tone. Our sample (100 mg.), on ozonolysis followed by hydrogenation over 10% palladium on charcoal, gave these two ketones (identified by v.p.c. retention times and infrared spectra) in yields of 28 and 12%, respectively. The n.m.r. spectrum showed a single-proton peak at 2.8 p.p.m. (allylic bridgehead) and a broad single-proton peak at 2.25 p.p.m. (C-4 bridgehead); the upfield pattern was complex and featured strong absorptions at 1.62, 1.48, and 1.29 p.p.m.

One-Step Olefin-to-Allene Conversion

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For other investigations, we prepared 1,2,6-cyclononatriene according to the general two-step method for synthesizing allenes,[1,2] *i.e.*, the addition of dibromocarbene (generated from bromoform) to the olefin[3] followed by reaction of the dibromocyclopropane derivative with an alkyllithium reagent. The reported overall conversion of 1,5-cyclooctadiene to 1,2,6-cyclononatriene by this method is 23% (based on olefin).[4] Skattebøl has since obtained *ca.* 45% yields of 1,2,6-cyclononatriene by this two-step sequence using 1 equiv. of olefin to 1 equiv. of bromoform.[5] Since the triene was to be our starting material, an improvement in the yield was desirable.

Prompted by the report of Skattebøl[2] that trimethylethylene and carbon tetrabromide in the presence of excess methyllithium gave a 50% yield of 2-methylpenta-2,3-diene (the two-step sequence gave 58% yield), we treated a fourfold excess of 1,5-cyclooctadiene with 1 equiv. of carbon tetrabromide and 2 equiv. of methyllithium in diethyl ether at *ca.* −65°. This one-step conversion gave *ca.* 70% of 1,2,6-cyclononatriene (based on carbon tetrabromide) in four experiments (Table I). When the same reaction was carried out using *n*-butyllithium in hexane, instead of methyllithium in ether, a 37% yield of 1,2,6-cyclononatriene was obtained.

TABLE I

OLEFIN-TO-ALLENE CONVERSIONS WITH CARBON TETRABROMIDE AND ALKYLLITHIUM (RLi)

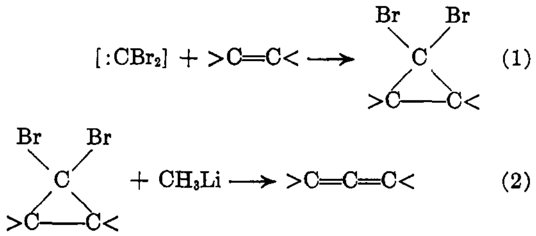
Olefin	R	Allene	Temp., °C.	Yield,[a] %
1,5-Cyclooctadiene	C_4H_9[b]	1,2,6-Cyclononatriene	*ca.* −65	36.8
1,5-Cyclooctadiene	CH_3[c]	1,2,6-Cyclononatriene	*ca.* −65	67.8
1,5-Cyclooctadiene	CH_3[c]	1,2,6-Cyclononatriene	*ca.* −65	71.2
1,5-Cyclooctadiene	CH_3[c]	1,2,6-Cyclononatriene	*ca.* −65	67.9
1,5-Cyclooctadiene	CH_3[c]	1,2,6-Cyclononatriene	*ca.* −65	64.4
cis-Cyclooctene	C_4H_9[b]	1,2-Cyclononadiene	0	*ca.* 30
cis-Cyclooctene	CH_3[c]	1,2-Cyclononadiene	*ca.* −65	73.7

[a] The yields are based on the amount of carbon tetrabromide used and were determined by g.l.p.c. (see Experimental Section). [b] In hexane. [c] In diethyl ether.

