[Contribution from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co.]

Chemistry of Allene. IV. Carbonylation Reactions of Allene

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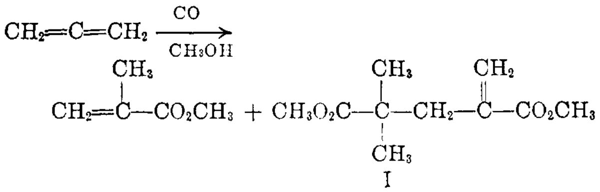
The carbonylation of allene in water in the presence of ruthenium catalysts has given methacrylic acid. Derivatives of methacrylic acid were obtained when the reaction was conducted in the presence of methanol or amines. Under certain conditions a lactone, 3-hydroxy-1,3,4-trimethylcyclohexanecarboxylic acid lactone, or an ester, dimethyl α,α-dimethyl-α'-methyleneglutarate, were the major products of the carbonylation reaction in water and methanol, respectively.

This paper reports the results of continued study of reactions of allene that are catalyzed by transition metal derivatives. It was previously found that certain nickel carbonyl compounds catalyze the cyclopolymerization of allene to a mixture of 1,2,4- and 1,3,5-trimethylenecyclohexanes,[1] and that nickel acetylacetonate catalyzes its reaction with acetylene to yield 3,5-dimethylenecyclohexene.[2,3] The present paper describes the reactions of allene with carbon monoxide and various third components in the presence of diruthenium nonacarbonyl and ruthenium chloride catalysts at pressures up to 1000 atm.

Carbonylation in methanol. One other instance of the carbonylation of allene has been reported; methyl methacrylate is obtained in 40% yield using a platinum chloride–stannous chloride catalyst in methanol.[4] In our work it was found that methyl methacrylate was obtained in 50% yield from allene, carbon monoxide, and methanol at 140° in the presence of diruthenium nonacarbonyl catalyst. When the reaction was carried out first at 140° and then completed at 190°, dimethyl α,α-dimethyl-α'-methyleneglutarate (I) was obtained in 23% yield together with methyl methacrylate in 18% yield.



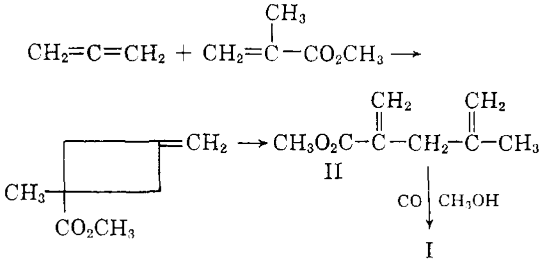
$$CH_2{=}C{=}CH_2 \xrightarrow[CH_3OH]{CO} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CO_2CH_3 + CH_3O_2C{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}CH_2{-}\overset{CH_2}{\overset{\|}{C}}{-}CO_2CH_3$$

I

The origin of the ester I is not obvious. Although I[5] corresponds in composition to a dimer of methyl methacrylate, it has been reported[6] that only one dimer, dimethyl α-methyl-α'-methyleneadipate is isolated when methyl methacrylate is heated to 225°.

In our work, the glutarate I was not obtained when methyl methacrylate was heated to 190° with the ruthenium carbonyl catalyst in the presence of carbon monoxide and methanol. On this basis, it appears that I is not formed by a catalyzed dimerization of methyl methacrylate.

Methyl α,γ-dimethylenevalerate (II) appears to be the most likely intermediate in the glutarate I synthesis. The ester II could be formed by the catalyzed cleavage of methyl 1-methyl-3-methylenecyclobutane carboxylate,[7] the cycloaddition product of allene and methyl methacrylate, which on pyrolysis at 650° (2–4 mm.) affords the ester II.[8] Carbonylation of II would be expected to yield the glutarate I. However, this route was eliminated from consideration when the cyclobutane ester failed to yield I under the conditions used for the carbonylation of allene.



