this reaction, isomerization of the 1,4-dienes to 2,4-isomers proceeded at a higher reaction temperature, and the second molecule of ethylene added to the conjugated dienes to yield C_9-dienes. As the isomerization increased, more of the 4-methyl isomer was found in the product. It indicated that the 5-methyl isomer was apt to isomerize to the conjugated isomer more easily than the 4-methyl isomer did. Careful control of the reaction temperature is desirable to obtain methyl-1,4-hexadienes selectively.

Experimental Section

Reaction of Butadiene with Ethylene.—A 200-ml pressure vessel equipped with a magnetic stirrer was charged with 50 ml of 1,2-dichloroethane, 33.5 g of liquefied butadiene, 0.09 g of cobaltous chloride–1,2-bis(diphenylphosphino)ethane complex, and 0.456 g of pure triethylaluminum and then was tightly closed. After the temperature was raised to 80°, ethylene was injected directly from a cylinder to a pressure of 40 kg/cm^2 and the pressure was held constant for 2 hr. A remarkable absorption of ethylene was observed during the first 0.5 hr. After cooling to room temperature, unreacted ethylene was vented and the catalyst was deactivated by adding a small quantity of methanol, and then the reaction mixture was washed with water containing a small amount of hydrochloric acid. A distillation of the organic phase was performed at atmospheric pressure. The distillate taken up to a bath temperature of 200° was assayed by vpc (relative peak areas) with toluene as an internal standard (Apiezon Grease L packing column 3 m, 100°), and 0.22 g of 1,4-hexadiene, 2.8 g of 2,4-hexadiene, and 38.3 g of a major product were found. Further, analysis by vpc using a 5-m, paraffin wax coated column showed that the main product consisted of two components. Each of the two components was purified by preparative vpc. Since both components showed the same molecular peak at *m/e* 110 in the mass spectra, they should be C_8-dienes. The characteristic absorptions of the terminal double bond, *cis* unsaturation, methyl group, and nonconjugated system were shown in the infrared spectra. Hydrogenation of the components gave a mixture of 3-methylheptane and 3-ethylhexane, which were identified by their mass spectral cracking patterns. From these data it was concluded that two kinds of C_8-diene were 3-methyl-1,4-heptadiene and 3-ethyl-1,4-hexadiene. Proton nmr spectra were consistent with these structures.

Reaction of 1,4-Hexadiene with Ethylene.—Reactions of 1-*cis*-4-hexadiene with ethylene were carried out in a manner similar to that described above. A mixture of 56 g of 1,4-hexadiene, 0.24 g of the cobalt complex, and 1.5 g of triethylaluminum was charged into the vessel. At various reaction temperatures, a series of reactions was carried out for 2 hr under a constant ethylene pressure of 40 kg/cm^2. The results are shown in Table I.

Isomerization of 1,4-Hexadiene.—A 2-l. pressure vessel was charged with 1 kg of 1-*cis*-4-hexadiene, 2 g of the cobalt complex, and 12.5 g of triethylaluminum. The temperature was raised to 150° during 3.5 hr and was kept there for an additional 4 hr. The product consisted of 0.7% of 1,4-hexadiene, 2.1% of 1,3-isomer, and 97.2% of the 2,4-isomer which was fractionally distilled under atmospheric pressure to give the 2,4-isomer of 99.8% purity. The 2,4-isomer thus obtained contained three structural isomers and their proportion was slightly varied with the reaction conditions. In order to determine the proportion, analysis by vpc using a column packed with benzylcyanide-silver nitrate coated on Celite 545 was carried out at 35°.

Reaction of 2,4-Hexadiene with Ethylene.—A mixture of 56 g of 2,4-hexadiene, 0.24 g of the cobalt complex, and 1.5 g of triethylaluminum was charged into the vessel and then ethylene was injected at a pressure of 40 kg/cm^2. The reaction was carried out at 100° for 19 hr. After a work-up similar to that already described, 48.6 g of a distillate, bp 80–130°, was obtained. The distillate gave 28.1 g of the C_8-dienes, which consisted of 84.2% of 3-methyl-1,4-heptadiene and 15.8% of 3-ethyl-1,4-hexadiene.

