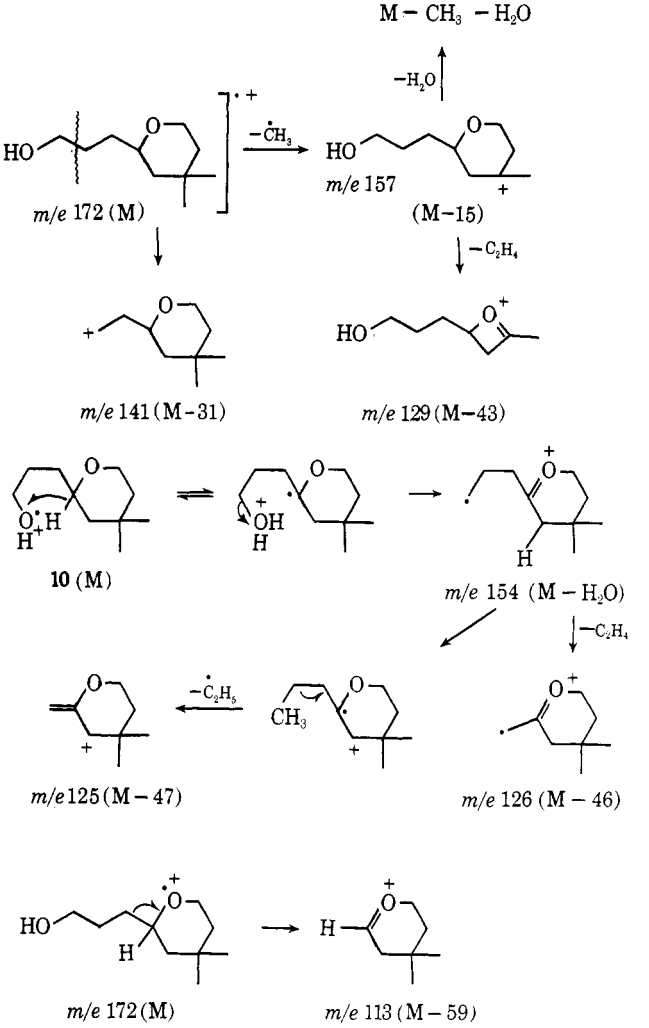


Table II. Hydrogen–Deuterium Exchange[a]

m/e						
170	171	172	173	174	175	176
			9a[b]			
3	44	6	46	1	0	
			9b[c]			
4	23	25	12	28	6	1

m/e					
111	112	113	114	115	116
			9a		
1	3	90	0	6	0
			9b		
0	2	14	77	0	6

[a] Corrected for ^{13}C isotopic contributions; all values in per cent; each peak normalized to 100%; reproducibility ±1%. [b] 2-(3′-Hydroxypropyl)-4,4-dimethyltetrahydropyran. [c] 2-(3′-Hydroxypropyl)-4,4-dimethyltetrahydropyran-2-*d*.

(9) Based on the extent of deuterium incorporation during steroidal sapogenin reductions (see ref 2b) this assumption seems reasonable.

Perhaps either the orbital overlap is different,[10] thus making the exchange transition state more favored in the sapogenin system, or the rate of fragmentation to exchange is increased in the case of alcohol **9b**.

The preceding results clearly established that lithium aluminum hydride–aluminum chloride reduction of spiroketal **8** proceeds by transfer of hydride from the reagent directly to C-2 of the tetrahydropyran ring and that the direction of ring opening is opposite to that experienced with spiroketals of the steroidal sapogenin type. Unless the geminal dimethyl group of spiroketal **8** introduces an unusual steric effect, it seems apparent that the direction of reductive ring opening in spiroketals related to **8** may generally involve the tetrahydrofuran ring. At this point it would seem that the pronounced steric compression usually associated with substituted steroid D rings may account for the course of steroidal sapogenin spiroketal ring opening and that the new reaction course described herein for spiroketal **8** may more generally be applicable. On this basis, lithium aluminum hydride–aluminum chloride reduction of spiroketals related to **8** may present a new synthetic route to otherwise difficulty accessible tetrahydropyrans. Extension of this study to the parent 1,6-dioxaspiro[4.5]decane and other spiroketal systems should prove of interest.

