(VI), was collected at 200–205° (745 mm.); yield 0.85 g. (21% from the acid chloride). Hydrolysis with 10% alcoholic potassium hydroxide furnished the viscous free acid VI,[5] which was not purified but was characterized, in part, as the *amide* by the thionyl chloride–ammonia procedure. After recrystallization from benzene–petroleum ether (b.p. 40–60°), this derivative was obtained in fine plates, m.p. 140–140.5°.

Anal. Calcd. for $C_8H_{15}ON$ (141.21): C, 68.04; H, 10.71. Found: C, 67.83; H, 10.95.

A mixed m.p. of this derivative with the amide,[4] m.p. 140–141°, of the solid isomer of IV,[4] m.p. 84–85° (samples kindly supplied by Professor Melvin S. Newman), was depressed to 106–129°. The infrared spectra and the ultraviolet end-absorption of the two specimens were also characteristically different. In addition, tetranitromethane produced a light yellow color with the free acid VI but no color with the crystalline sample of IV, in accord with the conjugated structure of the latter.

Treatment of the remaining portion (*ca.* 0.3 g.) of the crude acid VI with 20 ml. of 50% sulfuric acid on the steam-bath for 1 hr., and then isolation of the neutral product by extraction with ether, furnished 145 mg. of fine prisms, m.p. 93–98°. After two recrystallizations from benzene–petroleum ether (b.p. 60–70°), these melted at 99–100° and did not depress the m.p. of the lactone obtained from I. The infrared spectra of the two preparations were also identical, and a sample of V kindly furnished by Professor Henry E. Baumgarten[5] was likewise indistinguishable from them both.

α,β,γ,γ-Tetramethyl-β-valerolactone (VIIa). Ethyl 3-hydroxy-2,3,4,4-tetramethylpentanoate, b.p. 62–64° (0.6 mm.), was obtained in 72% yield in a 0.1-mole run by the Reformatsky procedure from pinacolone and ethyl α-bromopropionate. Hydrolysis of this ester with 5% aqueous-alcoholic sodium hydroxide afforded the corresponding acid Ia, m.p. 108–110°, in 81% yield after crystallization from dilute ethanol. Two additional crystallizations from the same solvent furnished the pure acid as fine prisms, m.p. 109–110°.

Anal. Calcd. for $C_9H_{18}O_3$ (174.23): C, 62.04; H, 10.41. Found: C, 62.34; H, 10.36.

For conversion to the corresponding β-lactone, 1.0 g. of the foregoing acid was dissolved in 20 ml. of benzene and treated with 0.75 g. of freshly prepared *N,N'*-diisopropylcarbodiimide.[1e] After a reaction period of 24 hr. at 25° the precipitate of *N,N'*-diisopropylurea was collected, and the filtrate diluted with petroleum ether (b.p. 40–60°), washed rapidly with cold 5% sodium carbonate-bicarbonate solution, and dried over anhydrous magnesium sulfate. Filtration and concentration of the solution under reduced pressure afforded an oily residue which crystallized readily at −20° from petroleum ether (b.p. 40–60°), forming large prism clusters of α,β,γ,γ-tetramethyl-β-valerolactone (VIIa), m.p. 46–47°; IR, 5.52 μ; yield 0.55 g. (61%).

Anal. Calcd. for $C_9H_{16}O_2$ (156.22): C, 69.19; H, 10.32. Found: C, 69.34; H, 10.17.

When heated to 110–130° this product liberated carbon dioxide and furnished an olefin, b.p. 104–106° (735 mm.), n_D^{20}, 1.4224; IR, 12.2 μ (CS_2), which is probably largely 3,4,4-trimethyl-2-pentene [lit.[9] b.p. 109° (740 mm.), n_D^{20}, 1.4232]. Attempted lactonization of I gave only noncrystalline neutral products whose infrared spectra showed carbonyl peaks at 5.5 and 5.8 μ. Efforts to isolate a pure β-lactone from the mixture by evaporative distillation at reduced pressure[1f] were unsuccessful.