Preparation of 1,3-Hexadiene.—To dried ethanol, deoxygenated and saturated with butadiene in the 2-l. autoclave, 6.4 g of cobaltous nitrate hexahydrate and 3.8 g of sodium borohydride were added and dissolved. About 400 g of butadiene was condensed into the autoclave. Under 60 kg/cm^2 of ethylene pressure at 60°, reaction was carried out for 17.5 hr. The reaction mixture consisted of C_6-dienes and linear dimers of butadiene. 1,3-Hexadiene of 96.5% purity was obtained by a rectification through 1.5-m packed column.

Reaction of 1,3-Hexadiene with Ethylene.—The reaction mixture consisted of 50 ml of toluene, 15 g of the 1,3-hexadiene, 0.24 g of the cobalt complex, and 1.5 g of triethylaluminum which were charged into the vessel. The reaction was carried out under 40 kg/cm^2 of ethylene pressure at 80° for 18.5 hr. The C_8-dienes thus obtained consisted of 3.3% of 3-methyl-1,4-heptadiene and 96.7% of 3-ethyl-1,4-hexadiene.

Reaction of Butadiene with Propylene.—The reaction vessel was charged with 20 ml of 1,2-dichloroethane, 0.08 g of the cobalt complex, 0.83 g of triethylaluminum, 22.8 g of butadiene, and 28 g of propylene. The temperature was raised to 80° and was held there for 5 hr. After the similar work-up, the diene fraction obtained by 1,1 addition was composed of three components. They were separated by preparative vpc, and a major product which was 84.7% of the fraction, was identified by infrared and mass spectra as 2-methyl-1,4-hexadiene. Two minor components were identified, by means of infrared and mass spectra and hydrogenation over a palladium catalyst, as *n*-heptadiene (10.8%) and 2-methyl-1,3-hexadiene (4.8%).

Reaction of Isoprene with Ethylene.—In a similar manner described above, a mixture of 20 ml of 1,2-dichloroethane, 102 g of isoprene, 0.08 g of the cobalt complex, and 0.83 g of triethylaluminum was treated under 40 kg/cm^2 of ethylene pressure at 100°. Immediately, a reaction was started and a vigorous absorption of ethylene and a rapid rise of the reaction temperature were occurred. A good control of the reaction temperature is needed in order to obtain a selective formation of methyl-1,4-hexadiene. After the work-up, a fraction containing 67.9 g of methyl-1,4-hexadienes and 5.6 g of conjugated dienes was separated. A conversion based on the charged isoprene was 51%. Analysis of the isomer content of methyl-1,4-hexadienes by vpc using a column packed with benzylcyanide-silver nitrate on Celite 545 at 45° showed that 4-methyl-1,4-hexadiene in this example was 81.3%. The results are shown in Table II.

The Reaction of Di-*n*-butylcadmium with Derivatives of Ketal Acids[1]

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Perhaps no other method of ketone preparation has the scope of the method utilizing organocadmium reagents in their reaction with acid chlorides[2] or mixed carboxylic–carbonic anhydrides.[3] However, treatment of either the acid chloride or the mixed carboxylic–carbonic anhydride I from 2-methyl-2-(3-carboxyethyl)-1,3-dioxolane[4] with di-*n*-butylcadmium gave only the dioxocane derivative II and none of the expected ketone I (R = n-C_4H_9). The structure of II is based on the infrared spectrum (5.75 μ), the nmr spectrum (a two-hydrogen multiplet centered at τ 5.64 for $-CH_2O\overset{|}{C}{=}O$ and a two-hydrogen multiplet centered at τ 6.38 for $-OCH_2-$), and the elemental analysis. Basic hydrolysis of II followed by esterification with diazomethane gave the hydroxy ester III while hydrolysis with 3 *N*

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[1] Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

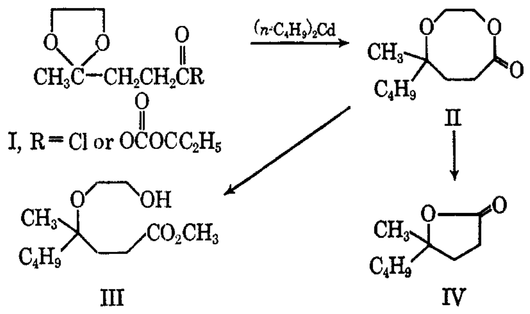
[2] J. Cason, *Chem. Rev.*, **40**, 15 (1947).

[3] D. S. Tarbell and J. A. Price, *J. Org. Chem.*, **22**, 245 (1957).