Cyclooctene, under the same conditions (fourfold excess, carbon tetrabromide and methyllithium), gave a 74% yield of 1,2-cyclononadiene. When cyclooctene was treated with carbon tetrabromide and *n*-butyllithium in hexane at 0°, *ca.* a 30% yield of 1,2-cyclononadiene resulted. The amounts of cyclic allene obtained in these two latter cases are not readily comparable to those reported for the two-step sequence separately by Moore and Ward[1] (55%) and by Skattebøl[2] (60%) for cyclooctene, since their yields are based on olefin used, whereas here the yields are based on the amount of carbon tetrabromide used.

This modification of the general allene synthesis combines the two-step sequence into one as shown in eq. 1 and 2. The marked decrease in the yield of 1,2,6-cyclononatriene when *n*-butyllithium was used could be due to either part (1 or 2) of the transformation, to both, or to a separate side reaction. In those cases where Moore and Ward,[1] and Skattebøl[2] treated a dibromocyclopropane derivative with both *n*-butyllithium and methyllithium, the yields of the corresponding allene show that methyllithium provides the better result.

$$>C{=}C< + CBr_4 + CH_3Li \longrightarrow$$



In conclusion, the ease with which the reaction can be carried out makes this modification preferable, whether the yield of allene obtained by the one-step conversion is higher than the two-step sequence or not.

Experimental Section

1,2,6-Cyclononatriene.—To a stirred mixture of 54.0 g. (0.50 mole) of 1,5-cyclooctadiene and 41.5 g. (0.125 mole) of carbon tetrabromide (under a nitrogen atmosphere), cooled to *ca.* −65°, were added 74.0 ml. (0.125 mole) of methyllithium in diethyl ether (Foote Mineral Co.) during a 45-min. period. The stirred mixture was kept between −65 and −68° for an additional 30 min., then 80.5 ml. (0.135 mole) of the ethereal methyllithium solution was added during a 30-min. period. The reaction mixture was further stirred for 30 min. at −68° and allowed to come to 0°, and the water was added. The ethereal layer was separated, washed with water until neutral, and dried over sodium sulfate. The bulk of the ether was removed by distillation and the concentrated ethereal solution was analyzed by g.l.p.c.

The yields (based on carbon tetrabromide) of 1,2,6-cyclononatriene for four such experiments were obtained by isothermal (100°) g.l.p.c. analyses using a 6 ft. × 0.25 in. column containing 10% Apiezon L on 80–90-mesh Anakrom ABS in conjunction with an F & M Scientific Corp., Model 500 chromatograph. The planimetered peak areas corresponding to 1,5-cyclooctadiene and 1,2,6-cyclononatriene (identical retention times with pure samples) gave the ratio of starting material to product. Fractional distillation of the reaction mixtures gave 1,2,6-cyclononatriene (*ca.* 80% of that present, determined by g.l.p.c. analysis), b.p. 65–66° (16 mm.), $n^{19.8}D$ 1.5234, infrared and n.m.r. spectra identical with those of a sample prepared according to Skattebøl.[2] The above procedure for the preparation using *n*-butyllithium in hexane (Foote Mineral Co.) was followed.

1,2-Cyclononadiene.—The above procedure was followed using 55.0 g. (0.50 mole) of cyclooctene, 41.5 g. (0.125 mole) of carbon tetrabromide, and 154.5 ml. (0.260 mole) of methyllithium in ether. The fractionally distilled allene, b.p. 77–79° (*ca.* 30 mm.),

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(1) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962).

(2) L. Skattebøl, *Tetrahedron Letters*, 167 (1961); *Acta Chem. Scand.*, **17**, 1683 (1963).

(3) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954), and subsequent papers.

(4) This yield can easily be raised by using the olefin in excess, but it is clear that Dr. Skattebøl was interested in preparing the bisdibromocyclopropane derivative of 1,5-cyclooctadiene as well, which he converted into cyclodeca-1,2,6,7-tetraene.

(5) Private communication.

exhibited an infrared spectrum identical with that published.[2] The reaction using *n*-butyllithium in hexane was kept at 0° throughout the addition and stirring periods, otherwise the procedure was the same as above.