The ester II could also arise *via* a catalyzed addition of methyl methacrylate to allene in a manner analogous to the thermal dimerization[6] of methyl

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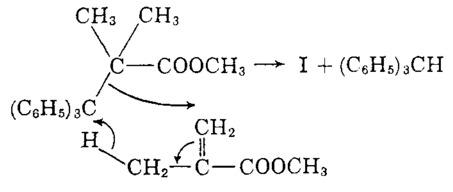
[1] R. E. Benson and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, 81, 4247 (1959).

[2] R. E. Benson and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, 81, 4250 (1959).

[3] R. E. Benson, R. V. Lindsey, Jr., and B. C. Anderson, *J. Am. Chem. Soc.*, 81, 4253 (1959).

[4] E. L. Jenner and R. V. Lindsey, Jr., U. S. Pat. 2,876,254, March 3, 1959.

[5] The glutarate I has been previously prepared by reaction of trityl bromide with dimethylketene dimethylacetal. It is postulated that the initially formed methyl β,β,β-triphenylpivalate undergoes pyrolysis *via* a concerted process to give methyl methacrylate, which in turn reacts in a concerted manner with additional methyl β,β,β-triphenylpivalate to yield the glutarate I [S. M. McElvain and C. L. Aldridge, *J. Am. Chem. Soc.*, 75, 3987 (1953)].

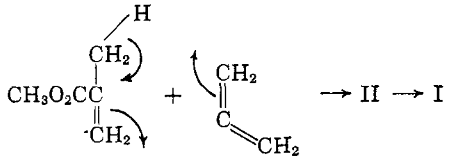


[6] C. J. Albisetti, D. C. England, M. J. Hogsed, and R. M. Joyce, *J. Am. Chem. Soc.*, 78, 472 (1956).

[7] H. N. Cripps, J. K. Williams, and W. H. Sharkey, *J. Am. Chem. Soc.*, 81, 2723 (1959).

[8] J. J. Drysdale, H. B. Stevenson, and W. H. Sharkey, *J. Am. Chem. Soc.*, 81, 4908 (1959).

methacrylate itself. This route to I is preferred, although an attempt to isolate the proposed intermediate II from the reaction of allene and methyl methacrylate at 190–200° in the presence of diruthenium nonacarbonyl catalyst but in the absence of carbon monoxide was unsuccessful. Polymeric material and a small amount of methyl 1-methyl-3-methylenecyclobutanecarboxylate were obtained. The stability of the catalyst and of the diene ester II under these conditions was not established.

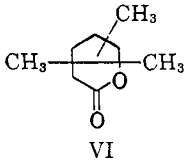


Carbonylation in water. Methacrylic acid was obtained in 20% yield by the reaction of allene with carbon monoxide and water in the presence of a ruthenium chloride–pyridine catalyst at 120° and 700–1000 atm. However, when the reactants were quickly brought to 175°, which frequently resulted in a flash to 200° or higher, the yield of methacrylic acid dropped to 5% and isomeric $C_{10}H_{16}O_2$ lactones could be isolated in about 20% yield together with a trace amount of *n*-butyraldehyde. No lactone could be detected when the reaction was carried out at 120°.

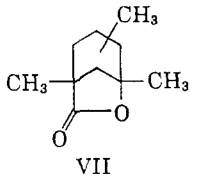
The lactone product was found to contain two main components, designated as lactone A (III) and lactone B (IV), in a ratio of about 7:1, respectively. The composition of the lactones corresponds to the reaction of three moles of allene with one mole each of carbon monoxide, water, and hydrogen.[9] Infrared, NMR, and hydrogenation studies established that the lactones were free of unsaturation and therefore, in order to conform with the molecular formula, must be bicyclic.

Lactone A was shown to be a γ-lactone from the position of its carbonyl stretch in the infrared[10] (λ_{max} 1770 cm.$^{-1}$) and by the fact that saponification of it followed by careful acidification of the solution regenerated the lactone unchanged. An attempted oxidation of lactone A with dilute nitric acid afforded a $C_{10}H_{15}NO_4$ nitrolactone (V) which was unaffected by further treatment with dilute nitric acid. Similar results have been obtained by other investigators[11] in attempting to oxidize lactones derived from tertiary alcohols and containing a R_3CH grouping.