[4] C. K. Warren and B. C. L. Weedon, *J. Chem. Soc.*, 3979 (1958).

hydrochloric acid proceeded with cleavage to γ-butyl-γ-valerolactone (IV) (Scheme I).

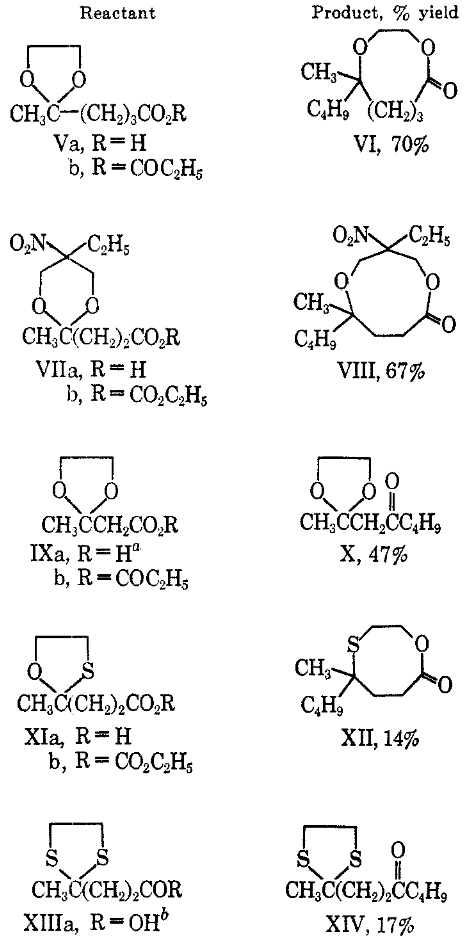
SCHEME I



The acid cleavage probably proceeds by lactone hydrolysis, cleavage of the tertiary ether linkage, and relactonization of the unsaturated acid.

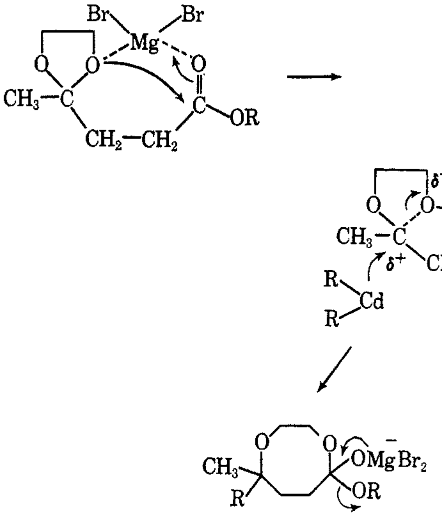
Additional work which concerns the scope of this reaction is reported in Chart I.

CHART I



[a] Compound IXa was prepared as described by L. Willimann and H. Schinz, *Helv. Chim. Acta*, **32**, 2161 (1949). [b] Compound XIIIa was prepared as described by J. F. Harris, Jr., U. S. Patent 2,839,445 (1958). All other compounds are described in the Experimental Section.

The initial step in the formation of these lactones could be bond formation between the oxygen of the ketal and the carbonyl carbon. This may be thought to arise through complexing of the ketal and the carbonyl oxygen with magnesium bromide. The positive charge can be spread over oxygen and carbon by partial breaking of the carbon–oxygen bond of the ketal, and attack by the dialkylcadmium reagent leads to the observed product. Evidently bond formation between the ketal oxygen and the carbonyl carbon must occur before the carbon–oxygen bond of the ketal is broken in order to explain formation of the large ring. It is significant that IXb gave the ketone X as the only isolable product.



In this case attack of the ketal oxygen on the carbonyl would lead to a four-membered-ring transition state and apparently the strain involved is prohibitive.

In view of a recent publication on the activating effect of magnesium salts in organocadmium reactions,[5] it seemed desirable to determine if they were also essential for these reactions. Treatment of the mixed carboxylic-carbonic anhydride I with commercially available salt-free dimethylcadmium gave only the ketal ester I ($R = OC_2H_5$). This type of reaction has been observed earlier during the attempted acylation of alcohols by mixed anhydrides.[3] In the presence of magnesium bromide, I reacted with dimethylcadmium to give a 37% yield of the methyl analog of dioxocane II. An identical yield was obtained with dimethylcadmium prepared *in situ*.

That this reaction could be extended to the preparation of nine-membered ring lactones was shown by formation of VI and VIII in good yield. Acid cleavage of VI yielded δ-butyl-δ-caprolactone while VIII gave γ-butyl-γ-valerolactone (IV).

