tures at which the rearrangement is generally executed.[5]

EXPERIMENTAL[6]

2,2-Dibromocyclopropylcarbinyl phenyl ether (II). To a stirred suspension of anhydrous potassium *t*-butoxide (0.5 mole) in a solution of 165 g. (1.2 moles) of allyl phenyl ether and 100 ml. of pentane there was added, during 1 hr., 126.5 g. (0.5 mole) of bromoform. After 5 hr. at room temperature (200 ml. of pentane was added to facilitate stirring), hydrolysis, extraction with pentane, drying over magnesium sulfate and distillation gave 133 g. of recovered allyl phenyl ether and 41.2 g. of material, b.p. 119–126° at 1 mm. which solidified at room temperature. After several recrystallizations from ethanol, the product (31.5 g., 21%) melted at 53–54°.

Anal. Calcd. for $C_{10}H_{10}Br_2O$: C, 39.23; H, 3.27; Br, 52.32. Found: C, 39.21; H, 3.31; Br, 52.43.

Cyclopropylcarbinyl phenyl ether (I). *A. Reduction of* II. To a mixture of 100 ml. of 95% ethanol, 60 g. of Raney nickel-aluminum alloy, and 10 g. (0.033 mole) of II was added in 1 hr. 600 ml. of 10% sodium hydroxide.[7] After two additional hours of reflux the mixture was filtered and the nickel was washed successively with 100 ml. of 10% sodium hydroxide and with 400 ml. of pentane. The aqueous layers were poured into 400 ml. of concd. hydrochloric acid, then extracted with pentane. The combined pentane extracts gave 3.0 g. (62%) of cyclopropylcarbinyl phenyl ether (I), b.p. 51–53° at 2 mm., n_D^{25} 1.5199.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.17. Found: C, 81.11; H, 8.29.

B. Displacement on cyclopropylcarbinyl tosylate by phenoxide ion. Cyclopropylcarbinyl tosylate was prepared by a procedure analogous to that used by Bergstrom and Siegel[8] for the benzenesulfonate. *p*-Toluenesulfonyl chloride (19.0 g., 0.1 mole) and 50 ml. of methylene chloride was added, at −3 to +3° during 45 min. to a mixture of 26.4 ml. of 2,4,6-collidine and 7.2 g. (0.1 mole) of cyclopropylcarbinol. Additional methylene chloride (25 ml.) was added, the mixture was stirred at 0° for 2 hr., and the collidine then neutralized with 25 ml. of 10*N* sulfuric acid, the temperature being kept below 15°. Layers were separated, the aqueous layer was extracted with methylene chloride, and the combined organic layers extracted with three 20-ml. portions of ice cold 2.5*N* sulfuric acid, then dried over potassium carbonate. The solvent was removed under reduced pressure with no external heat.

The red oil which remained was dissolved in 50 ml. of anhydrous ether and added at 0° over 30 min. to a suspension of sodium phenoxide (from 250 g. of phenol and 34.5 g. of sodium) in 200 ml. of ether. The solution was stirred at room temperature for 1.5 days, refluxed for 4 days, filtered, and washed successively with 10% alkali and with water. After drying and removal of the solvent there was obtained 3.5 g. (23%) of crude product which on fractionation gave 1.0 g. of pure cyclopropylcarbinyl phenyl ether, n_D^{25} 1.5199, whose infrared spectrum was identical with that prepared above.

Attempted thermal rearrangement of I. One milliliter of I was refluxed (214°) at atmospheric pressure for 6 hr. The infrared spectrum was unchanged, and 12 hr. of additional reflux also resulted in no change. One milliliter of I, sealed in an 11-ml. tube, was heated at 300 ± 4° for 10 hr., and recovered unchanged (infrared spectrum, negative ferric chloride test).

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KEDZIE CHEMICAL LABORATORY
MICHIGAN STATE UNIVERSITY
EAST LANSING, MICH.

(5) Pyrolysis of certain cyclopropylcarbinyl derivatives at 500–520°, however, does lead to rearrangements; see C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007 (1960).

(6) Analyses by Spang Microanalytical Laboratory, P. O. Box 1111, Ann Arbor, Mich.

(7) D. Papa, E. Schwenk, and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942).

(8) C. G. Bergstrom and S. Siegel, *J. Am. Chem. Soc.*, **74**, 145 (1952).