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Magnesium Methoxide Cyclization of Biacetyl Derivatives[1]

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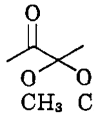
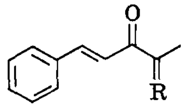
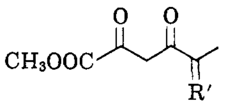
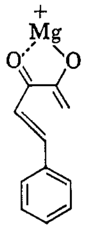
As part of another program a synthesis of cyclic α-diketo compounds was required which would involve intramolecular reaction of an acyclic progenitor. For this purpose model reactions were carried out with certain derivatives of 2,2-dimethoxy-3-butanone (I),[2] such as II and III, which were obtained from basic condensation of I with benzaldehyde and dimethyl oxalate, respectively. Deketalization of II and III led to the corresponding α-diketo compounds (IIa)[3a,b] and IIIa.

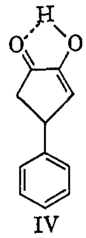

I

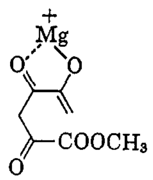

II, R = $-(OCH_3)_2$
IIa, R = O

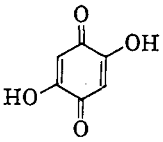

III, R′ = $-(OCH_3)_2$
IIIa, R′ = O

Attempts were now made to convert IIa by an intramolecular Michael reaction to 4-phenylcyclopentane-1,2-dione (IV).[4a,b] Analogously the preparation of 2,5-dihydroxy-*p*-benzoquinone (V)[5] was attempted *via* an intramolecular Claisen condensation. Both reactions did proceed smoothly in the expected manner when magnesium methoxide was chosen as the base; however, when other bases such as sodium alkoxides, secondary and tertiary amines, or quaternary ammonium salts were employed, a number of unidentified products were formed, none of which were the desired compounds. These results can be explained by postulation of a magnesium ion complex, formed from the enolate of the α-dicarbonyl system, which would hold the progenitor in the proper conformation. This communication thus establishes a convenient synthesis of cyclic compounds, such as IV and V, from acyclic α-dicarbonyl precursors.




IV




V

Experimental Section

4,4-Dimethoxy-3-oxo-1-phenyl-1-pentene (II).—A mixture of 3 g. of 3,3-dimethoxy-2-butanone and 2.6 g. of benzaldehyde was dissolved in a solution consisting of 25 ml. of methanol and 20 ml. of 20% sodium hydroxide. After 10 hr. at room temperature some of the methanol was evaporated under vacuum and the solution was extracted with ether and dried over sodium sulfate. The yellow-green liquid remaining after evaporation of the ether was purified by distillation at 104° (0.25 mm.). A total of 4.0 g. (80%) of II was obtained: $\lambda_{\max}^{CH_3OH}$ 299 mμ (ϵ 20,700), 229 (8400), 223 (8670); $\lambda_{\max}^{CHCl_3}$ 5.92, 6.24, 6.36, 6.73, 6.94 μ; the n.m.r. spectrum showed singlets at τ 8.66 (3H) and 6.77 (6H) and a complex group of peaks centered at τ 2.6 (7H) which includes phenyl and vinyl protons.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.45; H, 7.20.

Benzalbiacetyl (IIa).—To a solution of 0.50 g. of *p*-toluenesulfonic acid in 150 ml. of acetone was added 2.8 g. of II. After 15 hr. at room temperature the acetone was removed under vacuum, the resulting yellow oil dissolved in benzene, and the organic phase was extracted with water until neutral. Drying and evaporation of the benzene followed by crystallization from petroleum ether (b.p. 60–68°) yielded 1.98 g. (89%) of benzalbiacetyl: m.p. 48–50° (lit.[3] m.p. 52–53°); $\lambda_{\max}^{CH_3OH}$ 302 mμ (ϵ 17,900), 228 (8290), 223 (8170); $\lambda_{\max}^{CHCl_3}$ 5.83, 5.95, 6.33, 6.69, 6.91 μ; the n.m.r. spectrum had a τ 7.64 (3H) singlet and a complex group of peaks due to vinyl and phenyl protons at τ 2.5 (7H).