Hemithioketal XIb gave the oxathiolane XII in much lower yield along with a considerable amount of nonvolatile material. The structure of XII is based on the infrared spectrum (5.78 μ) and the nmr spectrum (a two-hydrogen triplet centered at τ 5.53 for $-CH_2O\overset{|}{C}{=}O$ and a two-hydrogen triplet centered at τ 7.24 for $-CH_2S-$). No thiolactone could be detected as a reaction product. Cleavage of XII with 3 *N* hydrochloric acid solution also gave γ-butyl-γ-valerolactone (IV). The failure to obtain any thio lactone from XIb may be due to instability of the thio lactone in the reaction mixture. Hydrogens α to a thio ester are known to be more acidic than those α to a carbethoxy group, and ethyl thioacetate undergoes the Claisen condensa-

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[5] J. Kollonitsch, *J. Chem. Soc., Sect. A*, 453 (1966).

tion with isopropylmagnesium bromide.[6] The nonvolatile material formed on treatment of XIb with dibutylcadmium may also be due to Claisen condensation products.

The only isolable product from dithioketal XIIIb was ketone XIV ($\lambda_{max}^{CHCl_3}$ 5.84 μ; four-hydrogen singlet at τ 6.68 for thioketal hydrogens in the nmr spectrum), and the yield was again very low.

Experimental Section[7]

2-(3-Carboxypropyl)-2-methyl-1,3-dioxolane (Va).—Ethyl-γ-acetylbutyrate was prepared as described,[8] ketalized,[9] and hydrolyzed with 5 *N* sodium hydroxide to give the ketal acid (Va): bp 105–112° (0.4 mm); $\lambda_{max}^{CHCl_3}$ 5.83 μ; nmr ($CDCl_3$) 4 H singlet at τ 6.08 ($-OCH_2CH_2O-$), 3 H singlet at 8.69 ($CH_3\overset{|}{C}<$).

2-(2-Carboxyethyl)-5-ethyl-2-methyl-5-nitro-1,3-dioxolane (VIIa).—The corresponding ethyl ester was prepared as described[10] and hydrolyzed with 5 *N* sodium hydroxide to give the ketal acid VIIa: mp 134.5–136° (from ether); $\lambda_{max}^{CHCl_3}$ 5.81 and 6.43 μ; nmr ($CDCl_3$) 2 H doublet (J = 12 cps) centered at τ 5.42 ($-OCH_2\overset{|}{C}<$), 2 H doublet (J = 12 cps) centered at 6.10 ($-OCH_2\overset{|}{C}<$), 3 H singlet at 8.58 ($CH_3\overset{|}{C}<$), 3 H triplet at 9.13 ($\mathit{CH_3}CH_2-$).

Anal. Calcd for $C_{10}H_{17}O_6N$: C, 48.58; H, 6.93; N, 5.67. Found: C, 48.94; H, 6.63; N, 6.04.

2-(2-Carboxyethyl)-2-methyl-1,3-oxathiolane (XIa).—Ethyl levulinate (72.1 g, 0.5 mole), 2,2-dimethyl-1,3-oxathiolane (288.7 g, 2.4 mole), and *p*-toluenesulfonic acid monohydrate (0.64 g) were stirred and heated under a partial takeoff head for 16 hr during which time the acetone (31 ml) was removed as it was formed. The excess 2,2-dimethyl-1,3-oxathiolane was removed at reduced pressure, and the residual liquid was taken up in ether and filtered to remove the solids. After washing with 5% sodium bicarbonate, the organic layer was dried ($MgSO_4$), concentrated at reduced pressure, and distilled to yield 68.7 g (67%) of the hemithioketal ester: bp 79–84° (0.5 mm); $n^{28}D$ 1.4783; $\lambda_{max}^{CHCl_3}$ 5.79 μ. The hemithioketal ester (40.74 g), 47 ml of 5 *N* sodium hydroxide, and 50 ml of methanol were combined and refluxed 30 min. Water (20 ml) was added, and reflux was continued for 1 hr. The reaction mixture was evaporated to dryness at reduced pressure, and 100 ml of water was added. After acidification to pH 2, the product was extracted with ether. Concentration of the dried ether extract gave an oil (33.86 g, 95%) which crystallized on cooling: mp 67.5–69°; $\lambda_{max}^{CHCl_3}$ 5.84 μ; nmr ($CDCl_3$) 2 H multiplet centered at τ 5.87 ($-O\mathit{CH_2}CH_2S-$), 2 H multiplet centered at 6.93 ($-S\mathit{CH_2}CH_2O-$), 3 H singlet at 8.40 ($CH_3\overset{|}{C}<$).