It was thus assumed that in lactone A the carbon bearing the ether oxygen of the lactone grouping was the site of a methyl group and one of the positions of ring juncture. As a starting point it was further assumed that the lactone contained only one R_3CH grouping since only a mononitro derivative could be obtained. This led to a consideration of partial structures VI and VII for lactone A, with VII preferred on the basis of the previous experiments which show that carbonylation of allene occurs primarily on the 2-carbon atom. Attempts to oxidize lactone A with permanganate or to aromatize it with sulfur or palladium on carbon were unsuccessful.

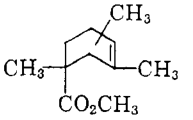


VI



VII

The reaction of allene and carbon monoxide in the presence of methanol under the conditions of the lactone synthesis was then investigated in the hope of obtaining a more readily identifiable product that might aid in identifying the lactone. Under these conditions (a ruthenium chloride–pyridine catalyst at 175°) a $C_{11}H_{18}O_2$ ester (VIII) was obtained in 12% yield together with methyl methacrylate in 10% yield. The composition of the C_{11} ester corresponded to the reaction of three moles of allene and one mole each of carbon monoxide, methanol and hydrogen. Hydrolysis of the ester afforded the acid which on treatment with dilute hydrochloric acid yielded lactone A. Furthermore, reaction of the ester with dilute nitric acid afforded the same nitrolactone as had previously been obtained from lactone A. Thus, partial structure IX was tentatively assigned to the ester.



IX

Hydrogenation of the double bond of the ester was unsuccessful in alcohol solvents but could be effected in acetic acid using a platinum oxide catalyst. This behavior was considered indicative of the presence of a highly substituted double bond and, accordingly, the remaining methyl group was placed on the doubly-bonded carbon. This product was then recognized as the Diels-Alder adduct of methyl methacrylate and 2,3-dimethylbutadiene,[12] which was confirmed by preparing the ester in this manner. Thus the identification of the ester VIII as methyl 1,3,4-trimethyl-3-cyclohexenecarboxylate established the structure of lactone A as 3-hydroxy-1,3,4-trimethylcyclohexanecarboxylic acid lactone (III); see Fig. 1.

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(9) The hydrogen is apparently derived from a water gas type reaction. W. Reppe, *et al.*, *Ann.*, **582**, 87 (1953).

(10) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, second ed., Wiley, New York, 1958, p. 186; F. Korte, K. H. Büchel, and Kl. Göhring, *Angew. Chem.*, **71**, 523 (1959); R. N. Jones, C. L. Angell, T. Ito, and R. J. D. Smith, *Can. J. Chem.*, **37**, 2007 (1959).

(11) P. K. Porter and W. A. Noyes, *J. Am. Chem. Soc.*, **45**, 2366 (1923); J. Kachler and F. V. Spitzer, *Monatsh.*, **4**, 643 (1883).

(12) E. H. Farmer and R. C. Pitkethly, *J. Chem. Soc.*, 11 (1938).

