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.

Acknowledgment.—The authors are grateful to Mr. W. R. Freeman for the g.l.p.c. analyses.

Magnesium Methoxide Cyclization of Biacetyl Derivatives[1]

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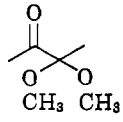
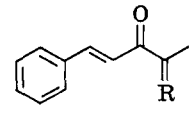
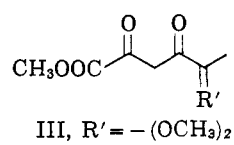
As part of another program a synthesis of cyclic α-diketo compounds was required which would involve intramolecular reaction of an acyclic progenitor. For this purpose model reactions were carried out with certain derivatives of 2,2-dimethoxy-3-butanone (I),[2] such as II and III, which were obtained 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

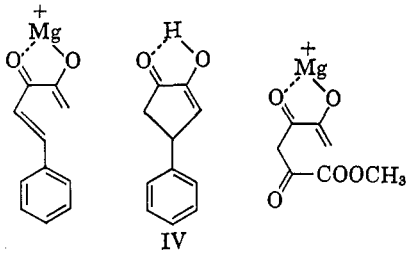


II, R = $-(OCH_3)_2$
IIa, R = O

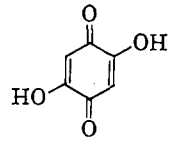


III, R′ = $-(OCH_3)_2$
IIIa, R′ = O

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*



IV



V

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.

(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).

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: λ_{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

for 3 hr., then diluted with ether, and extracted with 10% acetic acid. The aqueous phase, which was deep red, was further acidified with dilute hydrochloric acid, whereupon the color changed to yellow. The acidified aqueous mixture was extracted with ether–ethyl acetate. The organic extract was washed with water until neutral and dried over sodium sulfate. On partial evaporation of the solvent, there crystallized 165 mg. of V (28.3%) as fine orange needles: m.p. 208–212° dec., lit.[5] m.p. 211° dec.; $\lambda_{max}^{dioxane}$ 6.05, 6.14 μ; $\lambda_{max}^{ethanol}$ 285 mμ (ϵ 18,350), lit.[5] log ϵ 4.27.

Aziridines. XIII. Reactions of Cyclohexenimine Derivatives[1]

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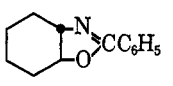
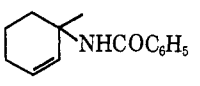
In 1956, it was reported[2] that pyrolysis of a sample of N-benzoylcyclohexenimine (Ia), m.p. 70–72°, at 120° followed by distillation at 180° (20 mm.) and chromatography on alumina gave a 20% yield of a product to which was ascribed the isomeric *trans*-oxazoline structure II. The assignment of structure was based only on the observation of a melting point of 66–67° (lit. m.p. 66.2–67.6°[3] and 68.5–69.0°[4] for authentic II) and an elemental analysis for nitrogen. In view of the similarity of melting points of Ia and II, this conclusion seems open to question. Furthermore, by analogy with a number of reported pyrolytic isomerizations of acyl aziridines, the anticipated product is the unsaturated amide III.[5,6]

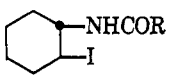
Ia, R = C_6H_5
b, R = $C_6H_4NO_2$-*p*



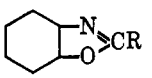
II



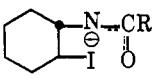
III



IVa, = R C_6H_5
b, = $C_6H_4NO_2$-*p*



Va, R = C_6H_5
b, R = $C_6H_4NO_2$-*p*



VIa, R = C_6H_5
b, R = $C_6H_4NO_2$-*p*

Therefore a reinvestigation of the pyrolysis was undertaken. It was found that heating compound Ia either alone as described,[2] or in a benzene solution at 150° for 10 hr., gave only unreacted starting material. In benzene solution at 200–210°, compound Ia was isomerized to the unsaturated amide III, which was conclusively identified by comparison with an authentic sample. The pyrolysis of Ia is therefore not anomalous, but follows the previously observed pattern.

In previous papers in this series we described the preparation of the quaternary methiodides of cycloheptenimine, cyclooctenimine, and *trans*-cyclododecenimine.[6,7] These are all stable, crystalline compounds which were found to be particularly suitable for structure determination by the three-dimensional single-crystal X-ray diffraction technique.[8] In contrast, it was reported that attempted quaternization of cyclohexenimine gave only ring-opened products.[9] These observations were confirmed in our laboratory. In view of these results, we prepared a number of N-aroyl and N-arenesulfonyl derivatives of cyclohexenimine containing a heavy element. Of these, the N-*p*-iodobenzenesulfonyl derivative was found suitable for X-ray study, and its structure was determined in the laboratory of L. M. Trefonas.[8]

A comparison of the structures reported by Trefonas for cyclohexenimine and cycloheptenimine provides an excellent rationalization for the difference in stability of the quaternary iodides. The six-membered ring of cyclohexenimine is very nearly planar and presumably there are no axial hydrogens to obstruct the nucleophilic back-side attack by iodide ion. In contrast, the seven-membered ring in cycloheptenimine is considerably puckered and appears to have four hydrogens in approximately axial positions which can block back-side approach of the iodide ion.

Examples of the isomerization of N-acyl aziridines by treatment with sodium iodide in acetone or acetonitrile have been reported,[5] and an iodo amide was suggested as a possible intermediate in this reaction. We have now found that treatment of N-benzoylcyclohexenimine Ia with sodium iodide in acetonitrile or acetone indeed gives an iodo amide, N-(*trans*-2-iodocyclohexyl)benzamide (IVa). On the other hand, the analogous *p*-nitrobenzoyl derivative Ib on treatment with sodium iodide in acetone gave primarily the oxazoline Vb, and only a small amount of the iodo amide IVb. In acetonitrile, Vb was formed exclusively, in 95% yield.

A possible explanation of this difference in reactivity is that the more strongly basic intermediate ion VIa preferentially abstracts a proton from the solvent (which may possibly contain some water) to form the amide IVa, whereas the more stable and less basic ion VIb undergoes cyclization.[10]

The iodo amide IVa was not cyclized to the oxazoline Va even on treatment with sodium ethoxide in ethanol, a result which was unexpected in view of the ready cyclization of the corresponding tosylate.[11]

(1) This investigation was supported in part by Public Health Service Research Grant No. GM-11883 from the National Institute of General Medical Sciences.

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(10) This explanation was suggested by a referee and is analogous to that offered by G. E. Ham, Abstracts of the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p. 16N, for results obtained from the reaction of O-ethyl-N,N-ethyleneurethan and sodium iodide.

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