Anal. Calcd for $C_7H_{12}O_3S$: C, 47.70; H, 6.88; S, 18.19. Found: C, 47.82; H, 6.77; S, 18.01.

Preparation of Mixed Carboxylic–Carbonic Anhydrides.—The procedure of Tarbell and Leister[11] was followed, and the crude products obtained (after filtration of triethylamine hydrochloride and removal of solvent) were used directly. All mixed carboxylic–carbonic anhydrides prepared gave the typical anhydride double peaks at 5.48–5.52 and 5.66–5.70 μ in the carbonyl region of the infrared spectrum.

General Procedure for Dibutylcadmium Reactions.—Butylmagnesium bromide was prepared by addition of 15.07 g (0.11 mole) of butyl bromide in 50 ml of anhydrous ether to 2.43 g (0.10 g-atom) of magnesium under a nitrogen atmosphere. After complete reaction of the magnesium, the Grignard solution was cooled in an ice bath and stirred vigorously during the portionwise addition of 12.10 g (0.066 mole) of cadmium chloride (predried in an oven at 110°) over 15 min. Following 30 min of reflux, the Gilman test was negative. The ether was removed in a stream of nitrogen and replaced with 50 ml of anhydrous benzene. After the solution was cooled in an ice bath, the mixed carboxylic–carbonic anhydride or acid chloride (0.05 mole) in 25 ml of anhydrous benzene was added dropwise with vigorous stirring over 1 hr. Stirring was continued at room temperature for 15 hr, and the reaction mixture which contained a heavy precipitate was hydrolyzed by addition of 0.10 equiv of dilute sulfuric acid with ice bath cooling. The organic layer was separated and the aqueous layer was extracted with two 50-ml portions of ether. The combined organic layers were washed with two 50-ml portions of 5% sodium bicarbonate, dried ($MgSO_4$), concentrated under reduced pressure, and distilled.

8-*n*-Butyl-8-methyl-1,4-dioxocan-5-one (II).—Butylmagnesium bromide (from 9.96 g (0.41 g-atom) of magnesium), 49.84 g (0.27 mole) of cadmium chloride, and 47.72 g (0.205 mole) of mixed anhydride I gave 19.92 g (49%) of dioxocane II: bp 82–87° (0.13 mm); $n^{28}D$ 1.4609; $\lambda_{max}^{CHCl_3}$ 5.75 μ; nmr ($CDCl_3$) 2 H multiplet centered at τ 5.64 ($-CH_2O\overset{|}{C}{=}O$), 2 H multiplet centered at 6.38 ($-CH_2O-$), 3 H singlet at 8.84 ($CH_3\overset{|}{C}<$), broad 3 H triplet at 9.09 ($\mathit{CH_3}CH_2-$).

Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.80; H, 10.03.

9-*n*-Butyl-9-methyl-1,4-dioxonan-5-one (VI).—Butylmagnesium bromide (from 3.40 g (0.14 g-atom) of magnesium), 15.80 g (0.986 mole) of cadmium chloride, and 17.62 g (0.072 mole) mixed anhydride Vb gave 11.85 g (71%) of dioxonane VI: bp 78–83° (0.20 mm); $n^{30}D$ 1.4613; $\lambda_{max}^{CHCl_3}$ 5.75 μ; nmr ($CDCl_3$) 2 H multiplet centered at τ 5.70 ($-CH_2O\overset{|}{C}{=}O$), 2 H multiplet centered at 6.43 ($-CH_2O-$), 3 H singlet at τ 8.88 ($CH_3\overset{|}{C}<$), broad 3 H triplet centered at 9.10 ($\mathit{CH_3}CH_2-$).

Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 66.99; H, 10.22.

9-*n*-Butyl-3-ethyl-9-methyl-3-nitro-1,5-dioxonan-6-one (VIII).—Butylmagnesium bromide (from 1.73 g (0.071 g-atom) of magnesium), 8.60 g (0.047 mole) of cadmium chloride, and 11.32 g (0.036 mole) mixed anhydride VIIb gave 6.44 g (67%) of dioxonane VIII: bp 120–130° (0.08 mm); $n^{26}D$ 1.4736; $\lambda_{max}^{CHCl_3}$ 5.71 and 6.45 μ; nmr ($CDCl_3$) 2 H multiplet centered at τ 5.22 ($-CH_2O\overset{|}{C}{=}O$), 2 H multiplet centered at 6.17 ($-CH_2O-$), 3 H singlet at 8.87 ($CH_3\overset{|}{C}<$).