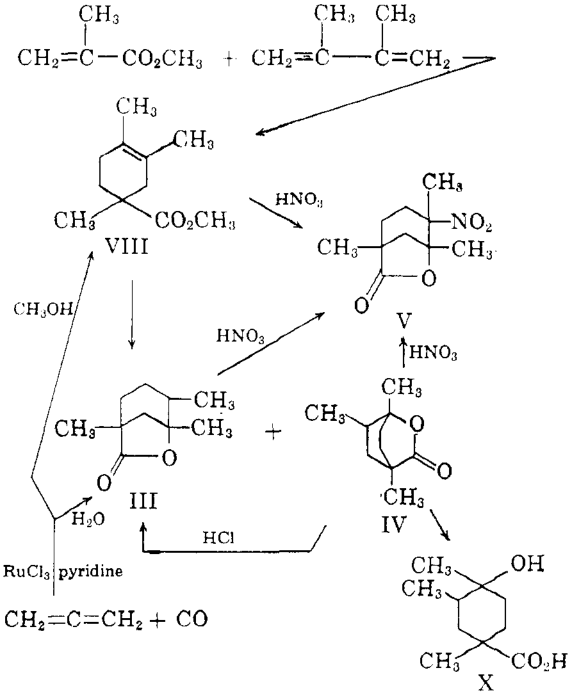
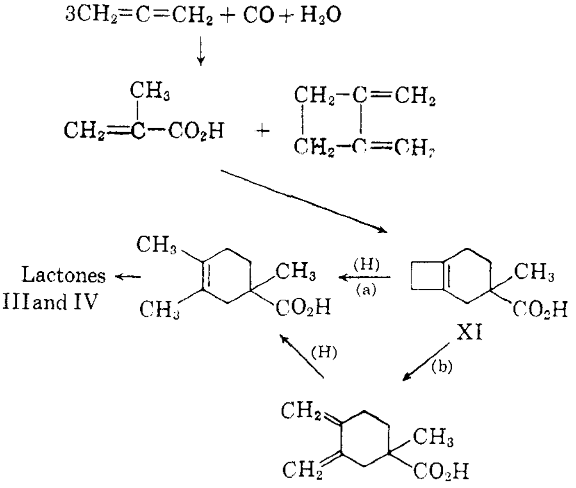


Figure 1

IDENTIFICATION OF LACTONES

Lactone B on saponification afforded the hydroxy acid (X) which indicated that it was a δ-lactone in agreement with the position of the lactone carbonyl stretch in the infrared (1750 cm.$^{-1}$). Dilute hydrochloric acid at reflux converted lactone B to lactone A and treatment of lactone B with dilute nitric acid also afforded the same nitrolactone as was obtained from lactone A and ester VIII. Thus the difference between lactones A and B is the point of attachment of the ether oxygen of the lactone grouping and lactone B is therefore 4-hydroxy-1,3,4-trimethylcyclohexanecarboxylic acid lactone (IV); see Fig. 1.

In view of the known trimerization of allene to 1,2,4- and 1,3,5-trimethylenecyclohexane[1] in a ratio of 4:1, respectively, the possibility that allene trimer was the lactone (and ester) intermediate was considered early in the investigation. However, the lactone could not be isolated when allene was replaced by the trimer mixture in the aqueous carbonylation, other conditions being identical. It is proposed that 1,2-dimethylenecyclobutane (allene dimer) and methacrylic acid are the intermediates in this synthesis according to the following scheme. The fact that high temperature favors the formation of the lactones (or ester VIII) is in accord with the previous finding of Alder and Ackermann[13] that the reaction of allene and maleic anhydride at 175° affords products derived from allene dimer. Other negatively substituted olefins, including acrylates, behave similarly on reaction with allene at 200° to give octahydronaphthalene derivatives.[7] It has been proposed that this reaction involves the thermal rearrangement of intermediate Diels-Alder adducts of the type XI to give 1,2-dimethylenecyclohexanes which then afford octahydronaphthalenes by a second Diels-Alder reaction.[7,13] In the lactone synthesis, however, it is visualized that the incorporation of hydrogen by either a) hydrogenolysis of XI or b) the addition of hydrogen to the 1,2-dimethylenecyclohexane takes precedence over octahydronaphthalene formation.



Other carbonylations. In an unusual reaction, the carbonylation of allene in the presence of both water and acetylene and a ruthenium chloride-pyridine catalyst at 130–150° afforded 3-methyl-2-cyclopentenone in low yield. The methylcyclopentenone corresponds in composition to the reaction of allene, carbon monoxide, acetylene and hydrogen.

Carbonylation of allene at 135° in the presence of cyclohexylamine and a ruthenium chloride catalyst afforded *N*-cyclohexylmethacrylamide in 16% yield. In the presence of excess cyclohexylamine, a mixture of the methacrylamide and *N*-cyclohexylformamide was obtained in a combined yield of 40%.