Acknowledgment. We wish to thank Professor Melvin S. Newman for helpful advice and for samples of the solid isomer of IV and its amide, and Professor Henry E. Baumgarten for an authentic specimen of V. We are also grateful to Dr. James N. Shoolery (Varian Associates, Palo Alto, Calif.) for the NMR spectrum of V and its interpretation, and the University of Kansas for a grant from the General Research Fund.

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A Convenient Synthesis of *cis*-Cyclononene

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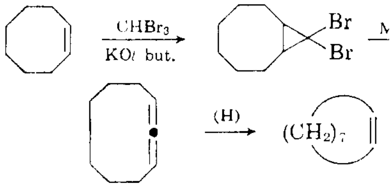
Unambiguous syntheses of both *cis-* and *trans-*cyclononene have been reported.[1] However, because they are multi-stepped and include almost prohibitively low-yield steps they do not lend themselves easily to the preparation of substantial quantities of these interesting olefins. The need for such quantities prompted the search for a more efficient process, the results of which are the subject of this report.

The two-step allene synthesis reported by Doering and LaFlamme[2] was found to be nicely adaptable to the synthesis of 1,2-cyclononadiene. The required starting material, cyclooctene, was prepared by reduction of commercially available 1,5-cyclooctadiene essentially as described for cyclooctatetraene.[3] Its transformation is summarized below.

cis-Cyclononene was prepared from 1,2-cyclononadiene by either catalytic hydrogenation or sodium-ammonia reduction. The complete absence of the *trans* isomer in both of these reaction products is as expected. The *cis* isomer is the energetically more stable of the two[4] and it is probably this factor which determines the stereochemical course



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of the sodium-ammonia reduction. A molecular-model construction of the allene suggests that *only* the *cis* isomer could be formed by catalytic hydrogenation.

EXPERIMENTAL

cis-Cyclooctene. A solution of 21.6 g. of 1,5-cyclooctadiene[5] in 75 ml. of methanol was shaken with 0.5 g. of 5% palladium-calcium carbonate[3] under 2 atm. of hydrogen. The heat of reaction was conveniently dissipated by wrapping the bottle with a towel and periodically saturating it with acetone. Following the uptake of 1 mole-equivalent of hydrogen the suspension was filtered, diluted with 200 ml. of ether and washed repeatedly with water. The organic phase was dried (sodium sulfate) and fractionally distilled to give 19.1 g. (87%) of *cis*-cyclooctene, b.p. 144–145° (750 mm.). This sample was identical with material from the reduction of cyclooctatetraene; both contained about 4% of cyclooctane and no other impurity (vapor-liquid chromatography).

9,9-Dibromobicyclo[6.1.0]nonane. Cyclooctene (50 g., 0.45 mole) was added to a solution prepared by dissolving 20 g. (0.51 g.-atom) of potassium in 600 ml. of dry *t*-butyl alcohol. The flask was surrounded with ice and, while stirring, 127 g. (0.50 mole) of bromoform was added dropwise. After the addition was complete, stirring was continued for an hour and the contents were poured into 500 ml. of water. The mixture was extracted with several portions of pentane and the combined extracts were washed with water (2.5 l.), dried (sodium sulfate) and freed of solvent on a steam cone. Distillation of the residue gave 42 g. (33%) of 9,9-dibromobicyclo[6.1.0]nonane, b.p. 45° (0.15 mm.), n_D^{27} 1.5105.

Anal. Calcd. for $C_9H_{14}Br_2$: C, 38.33; H, 5.00; Br, 56.67. Found: C, 38.63; H, 5.14; Br, 56.98.

The fore-run from the distillation (48 g.) consisted of unchanged cyclooctene and bromoform and was suitable for recycling. Vapor-liquid chromatography showed it to contain about 20 g. (40% recovery) of cyclooctene. A more efficient conversion was realized using the conventional large excess of olefin[2] but the procedure described is felt to be a satisfactory economic compromise.