Anal. Calcd for $C_{14}H_{25}O_5N$: C, 58.51; H, 8.77; N, 4.87. Found: C, 58.57; H, 8.37; N, 5.04.

2-Methyl-2-(2-oxohexyl)-1,3-dioxolane (X).—Butylmagnesium bromide (from 2.33 g (0.096 g-atom) of magnesium), 10.98 g (0.06 mole) of cadmium chloride, and 10.38 g (0.048 mole) of mixed anhydride IXb gave 4.49 g (47%) of ketone X: bp 60–70° (0.50 mm); $n^{30}D$ 1.4383; $\lambda_{max}^{CHCl_3}$ 5.84 μ; nmr ($CDCl_3$) 4 H singlet at τ 6.08 ($-OCH_2CH_2O-$), 2 H singlet at 7.28 ($-CH_2\overset{|}{C}{=}O$), 3 H singlet at 8.62 ($CH_3\overset{|}{C}<$), broad 3 H triplet centered at 9.12 ($\mathit{CH_3}CH_2-$).

Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.54. Found: C, 64.55; H, 9.54.

5-*n*-Butyl-5-methyl-1,4-oxathiolan-8-one (XII).—Butylmagnesium bromide (from 4.62 g (0.19 g-atom) of magnesium), 20.13 g (0.11 mole) of cadmium chloride, and 23.62 g (0.095 mole) of mixed anhydride XIb gave a first 5.12-g fraction (bp 68–97° (0.25 mm), $\lambda_{max}^{CHCl_3}$ 5.75 μ) which was shown to consist of three components by glpc on a 1% polyethylene glycol 4000 monostearate column. The component with the shortest retention time (8.4 min) comprised 46% of the mixture and was 2-(2-carbethoxyethyl)-2-methyl-1,3-oxathiolane (XI, R = C_2H_5). The nmr spectrum of the mixture exhibited a multiplet at τ 5.83, a multiplet at 6.92, a singlet at 8.40, and a triplet centered at 8.73; all of these peaks correspond to those in the pure hemithioketal ester. The component with a retention time of 9.8 min comprised 29% of the mixture and was not identified. The final component (25% of the mixture) had the same retention time (15.8 min) as pure oxathiolane XII. A higher boiling fraction contained 2.78 g (14%) of pure oxathiolane XII: bp 97–102° (0.18 mm); $n^{28}D$ 1.5001; $\lambda_{max}^{CHCl_3}$ 5.78 μ (thiolactones absorb at 5.97 μ); nmr ($CDCl_3$) 2 H triplet (J = 5 cps) centered at τ

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[6] M. W. Cronyn, M. P. Chang, and R. A. Wall, *J. Am. Chem. Soc.*, **77**, 3031 (1955).

[7] All melting points were taken in glass capillaries and are corrected. The infrared spectra were determined using a Beckman IR-9 spectrophotometer. The nmr spectra were determined using a Varian A-60 spectrometer with tetramethylsilane as the internal standard.

[8] H. Kappeler, D. Stauffacher, A. Eschenmoser, and H. Schinz, *Helv. Chim. Acta*, **37**, 957 (1954).

[9] R. I. Meltzer, A. D. Lewis, J. Volpe, and D. M. Lustgarten, *J. Org. Chem.*, **25**, 712 (1960).

[10] G. H. Morey, U. S. Patent 2,406,504 (1946).

[11] D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, **23**, 1149 (1958).

5.53 ($-CH_2O\overset{|}{C}=O$), 2 H triplet (J = 5 cps) centered at 7.24 ($-CH_2S-$), 3 H singlet at 8.72 ($CH_3\overset{|}{C}<$), broad 3 H triplet centered at 7.24 ($-CH_2S-$), 3 H singlet at 8.72 ($CH_3\overset{|}{C}<$), broad 3 H triplet centered at 9.07 (CH_3CH_2-).

Anal. Calcd for $C_{11}H_{20}O_2S$: C, 61.07; H, 9.33. Found: C, 60.81; H, 9.38.