EXPERIMENTAL

Preparation of methyl methacrylate.[14] A stainless steel pressure vessel of 400 ml. capacity was charged under nitrogen with 150 ml. of methanol and 2 g. of diruthenium nonacarbonyl. The vessel was cooled and evacuated and 40 g. of allene was added by distillation. Carbon monoxide was added to give a pressure of 300 atm. and the vessel was heated to 135–150°. Carbon monoxide was again added to maintain a pressure of 700–900 atm. for a total reaction time of about 12 hr. The resulting product (173 g.) was a dark liquid containing a small amount of solid. The reaction mixture was flash-distilled at reduced pressure to give a methyl methacrylate–methanol fraction (A), 6.3 g. of unidentified colorless oil, b.p. 58–60° (1 mm.), n^{25}_{D} 1.4560 and a residue of 6.3 g. The distillate (A) was washed three times with a saturated solution of calcium chloride. The organic layer was dried and distilled to obtain 45.2 g. (50% yield) of

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[13] K. Alder and O. Ackermann, *Chem. Ber.*, **87**, 1567 (1954); **90**, 1697 (1957).

[14] R. E. Benson, U. S. Pat. **2,871,262**, January 27, 1959.

methyl methacrylate, b.p. 61–62° (190 mm.), n^{25}_{D} 1.4110. The identity of the product was confirmed by infrared analysis.

This synthesis has also been effected in the presence of iron pentacarbonyl catalyst at 180–190°. Methyl methacrylate was obtained in 25% yield together with a small amount of methyl 1-methyl-3-methylenecyclobutanecarboxylate, b.p. 66° (33 mm.), n^{25}_{D} 1.4376; reported[7] b.p. 54–55° (15 mm.), n^{25}_{D} 1.4432. The identity of these products was established by infrared analysis.

Preparation of dimethyl α,α-dimethyl-α′-methyleneglutarate.[14] The pressure vessel was charged in the usual manner with 40 g. of allene, 150 ml. of methanol, and 2 g. of diruthenium nonacarbonyl catalyst. Carbon monoxide was added and the temperature was maintained at 140° for 3 hr. and at 200° for 6 hr. A pressure of 700–1000 atm. was maintained by further addition of carbon monoxide as needed. The product was distilled to obtain a methanol-methyl methacrylate fraction (A) and 37 g. of an orange liquid, b.p. 40–100° (0.2 mm.) (B). Fraction A was worked up in the usual manner to give methyl methacrylate in 18% yield. Distillation of fraction B gave 22 g. of dimethyl α,α-dimethyl-α′-methyleneglutarate as a colorless oil, b.p. 50° (0.9 mm.), n^{25}_{D} 1.4457; reported[5] b.p. 136–138° (50 mm.), n^{25}_{D} 1.4440. The infrared and proton magnetic resonance spectra were in agreement with the proposed structure.

Hydrogenation of the ester using a platinum oxide catalyst in methanol at room temperature afforded dimethyl α,α,α′-trimethylglutarate in 79% yield, b.p. 71° (2.2 mm.), n^{25}_{D} 1.4283; reported[5] b.p. 113° (24 mm.), n^{25}_{D} 1.4272. The proton magnetic resonance spectrum was in accord with the proposed structure. Hydrolysis of the saturated ester afforded α,α,α′-trimethylglutaric acid as clusters of fine needles m.p. 98–98.8°; reported[5] m.p. 98.5–99.5°.