Experimental Section

All solvents and boron trifluoride etherate were redistilled. Lithium aluminum hydride and lithium aluminum deuteride were used as supplied by the Metal Hydrides Division of Ventron Corporation. Solvent extracts of aqueous solutions were dried over sodium sulfate and concentrated under reduced pressure on a rotary evaporator. Merck (Rahway) "suitable for chromatography" alumina was used for column chromatography. Analytical thin-layer chromatography (tlc) plates were prepared using silica gel G or silica gel HF254 (Merck, Darmstadt). Development was effected by spraying with chromic acid or using ultraviolet light. Boiling points and melting points (Kofler hot stage apparatus) are uncorrected. Each analytical sample was colorless and exhibited a single spot upon thin-layer chromatography. The infrared (Beckman IR-12) and proton magnetic resonance (Varian A-60, tetramethylsilane internal standard) spectra were determined by Miss K. Reimer. The low-resolution mass spectra were determined (by R. Scott and E. Beebe) employing an Atlas CH4B mass spectrometer equipped with a molecular beam direct inlet system and the Atlas SMIB double focusing instrument was used for accurate mass measurements. Elemental microanalyses were provided by Dr. A. Bernhardt, Mikroanalytisches Lab., Engelskirchen, West Germany.

Ethyl α-(4,4-Dimethyl-2,4-dioxocyclohexyl)acetate (4a). By employing the general procedure of Stetter[5] and Rosenmund,[4] dimedone (**3**, 236 g) was added to a solution of sodium (39 g) in dry ethanol (360 ml) and treated with ethyl bromoacetate (282 g). The resulting colorless product (124 g) was collected and dried, mp 93–106°. One recrystallization from water gave 85 g (22%) of colorless needles: mp 112–114° (lit.[5] 110.5°); ir (KBr) 1745, 1650, 1568, 1260, 1215, and 1185 cm^{-1}; pmr ($CDCl_3$) δ 1.12 (s, 6), 1.25 (t, 3, J = 7 Hz), 2.39 (s, 4), 3.38 (s, 2), 4.14 (q, 2, J = 7 Hz), 10.36 ppm (s, 1, –OH).

α-(4,4-Dimethyl-2,6-dioxocyclohexyl)acetic Acid (4b). Ethyl ester **4a** (85 g) was heated in refluxing concentrated hydrochloric acid (170 ml) for about 20 hr. Upon cooling, the colorless solid which precipitated (32 g) was collected by filtration, washed with water, and recrystallized from water to give acid **4b**: mp 198–202° (lit.[4] 199°); ir (KBr) 1710, 1650, and 1580 cm^{-1}; pmr (K_2CO_3–D_2O) δ 1.01 (s, 6), 2.27 (s, 4), 3.11 ppm (s, 2); mass spectrum (70 eV) m/e (rel intensity) 198 (26, M^+), 180, (100), 124 (56), 98 (51), 83 (64), 55 (67).

4-Oxo-6,6-dimethyloctanedioic Acid (5a). The aqueous filtrate obtained above (when acid **4b** was isolated) was extracted with ether. The organic layer was washed with water and solvent removed to yield diacid **5a**. Further reaction of acid **4b** with concentrated hydrochloric acid produced an additional amount of diacid **5a**. This procedure was repeated until essentially no starting material (**4b**) was isolated. One recrystallization of the combined product from ether–ligroin (30–60°) gave 64 g (72%) of diacid **5a**; mp 70–75°. Further recrystallization from the same solvent afforded an analytical sample: mp 74–77°; ir (KBr) 1725 and 1710 cm^{-1}; pmr ($CDCl_3$) δ 1.12 (s, 6), 2.49 (s, 2), 2.65 (m, 6, br), 11.43 ppm (s, 2).

Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.43; H, 7.28.

Dimethyl 4-Oxo-6,6-dimethyloctanedioate (5b). Treatment of diacid **5a** (500 mg) with an excess of freshly distilled diazomethane in ether gave 560 mg of a colorless liquid. Distillation of a sample at 85° (bath) and 0.2 mm produced an analytical sample: ir (CCl_4) 1745, 1730, 1230, and 1180 cm^{-1}; pmr ($CDCl_3$) δ 1.10 (s, 6), 2.45 (s, 2), 2.62 (m, 6, br), 3.63 (s, 3), 3.67 ppm (s, 3); mass spectrum (70 eV) m/e (rel intensity) 244 (6, M^+), 231 (27), 181 (35), 157 (100), 130 (31), 115 (98).

Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.06; H, 8.18.

Diethyl 4-Oxo-6,6-dimethyloctanedioate (5c). A solution prepared from diacid **5a** (2.2 g), ethanol (20 ml), and concentrated hydrochloric acid (1 ml) was heated at reflux for 2.5 hr. After cooling to room temperature, the mixture was extracted with ether. The combined extract was washed with 1% sodium bicarbonate and water. Removal of solvent gave 2.3 g (81%) of liquid diester **5c**. An analytical sample was obtained by distillation: bp 130° (bath) (0.2 mm); ir (CCl_4) 1740, 1375, and 1190 cm^{-1}; pmr ($CDCl_3$) δ 1.12 (s, 6), 1.25 (t, 6, J = 7 Hz), 2.44 (s, 2), 2.65 (m, 6, br), 4.13 (q, 2, J = 7 Hz), 4.15 ppm (q, 2, J = 7 Hz).

Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.58; H, 9.05.

Diethyl 6,6-Dimethyloctanedioate 4-Ethylene Thioketal (6). Method A. From 4-Oxo-6,6-dimethyloctanedioic Acid (5a). A mixture of diacid **5a** (64 g), absolute ethanol (200 ml), and boron trifluoride etherate (70 ml) was heated at reflux for 2.5 hr. To the solution was added 1,2-ethanedithiol (50 ml) and an additional 80 ml of boron trifluoride etherate. After heating at reflux for 4 hr, the mixture was stirred at room temperature for about 4 days, poured into aqueous bicarbonate, and allowed to stand for 1 hr. When the pH was adjusted to 9 with sodium hydroxide (cooling with ice) a colorless solid separated and was removed by filtration. The filtrate was extracted with ether (4 × 200 ml) and the extract was washed with aqueous sodium hydroxide and water. Removal of the solvent yielded a viscous oil that was shown by vapor phase chromatography to still contain about 20% keto diester **5c**. Another treatment of the crude product with 1,2-ethanedithiol–boron trifluoride etherate gave no improvement in composition. The final yield was 82 g of viscous oil. Chromatography on activated alumina (1700 g) and elution with carbon tetrachloride–chloroform (6:1) afforded 57 g (55%) of diester thioketal **6** (light yellow oil), which displayed only one spot on tlc (acetone–carbon tetrachloride, 1:5). Distillation gave a colorless sample: bp 120° (bath) (0.014 mm); ir (CCl_4) 1743, 1375, and 1185 cm^{-1}; pmr ($CDCl_3$) δ 1.20 (s, 6), 1.25 (t, 6, J = 7 Hz), 2.25 (s, 2), 2.45 (s, 2), 2.52 (m, 4, br), 3.30 (s, 4), 4.07 ppm (q, 4, J = 7 Hz).

Anal. Calcd for $C_{16}H_{24}O_2S_2$: C, 55.14; H, 8.10. Found: C, 55.03; H, 7.88.

The analytical sample did not give acceptable elemental analytical data for sulfur. Values for sulfur ranged from about 1% low to 6% high.

Method B. From Diethyl 4-Oxo-6,6-dimethyloctanedioate (5c). To diketo diester **5c** (300 mg) was added 1,2-ethanedithiol (1 ml) and boron trifluoride etherate (2 ml). After standing at room temperature for 1 hr, the mixture was diluted with ether and washed with saturated sodium bicarbonate and water. Removal of the solvent gave 230 mg (60%) of ethylene thioketal **6**. Comparison of infrared and pmr spectra, as well as tlc and vapor phase chromatographic behavior, demonstrated that this product was identical with the ester **6** obtained directly from diacid **5a**.

9,9-Dimethyl-1,6-dioxaspiro[4.5]decane (8). Diester ethylene thioketal **5c** (3.6 g) in ether (120 ml) was added over 5 min to a stirred mixture (ice bath) of lithium aluminum hydride (1 g) in

(10) A similar argument is used by B. E. Legetter, U. E. Diner, and R. K. Brown (*Can. J. Chem.*, **42**, 2113 (1964)) to explain the preference for six-membered ring opening in sapogenin spiroketal systems. These chemists suggested that the direction of ring opening of the sapogenin spiroketal is based on a greater degree of p-orbital overlap between the developing empty p orbital of the carbon atom and the p orbital of the adjacent oxygen atom in the five-membered ring over that in the six-membered ring.

ether (100 ml). After stirring for an additional 20 min, water was cautiously added; the solution was filtered, and the water layer was separated. The ethereal phase was washed with 2 *N* sodium hydroxide and water. Removal of solvent gave 2.2 g (81%) of liquid 6,6-dimethyl-1,8-octanediol 4-ethylene thioketal (**7a**) which was used without further purification as follows. To diol ethylene thioketal **7a** (1.0 g) in acetone (30 ml) was added cadmium carbonate (2.0 g) followed by mercuric chloride (1.0 g). The mixture immediately became yellow and tlc indicated that all starting material had been replaced by a less polar product. After solid material was removed (filtration), the acetone was evaporated. The residue was dissolved in chloroform and washed with aqueous potassium iodide and water. Removal of solvent at room temperature and distillation of the liquid product gave 0.23 g (36%) of spiroketal **8**: bp 60° (bath) (0.2 mm); ir (CCl_4) 1045 and 815 cm^{-1}; pmr ($CDCl_3$) δ 0.93 (s, 3), 1.15 (s, 3), 1.30 (m), 1.54 (s), 1.85 (m), 3.80 ppm (m, 4); mass spectrum (rel intensity), 171 (M + 1, 11), 170 (52), 169 (3), 156 (12), 155 (82), 152 (7), 148 (10), 147 (8), 142 (7), 140 (20), 139 (3), 138 (2), 137 (29), 130 (2), 129 (48), 127 (3), 126 (19), 125 (49), 114 (20), 113 (43), 112 (19), 111 (36), 109 (4), 105 (5), 98 (8), 97 (2), 96 (3), 95 (4), 93 (4), 91 (5), 89 (3), 88 (29), 87 (100), 86 (51), 85 (29), 84 (86), 83 (33), 81 (4), 79 (5), 77 (6), 72 (9), 71 (14), 70 (16), 69 (88), 68 (18), 67 (20), 59 (12), 58 (8), 57 (22), 56 (91), 55 (48), 54 (25), 53 (15), 45 (31), 44 (22), 43 (56), 42 (30), 41 (56), 40 (22), 39 (33).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 70.43; H, 10.53.