2-Methyl-2-(3-oxoheptyl)-1,3-dithiolane (XIV).—Butylmagnesium bromide (from 1.26 g (0.056 g-atom) of magnesium), 6.09 g (0.033 mole) of cadmium chloride, and 5.27 g (0.025 mole) of acid chloride XIIIb gave 1.00 g (17%) of ketone XIV: bp 109–113° (0.15 mm); n^{24}D 1.5202; $\lambda_{\max}^{CHCl_3}$ 5.85 μ; nmr ($CDCl_3$) 4 H singlet at τ 6.68 ($-SCH_2CH_2S-$), 3 H singlet at 8.22 ($CH_3\overset{|}{C}<$), broad 3 H triplet centered at 9.08 (CH_3CH_2-).

Acid Cleavage of 8-*n*-Butyl-8-methyl-1,4-dioxocan-5-one (II).—A suspension of 0.5196 g of II in 10 ml of 3 N hydrochloric acid was heated on a steam bath for 2 hr. After saturation with salt, the product was extracted with three 15-ml portions of ether. The extract was washed with saturated sodium carbonate solution, dried ($MgSO_4$), concentrated at reduced pressure, and distilled to yield 0.176 g (48%) of γ-butyl-γ-valerolactone (IV): bp 60–65° (0.07 mm); n^{28}D 1.4426; $\lambda_{\max}^{CHCl_3}$ 5.67 μ. The infrared and nmr spectra as well as the glpc retention time were identical with those of the authentic compound prepared by the reaction of ethyl levulinate with butylmagnesium bromide.[12]

Base Hydrolysis of 8-*n*-Butyl-8-methyl-1,4-dioxocan-5-one (II).—A suspension of 0.991 g of II and 0.260 g of sodium hydroxide in 10 ml of water was refluxed 30 min. After cooling, the colorless solution was extracted with ether, and the aqueous layer was acidified with 6 N hydrochloric acid. The ether extract was dried ($MgSO_4$) and concentrated at reduced pressure to yield a colorless oil (0.916 g; $\lambda_{\max}^{CHCl_3}$ 2.78, 2.84, and 5.83 μ). Treatment with excess ethereal diazomethane gave 0.414 g of hydroxy ester III: bp 88–89° (0.05 mm); $\lambda_{\max}^{CHCl_3}$ 2.78 and 5.77 μ; nmr ($CDCl_3$) 3 H singlet at τ 6.33 ($-CO_2CH_3$), 2 H multiplet centered at 6.37 ($-CH_2OH$), 2 H multiplet at 6.58 ($-OCH_2-$), 1 H singlet (exchanged by D_2O) at 7.60 ($-OH$), 3 H singlet at 8.87 ($CH_3\overset{|}{C}<$), broad 3 H triplet centered at 9.08 (CH_3CH_2-).

Anal. Calcd for $C_{12}H_{24}O_4$: C, 62.04; H, 10.41. Found: C, 61.93; H, 10.32.

Acid Cleavage of 9-*n*-Butyl-9-methyl-1,4-dioxocan-5-one (VI).—A suspension of 3.00 g of VI in 60 ml of 3 N hydrochloric acid was stirred and refluxed for 2 hr. Work-up as above for II yielded 0.582 g of δ-butyl-δ-caprolactone: bp 73–76° (0.07 mm); $\lambda_{\max}^{CHCl_3}$ 5.82 μ; nmr ($CDCl_3$) 3 H singlet at τ 8.63 ($CH_3\overset{|}{C}<$), broad 3 H triplet at 9.17 (CH_3CH_2-). Acidification of the sodium carbonate wash yielded 0.884 g of an unsaturated acid: bp 83–90° (0.18 mm); $\lambda_{\max}^{CHCl_3}$ 5.86 μ; nmr ($CDCl_3$) τ 4.83 (broad, $>C=CH-CH_2-$). The unsaturated acid (56 mg) was stirred and refluxed for 24 hr with 5 ml of 20% sulfuric acid. Ether extraction yielded 36 mg of δ-butyl-δ-caprolactone which was identified by its infrared spectrum and retention time by vapor phase chromatography. Addition of butylmagnesium bromide to ethyl δ-acetylbutyrate at −10° gave authentic δ-butyl-δ-caprolactone: bp 74–75° (0.20 mm); n^{28}D 1.4562; $\lambda_{\max}^{CHCl_3}$ 5.82 μ. The nmr spectrum was identical with that of the product obtained by acid cleavage of VI.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.76; H, 10.53.