Methyl 1,3,4-trimethyl-3-cyclohexenecarboxylate. A mixture of 60 g. of allene, carbon monoxide, 1 g. of ruthenium chloride,[15] 1.2 g. of pyridine and 100 ml. of methanol was heated rapidly to 175°. The initial pressure of carbon monoxide was 200 atm. and the pressure was gradually increased to 1000 atm. for a total reaction time of about 16 hr. The product was combined with a similar product in which the run flashed momentarily to 196°. The combined product (304 g.) was distilled into three fractions: (A) 119 g., b.p. 52–56°; (B) 38 g., b.p. 30–53° (113 mm.–1 mm.); (C) 63 g., b.p. 84–115° (1 mm.). A dark residue (84 g.) remained. Fraction A was extracted several times with a saturated calcium chloride solution and the dried organic layer was combined with fraction B and the trap contents of the initial distillation. Distillation of this material afforded 28 g. (10% yield) of methyl methacrylate, b.p. 57° (147 mm.), n^{25}_{D} 1.4117–1.4121. Distillation of the high boiling fraction (C) afforded 22 g. (12% yield) of methyl 1,3,4-trimethyl-3-cyclohexenecarboxylate, b.p. 111–115° (29 mm.), n^{25}_{D} 1.4611–1.4640. A constant boiling fraction of the ester was obtained in this distillation, 10 g., b.p. 115° (29 mm.), n^{25}_{D} 1.4640; saponification gave the acid m.p. 50.5–51.5°. The infrared spectrum of the ester prepared by this method was found to be identical to that of the product obtained by the Diels-Alder reaction of methyl methacrylate and 2,3-dimethylbutadiene,[12] b.p. 111°(25 mm.), n^{25}_{D} 1.4638; acid m.p. 52.5–53.5°, lit.[12] b.p. 106° (19 mm.), n^{16}_{D} 1.4679; acid m.p. 56°.

The ester was obtained in 25% yield by gradually injecting allene into the reaction mixture heated at 190°.

Lactones of 3- and 4-hydroxy-1,3,4-trimethylcyclohexanecarboxylic acid. A mixture of 60 g. of allene, 1.5 g. of ruthenium chloride, 2 g. of pyridine, and 100 ml. of water was pressured with carbon monoxide to 200 atm. The temperature was quickly raised to 175° resulting in a momentary flash to 200° or higher. The pressure was gradually raised to 800–1000 atm. by further addition of carbon monoxide and the reaction was maintained at 175° for about 16 hr. The products from five such runs were combined, extracted with ether, and the ether solution filtered to free it from a small amount of solid. The filtrate was extracted with aqueous sodium carbonate (100 g. of sodium carbonate and 500 ml. of water) and then dried over calcium sulfate. Most of the solvent was removed by distillation and the residue was distilled under vacuum to obtain 40 g. of material in the trap, 9 g. of foreshot [b.p. up to 53° (6 mm.)], 92 g. (22% yield) of crude $C_{10}H_{16}O_2$ lactone, b.p. 69–95° (1 mm.), and 18 g. of tarry residue. The contents of the trap and the foreshot were combined with similar material (29 g.) obtained previously and distilled at atmospheric pressure to obtain 20 g. of ether and 5 g. of *n*-butyraldehyde, b.p. 72–73°, identified by infrared analysis. No other distillation flat was observed.

Acidification of the sodium carbonate solution and extraction of the product with ether afforded on distillation 32 g. (5% yield) of methacrylic acid and 41 g. of residue which is presumably polymerized methacrylic acid.

The lactone product could be separated into two fractions. After removing, by distillation, a 13-g. sample (n^{25}_{D} 1.4636) comprising largely the low-boiling isomer, the remainder of the lactone product was distilled through a 30-inch spinning brush column to obtain (A) 35 g., b.p. 140–142° (30 mm.), n^{25}_{D} 1.4628–1.4630; (B) 7 g., b.p. 151–152.5° (30 mm.), n^{25}_{D} 1.4682–1.4695; 9 g. of foreshot, 14 g. of an intermediate fraction, and a residue of 6 g. The ratio of lactone A to lactone B is thus about 7:1. The infrared spectrum of lactone A showed carbonyl absorption at 5.64 μ with a weak characteristic shoulder at 5.45 μ and strong bands at 7.85 and 9.57 μ; the spectrum of lactone B showed carbonyl absorption at 5.71 μ and strong bands at 9.03, 9.45, and 10.52 μ, which served to distinguish it from lactone A. Lactone A was identified as 3-hydroxy-1,3,4-trimethylcyclohexanecarboxylic acid lactone and lactone B was identified as 4-hydroxy-1,3,4-trimethylcyclohexanecarboxylic acid lactone.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found (A): C, 71.64; H, 9.59; (B): C, 71.75; H, 9.23.