Synthesis of β-Lactones from β-Hydroxyacids

E. TESTA, L. FONTANELLA, AND L. MARIANI

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As a part of a study on compounds active on the central nervous system[1] we recently described a new general method of synthesis of β-lactones, (diazotization of α,α-disubstituted β-aminoacids in acetic acid at low temperature).[2] The β-lactones are useful intermediates for pharmacologically active compounds (α-alkyltropic acids and derivatives,[3a,b] dihydro 1,3-oxazine-2,4-diones,[4] α-methylatropine[5]).

Many β-lactones are recorded in literature, which were obtained by different methods.[6] However, recently two processes for the preparation of β-lactones by dehydration of the corresponding β-hydroxyacids have been published: Diassi and Dylion[7] cyclized yohimbic acid to the corresponding β-lactone by means of pyridine and ethyl chloroformate; Sheehan, *et al.*[8] cyclized *N*-trityl-L-serine by means of *N*,*N*′-diisopropylcarbodiimide. Their work prompted us to communicate our experiences in this field.

EXPERIMENTAL

When a benzene solution of α,α-diethyl-β-hydroxypropionic acid[2,5,9] was treated at 10° to 15° with 1 mole of thionyl chloride and 1 mole of pyridine, and water added after 30 min. and the mixture extracted with benzene a crystalline compound separated from the aqueous layer.

(1) Paper XV of this series see E. Testa, L. Fontanella, G. F. Cristiani, and L. Mariani, *Helv. Chim. Acta*, **42**, 2370 (1959).

(2) E. Testa, L. Fontanella, G. F. Criastiani, and L. Mariani, *Ann.*, in press.

(3) (a) R. Fusco and E. Testa, *Farmaco* [*Ed. sci.*], **12**, 828 (1957); (b) E. Testa, *Farmaco* [*Ed. sci.*], **12**, 837 (1957).

(4) E. Testa, L. Fontanella, G. F. Cristiani, and G. G. Gallo, *J. Org. Chem.*, **24**, 1928 (1959).

(5) G. Melone, A. Vecchi, G. Pagani, and E. Testa, *J. Org. Chem.*, in press.

(6) H. E. Zaugg, *Org. Reactions*, 307 (1954).

(7) P. A. Diassi and C. M. Dylion, *J. Am. Chem. Soc.*, **80**, 3746 (1958).

(8) J. C. Sheehan, K. Hasspacher, and Y. Lieh Yeh, *J. Am. Chem. Soc.*, **81**, 6086 (1959).

(9) B. J. Ludwig, *J. Am. Chem. Soc.*, **72**, 5329 (1950).

The compound was identified as bis(β-carboxy-β-ethylbutyl) sulfite, m.p. 142–144° (from ethyl ether–petroleum ether (b.p. 45–60°)).

Anal. Calcd. for $C_{14}H_{26}O_7S$: C, 49.69; H, 7.71; S, 9.48. Found: C, 49.65; H, 7.65; S, 9.51.

The organic layer was dried over sodium sulfate and distilled; 8.5% of *α,α-diethyl-β-propiolactone* (I) was isolated, b.p. 65°–70° (7 mm., air bath).

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.43. Found: C, 65.59; H, 9.44.

Compound I was identical with an authentic sample of α,α-diethyl-β-propiolactone.[2] Its structure was confirmed by conversion of I into the known α,α-diethyl-β-hydroxypropionic acid[2,4,9] (m.p. 60–62°); the infrared spectrum of I shows a typical band at 1815 cm.$^{-1}$

The cyclization reaction with thionyl chloride and pyridine occurred also with α-phenyl-α-*n*-propyl-β-hydroxypropionic acid[2,4]: the corresponding β-lactone[2] (b.p. 110–115°/0.5 mm., air bath) was isolated in 5.3% yield. In this case, no formation of a sulfite derivative was noted. The lactone shows a typical band at 1815 cm.$^{-1}$ α-Phenyl-α-*n*-propyl-β-propiolactone was hydrolized to the known α-phenyl-α-*n*-propyl-β-hydroxypropionic acid[10] (m.p. 104–107°).

The method described allows the preparation of β-lactones directly from β-hydroxycarboxylic acids, though in low yields.