Acid Cleavage of 9-*n*-Butyl-3-ethyl-9-methyl-3-nitro-1,3-dioxonan-6-one (VIII).—A suspension of 0.973 g of VIII in 20 ml of 3 N hydrochloric acid was stirred and refluxed for 17 hr. Work-up as above yielded 0.103 g γ-butyl-γ-valerolactone (IV): bp 65–70° (0.06 mm); $\lambda_{\max}^{CHCl_3}$ 5.68 μ.

Acid Cleavage of 5-*n*-Butyl-5-methyl-1,4-oxathiolan-8-one (XII).—A suspension of 0.500 g of XII in 10 ml of 3 N hydrochloric acid was stirred and refluxed 2 hr. The usual work-up gave 0.037 g of γ-butyl-γ-valerolactone (IV); bp 70° (0.07 mm); $\lambda_{\max}^{CHCl_3}$ 5.68 μ. The infrared spectrum and the glpc retention time were identical with those of the authentic compound.

Reaction of Mixed Anhydride I with Dimethylcadmium.—A solution of 5.80 g (0.025 mole) of mixed anhydride I in 12 ml of anhydrous benzene was added dropwise with stirring to 3.5 g (0.025 mole) of pure dimethylcadmium (obtained from Orgmet Inc., Hampstead, N. H.) in 25 ml of anhydrous benzene. After stirring 15 hr at room temperature, the clear colorless solution was cooled in an ice bath during the dropwise addition of dilute sulfuric acid. The organic layer was separated, washed with 5% sodium bicarbonate solution, dried ($MgSO_4$), and concentrated under reduced pressure to yield 4.28 g of a colorless oil. Infrared and glpc analysis showed the product to be the ketal ester I (R = OC_2H_5).

8,8-Dimethyl-1,4-dioxocan-5-one.—Magnesium bromide was prepared by reaction of 14.10 g (0.075 mole) of 1,2-dibromoethane with 1.70 g (0.07 g atom) of magnesium in 40 ml of ether. The ether was removed in a stream of nitrogen and 3.5 g (0.025 mole) of pure dimethylcadmium in 30 ml of anhydrous benzene was added. A solution of 5.78 g (0.025 mole) of mixed anhydride I in 10 ml of benzene was then added dropwise at room temperature over a 15 min period. After stirring overnight at room temperature, the reaction mixture was cooled in an ice bath during the dropwise addition of dilute sulfuric acid. The organic layer was washed with 5% sodium bicarbonate, dried ($MgSO_4$), and concentrated under reduced pressure. Distillation yielded 1.46 g (37%) of a colorless liquid: bp 112–117° (20 mm); $\lambda_{\max}^{CHCl_3}$ 5.75 μ; nmr ($CDCl_3$) 2 H multiplet centered at τ 5.66 ($-CH_2O\overset{|}{C}=O$), 2 H multiplet centered at 6.42 ($-CH_2O-$), 6 H singlet at 8.83 ($(CH_3)_2C<$)).

Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.40; H, 8.92.

Registry No.—II, 14734-32-8; III, 14734-44-2; IV, 3285-00-5; Va, 5694-89-3; VI, 14734-43-1; VIIa, 14734-35-1; VIII, 14734-36-2; X, 14734-37-3; XIa, 14734-38-4; XII, 14746-17-9; XIV, 14734-39-5; δ-butyl-δ-caprolactone, 14734-40-8; 8,8-dimethyl-1,4-dioxocan-5-one, 14734-41-9; di-*n*-butylcadmium, 3431-67-2.

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Nonplanar Cyclobutane. Temperature Dependence of Infrared Spectra of *cis*- and *trans*-Methyl 3-Isopropylcyclobutanecarboxylate

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We have recently reported the basic equilibration of *cis*- and *trans*- methyl 3-isopropylcyclobutanecarboxylate and discussed the conformational implications in terms of cyclohexane analogies.[1] In such terms, the greater thermodynamic stability of the *cis* isomer may be ascribed to the difference between an equatorial and axial carboalkoxy group in a homogeneously puckered cyclobutane. K_{equil} would thus represent a *cis* (e,e) $\rightleftharpoons$ *trans* (e,a) $\rightleftharpoons$ (a,e) equilibrium. However, a comparison of ΔF and K_{equil} values for this system and its 3-methyl analog[2] with corresponding values for alkyl-

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