A suspension of 1.8 g. of 1,3,4-trimethyl-3-cyclohexenecarboxylic acid in dilute hydrochloric acid (4 ml. of 37% hydrochloric acid, 8 ml. of water) was refluxed for 2 hr. The reaction mixture was cooled and the product was extracted into ether. Distillation of the dried ether solution afforded 0.5 g. of 3-hydroxy-1,3,4-trimethylcyclohexanecarboxylic acid lactone, b.p. 107–113° (9 mm.), n^{25}_{D} 1.4624. The infrared spectrum of this product was identical to that of lactone A.

A suspension of lactone B was refluxed in 15% hydrochloric acid for 4 hr. The reaction mixture was steam distilled and the distillate was extracted into pentane. Removal of the solvent from the dried pentane solution afforded a residual oil, n^{25}_{D} 1.4641, whose infrared spectrum was identical to that of lactone A.

Further evidence that lactone B was a δ-lactone was obtained by its conversion to the corresponding hydroxy acid. Two grams of lactone B were refluxed in 10% sodium hydroxide for 1 hr.; the lactone dissolved after the first few minutes. The solution was cooled and acidified slowly with cold concentrated hydrochloric acid. The oily product was extracted into ether and the ether layer was washed once with water and dried over calcium sulfate. After the ether was removed on a steam bath the residue crystallized. The product was filtered and washed with petroleum naphtha (b.p. 100–140°) to obtain 1 g. of white crystalline solid, m.p. 107–113°. The material was recrystallized once from benzene to obtain 4-hydroxy-1,3,4-trimethylcyclohexanecarboxylic acid; m.p. 113–114°, neut. equiv. Calcd., 186; Found, 190.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.93; H, 9.75.

3-Hydroxy-4-nitro-1,3,4-trimethylcyclohexanecarboxylic acid lactone. Method A. A suspension of 1.3 g. of lactone A (n^{25}_{D} 1.4623) in a solution of 3 ml. of 70% nitric acid in 15 ml. of water was refluxed for 45 min. with stirring. A yellow

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(15) Ruthenium chloride was obtained from Engelhard Industries, Newark, N. J. Analysis of this material indicated the approximate composition $RuCl_4.H_2O/RuCl_3{\cdot}3H_2O$ 80/20.

insoluble oil was obtained which crystallized on cooling. The reaction mixture was filtered and the solid was washed with water and recrystallized from dilute ethanol to obtain 0.2 g. of 3-hydroxy-4-nitro-1,3,4-trimethylcyclohexanecarboxylic acid lactone as white needles, m.p. 112–113°.

Anal. Calcd. for $C_{10}H_{15}NO_4$: C, 56.32; H, 7.09; N, 6.57. Found: C, 56.64; H, 7.19; N, 6.65.

Method B. A suspension of 3 g. of lactone B (n_D^{25} 1.4692–1.4709) was refluxed 4 hr. in dilute nitric acid to obtain 1.45 g. (45% yield) of crude nitrolactone. Recrystallization of the product from dilute ethanol afforded 1 g. of white needles, m.p. 112–113° alone or mixed with the nitrolactone from lactone A. The infrared spectra (Nujol) of the nitrolactones were identical. Nitration of the mixed lactones A and B (n_D^{25} 1.4658) afforded crude nitrolactone in 58% yield, m.p. 99–105°.

Method C. Two grams of methyl 1,3,4-trimethyl-3-cyclohexenecarboxylate was refluxed for 2 hr. in a solution of 4 ml. of 70% nitric acid in 12 ml. of water. The cooled reaction mixture was filtered and the product was recrystallized from dilute ethanol to obtain white needles, m.p. 110.5–111.5°. The infrared spectrum of this product was identical to that of the above nitrolactone.