ORGANIC SYNTHESES DEPT.
RESEARCH LABORATORIES OF LEPETIT S.P.A.
MILAN, ITALY

(10) E. Testa, L. Fontanella, G. F. Cristiani, and F. Fava, *Ann.*, 619, 47 (1958).

α-Oximino Ketones. VIII. The Second Order Beckmann Rearrangement in Alcohols

ARTHUR F. FERRIS, GRANNIS S. JOHNSON, AND FRANCIS E. GOULD

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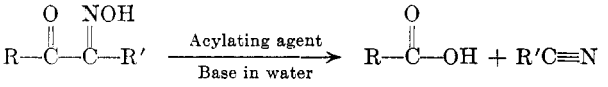
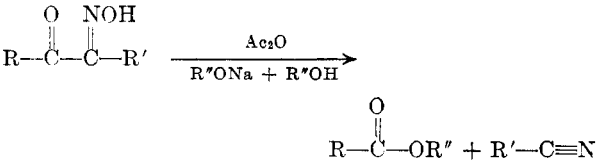
When α-oximino ketones possessing the *anti* configuration are treated with strong acids or acid chlorides, or when they are dissolved in aqueous base and treated with acylating agents, they are cleaved to nitriles and carboxylic acids, a reaction which has been termed a "second order" Beckmann rearrangement.[1] Recent work in this laboratory has shown that when a salt of 2,6-dioximinocyclohexanone in alcoholic base is treated with an acid anhydride, it is cleaved to ethyl 5-cyano-2-oximinovalerate.[2]

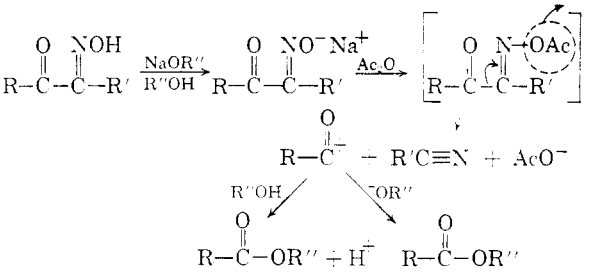


It has been found now that formation of esters is characteristic of simple α-oximino ketones as well as of 2,6-dioximinocyclohexanone when the second order Beckmann rearrangement is carried out in alcohols. The yields of esters obtained by the action of acetic anhydride on solutions of four



α-oximino ketones in alcoholic sodium alkoxides are reported in Table I. No attempt was made to isolate the low molecular weight nitrile products obtained when R′ was hydrogen or a methyl group, but when R′ was the phenyl group benzonitrile was obtained as expected. The tendency of the anhydride to react with the oxime instead of the alcohol can be explained on the basis discussed previously,[2] namely that the oxime anion is much more effective in attacking anhydride than the neutral alcohol molecule.

The fact that esters are obtained when the second order Beckmann rearrangement is carried out in alcohols provides additional confirmation for the mechanistic interpretation of the reaction presented previously.[1b] Thus if the rearrangement involves first formation of the acylated α-oximino ketone and second concurrent departure of the acetate anion and shift of the electron pair between the oxime carbon and the carbonyl carbon to form a nitrile and an oxocarbonium ion, it would be expected when the solvent is an alcohol that the oxocarbonium ion would attack the alcohol or combine with the alkoxide anion to form an ester, and that is exactly the result observed. The



alternative hypotheses that the reaction is initiated by attack of the alkoxide ion on the carbonyl carbon or involves concurrent attack at the carbonyl carbon and departure of the acetate ion have been considered in earlier work[3] and rejected on the basis of the fact that treatment of an α-acyloximino ketone in alcohol with an amine or other weak base leads to formation of the same ester product obtained when alkoxide is used.

EXPERIMENTAL[4]

α-Oximino ketones. 2-Oximino-1-phenyl-1-propanone and α-benzil monoxime were purchased from Distillation Prod-

(1) (a) A. H. Blatt and R. P. Barnes, *J. Am. Chem. Soc.*, 56, 1148 (1934); (b) A. F. Ferris, *J. Org. Chem.*, 25, 12 (1960). References to earlier work are given in these papers.

(2) A. F. Ferris, G. S. Johnson, F. E. Gould, and H. Stange, *J. Org. Chem.*, 25, 1302 (1960).

(3) A. F. Ferris, G. S. Johnson, and F. E. Gould, *J. Org. Chem.*, 25, 496 (1960).

(4) All melting points and boiling points are uncorrected.