2-(3′-Hydroxypropyl)-4,4-dimethyltetrahydropyran (9a). To a stirred mixture of lithium aluminum hydride (0.50 g) and aluminum chloride (6 g) in dry ether (100 ml) at room temperature was added (5 min) spiroketal **8** (0.23 g) in 20 ml of ether. The reaction mixture was maintained at room temperature 1.5 hr and heated at reflux for 30 min. Water and 6 *N* hydrochloric acid were cautiously added until two clear layers appeared. The ether layer was separated and washed with saturated sodium bicarbonate and water. Removal (*in vacuo*) of solvent afforded a quantitative yield of alcohol **9a** as a clear liquid. Distillation gave an analytical sample: bp 54° (bath) (0.014 mm); ir (CCl_4) 3440, 1112, and 1075 cm^{-1}; pmr ($CDCl_3$) δ 0.97 (s, 3), 1.02 (s, 3), 1.40 (m, 8, br), 3.60 (m, 5, br), 4.15 ppm (s, 1, br); mass spectrum (see Table I).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.55; H, 12.03.

2-(3′-Hydroxypropyl)-4,4-dimethyltetrahydropyran-2-*d* (9b). Deuteration of alcohol **9a** was accomplished using lithium aluminum deuteride in place of the hydride as described in the preceding experiment. The product **9b** boiled at 70° (bath) (0.03 mm); ir (neat) 3400, 2100, 1075, and 1050 cm^{-1}; pmr ($CDCl_3$) δ 0.97 (s, 3), 1.02 (s, 3), 1.40 (m, 8, br), 2.70 (m, 1, br), 3.65 ppm (m, 4).

An Analysis of Ketene Cycloadditions by Self-Consistent Perturbation Theory

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Abstract: The significance of the carbonyl group in ketene and the influence of substituents in ketenophiles are investigated by self-consistent perturbation theory (MINDO and CNDO/2 approximation) and by a variation perturbation treatment which is based on SCF wave functions (CNDO/2 approximation). The stabilization through the interaction of the ketenophile π system with the carbonyl π bond plays a dominant role in the orthogonal ($_\pi 2_s$ + $_\pi 2_a$) approach of the two reactants. This interaction is also responsible for the addition at the carbon–carbon double bond compared to a reaction at the carbonyl group of ketene. The high reactivity of "electron rich" and unsymmetrical ketenophiles is explained by the stabilization through the interaction with the unoccupied carbonyl π orbital and by electrostatic interactions.

The interpretation of ketene cycloadditions in terms of orbital symmetry remained controversial for several years. However, the formulation as a ($_\pi 2_s$ + $_\pi 2_a$) process[1] together with the subsequent experimental proof of the orthogonal approach by stereochemical investigations[2-4] and kinetic data[5] seemed to provide a satisfactory explanation. The concerted nature of the reaction which should be an attribute of the ($_\pi 2_s$ + $_\pi 2_a$) process was proven for several cases.[5-7]

Although the carbonyl group of ketene forms the arrowhead of the reaction, as is pointed out by Woodward and Hoffmann,[1] this qualitative picture does not elucidate its significance for the ($_\pi 2_s$ + $_\pi 2_a$) reaction path. Furthermore, there is no *a priori* reason why the cycloaddition normally occurs at the carbon–carbon double bond and not at the carbonyl group. Thermal (2 + 2) cycloadditions of carbonyl groups to olefins and acetylenes are known.[8,9] It was found only recently that the cumulated double bond of carbon dioxide adds to ynamines.[10] Cycloaddition at the carbonyl group was observed for the reaction of bis(trifluoromethyl)ketene with enol ethers or enol esters,[11] for diphenylketene with ynamines,[12] for ethoxyketene with cyclohexene,[13] and for the reaction of ketene with tetramethoxyethylene.[14] Another poorly understood aspect of this

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