N-Cyclohexylmethacrylamide. Thirty grams of allene (0.75 mole) was allowed to react with 150 g. of cyclohexylamine (1.5 moles) and carbon monoxide at 135° and 1000 atm. pressure for 14 hr. in the presence of 2 g. of diruthenium nonacarbonyl catalyst. The dark fluid product (200 g.) was flash distilled to leave a residue of 70 g. which was not volatile at 170° (3 mm.). The distillate was redistilled to obtain 89 g. of colorless oil, b.p. 70–94° (1 mm.), n_D^{25} 1.4890–1.4912. The oil partially solidified on standing and was filtered to obtain about 14 g. of white solid. This product was recrystallized from methanol-water to obtain *N*-cyclohexylmethacrylamide as white needles, m.p. 109.5–110.5°. The infrared spectrum of the product is consistent with the proposed structure.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25. Found: C, 71.74; H, 10.05.

Treatment of the filtrate with aqueous methanol afforded more of the crystalline methacrylamide, which was removed by filtration. There was finally obtained on distillation *N*-cyclohexylformamide, b.p. 143° (10 mm.), n_D^{25} 1.4846; reported[16] b.p. 140–142° (10 mm.), m.p. 39°. The infrared spectrum of the material is consistent with this structure.

3-Methyl-2-cyclopentenone. A mixture of 20 g. of allene (0.5 mole), 13 g. of acetylene (0.5 mole), 18 g. of water, 1 g. of ruthenium trichloride, and 1.2 g. of pyridine was heated to 130° in the presence of carbon monoxide at a final pressure of 1000 atm. The product (53 g.) was a dark red oil which was flash distilled at 25 mm. to obtain 35 g. of distillate. The distillate was extracted into ether and dried with calcium sulfate. Distillation afforded a 13-g. fraction of methacrylic acid and 2.5 g. of ketone fraction, b.p. 89–91° (25 mm.), n_D^{25} 1.4730. The ketone fraction was dissolved in ether and extracted with sodium carbonate solution to remove methacrylic acid and then dried over calcium sulfate. Removal of the ether by distillation afforded 3-methyl-2-cyclopentenone as a light yellow oil, n_D^{25} 1.4840, which was identified by infrared comparison with an authentic sample[17] (n_D^{25} 1.4855). The ketone afforded a semicarbazone, m.p. 210–211.5° dec. alone or on admixture with authentic 3-methyl-2-cyclopentenone semicarbazone, m.p. 212–213° dec. An orange red dinitrophenylhydrazone, m.p. 181° (from dilute acetic acid) was obtained which on admixture with authentic 3-methyl-2-cyclopentenone 2,4-dinitrophenylhydrazone, m. p. 179–180.5°, gave no melting point depression.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

Chemistry of Dimethylketene Dimer. II. Dehydration of *trans*-2,2,4,4-Tetramethyl-1,3-cyclobutanediol[1]

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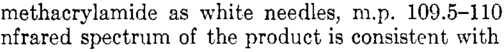
trans-2,2,4,4-Tetramethyl-1,3-cyclobutanediol was cleaved easily when refluxed in dilute sulfuric acid, while the *cis* isomer was unaffected. The cleavage product was the expected 2,2,4-trimethyl-3-pentenal. The dehydration reaction is interpreted in terms of a concerted transannular elimination mechanism.

The acid-catalyzed dehydration of certain 1,3-diols results in a characteristic cleavage to olefinic and carbonyl moieties[2]:



$$\underset{OH}{R_2C}CR_2\underset{OH}{CR_2} \longrightarrow H_2O + R_2C{=}CR_2 + R_2C{=}O$$

The steric effects of this reaction have been studied, and some pronounced differences in the rate or degree of cleavage have been noted for different isomers of acyclic glycols. There has been no similar study of the isomers of cyclic 1,3-diols. However, differences have been noted in susceptibility to cleavage of diols with differing ring size.[3,4] Thus, English and Brutcher[3] found an insignificant degree of acid-catalyzed cleavage of the cyclic glycol I, while Brutcher and Cenci[4] noted extensive cleavage of the indan derivative II. In neither instance was a comparison made of the behavior of *cis* and *trans* isomers of a particular cyclic glycol.

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