4-Phenylcyclopentane-1,2-dione (IV).—Benzalbiacetyl (IIa, 0.40 g.) in 40 ml. of dry methanol was added over 90 min. to a refluxing solution of 2.0 g. of magnesium methoxide in 225 ml. of dry methanol. After refluxing an additional 30 min., the methanol was evaporated under vacuum, the residue in ether was acidified, and the organic layer was washed until neutral. Drying the ether layer over sodium sulfate and subsequent evaporation yielded a light brown crystalline mass which was recrystallized from ether. Further purification by sublimation at 80° (0.5 mm.) provided 0.255 g. (64%) of colorless crystals: m.p. 111.5–113° (the mixture melting point of this material and IV obtained from the synthesis of Staudinger and Ruzicka[4a] was not depressed); $\lambda_{\max}^{CH_3OH}$ 253 mμ (ϵ 9500) which shifted to 292 mμ in 0.01 *N* methanolic sodium hydroxide; $\lambda_{\max}^{CHCl_3}$ 2.87, 2.98, 5.86, 6.05, 6.22, 6.70, 6.89 μ; the n.m.r. spectrum showed an ABX octet at τ 7.39 (2H, J_{AB} = 19 c.p.s., J_{AX} = 6 c.p.s., J_{BX} = 2.5 c.p.s.) for the nonequivalent methylene protons, a multiplet at τ 6.00 (1H) for the benzylic proton, a τ 3.42 (1H, J = 3 c.p.s.) doublet assigned to the vinylic proton, a broad singlet for the enol hydroxyl at τ 3.50 (1H), and the aromatic protons at τ 2.79 (5H).

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.78. Found: C, 75.83; H, 6.01.

Methyl 2,4-Dioxo-5,5-dimethoxyhexanoate (III).—A solution of 12 g. of dimethyl oxalate and 13.2 g. of ketal I in 50 ml. of methanol was added to a solution of 5.5 g. of sodium methoxide in 100 ml. of methanol. The mixture was kept overnight at room temperature and then an equal amount of ether was added. The sodium salt of III precipitated as a colorless crystalline solid. Filtration, followed by washing the filter cake several times with ether, provided 15 g. (62.5%) of the sodium salt of III: $\lambda_{\max}^{Nujol}$ 5.83, 6.08, 6.12 μ.

2,5-Dihydroxy-*p*-benzoquinone (V).—One gram of the sodium salt of III was suspended in 25 ml. of acetone. To this suspension was added, dropwise, concentrated sulfuric acid until the mixture was just slightly acidic. The reaction mixture was stirred for 3 hr. at room temperature and then filtered. The filtrate was concentrated under vacuum to one-fourth of its original volume, diluted with water, and immediately extracted with ether. The ether extract was washed with saturated sodium chloride solution, dried over sodium sulfate, and evaporated. The yellow oily residue (700 mg.) was taken up in a solution of 300 mg. of magnesium in 30 ml. of methanol which had been prepared in the meantime. The mixture was refluxed

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[1] This work was supported by the National Science Foundation (Grant No. 19242) and the Wisconsin Alumni Research Foundation.

[2] A. Braude and C. J. Timmons, *J. Am. Chem. Soc.*, **75**, 3135 (1953).

[3] (a) O. Diels and E. Andersonn, *Ber.*, **44**, 883 (1911); (b) O. Diels, *Ann.*, **434**, 1 (1923).

[4] (a) H. Staudinger and L. Ruzicka, *Helv. Chim. Acta*, **7**, 442 (1924). (b) W. Dieckman, *Ber.*, **32**, 1932 (1899); **55**, 2470 (1922).

[5] R. Scholl and P. Dahll, *ibid.*, **57**, 82 (1924).