1,2-Cyclononadiene. In a 500 ml., three-necked flask, equipped with a stirrer and over-size Dry Ice condenser, was placed 22 g. (0.92-g.-atom) of magnesium turnings and 200 ml. of anhydrous ether. While stirring and heating, 50 g. (0.18 mole) of 9,9-dibromobicyclo[6.1.0]nonane dissolved in 120 ml. of anhydrous ether was added in a dropwise manner. The need for the large surge-capacity of the condenser was due to the very rapid rate of reaction. Frequently, the reaction did not start until 20 min. to an hour after the addition was complete but after starting it was essentially complete in 3 or 4 min. Following this, stirring under reflux was continued for an additional 3 hr. and then ice and water were cautiously added. The mixture was processed as described for other cases[2] and the crude product distilled through an efficient column. There was obtained 13.0 g. (59%) of 1,2-cyclononadiene, b.p. 94° (44 mm.), n_D^{27} 1.4953. Repeated attempts to obtain satisfactory analytical data suggested that the allene slowly absorbs oxygen.

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 86.53; H, 11.55.

Vapor-liquid chromatography of a freshly distilled sample indicated it to be a single compound. The infrared spectrum possessed a medium-strong band at 5.10 μ (allene) but had no absorption in the 4.5–4.7 μ (acetylene) region.

CIS-*Cyclononene* A. *Hydrogenation*. 1,2-Cyclononadiene (7.0 g.) was shaken in a suspension of 150 mg. of 10% palladium-charcoal and 200 ml. of methanol under a pressure of 2 atm. The theoretical quantity of hydrogen was absorbed in 1 hr. when the rate dropped abruptly. The usual isolation procedure and distillation of the product gave 5.4 g. (76%) of *cis*-cyclononene, b.p. 85–86° (45 mm.), n_D^{27} 1.4748 [lit.[1] b.p. 167–169° (740 mm.), n_D^{20} 1.4799]. The infrared spectrum was identical with that reported and had no absorption in the 10.25 μ region which is reported to be characteristic of the *trans* isomer.[1] Chromatography showed the sample to be a single substance.

Anal. Calcd. for C_9H_{16}: C, 87.01; H, 12.99. Found: C, 86.93; H, 12.87.

B. *Sodium-ammonia.* To a solution of 9.0 g of sodium dissolved in 250 ml. of liquid ammonia (used without purification) was added 11.0 g. of 1,2-cyclononadiene in 50 ml. of anhydrous ether. The solution was stirred at its boiling temperature for 1 hr. and then treated with excess ammonium chloride. Evaporation of ammonia and processing of the residue in the usual manner gave 9.5 g. (85%) of *cis*-cyclononene, b.p. 81–82° (38 mm.) which was identical in all respects with that obtained by hydrogenation.

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[5] Cities Service Research and Development Co.

The Rate of Reaction of Hexyne-1 with Substituted Phenylmagnesium Bromides

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Previous kinetic studies of the reactions of Grignard reagents with weak acids have been limited to the alkyl series because the gasometric method in common use required that a volatile hydrocarbon be evolved in the reaction[1]:

$$\mathrm{RMgX} + \mathrm{RC{\equiv}CH} \longrightarrow \mathrm{RH} + \mathrm{RC{\equiv}CMgX} \qquad (1)$$

Several approaches to the problem of following the kinetics of reactions which do not yield volatile products have been made by groups at the University of Pittsburgh[2] and in our laboratory. The Pittsburgh group has recently completed a preliminary study of the reaction of phenylmagnesium bromide with hexyne-1 using VPC as a tool.[3] Their data will be published in the near future.

We have determined the rates of reaction of a series of substituted phenylmagnesium bromides with hexyne-1 in ether by following the rate of change of the dielectric constant of the reaction mixture with time. The reactions were run under pseudo-first order conditions in ether with a

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