[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

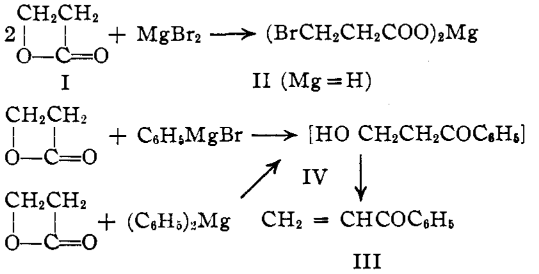
β-Propiolactone. VII.[1] Reactions with Grignard Reagents

BY T. L. GRESHAM, J. E. JANSEN, F. W. SHAVER AND R. A. BANKERT

Previous studies[1] demonstrated the great ease with which the ring opening of β-propiolactone (I) occurs at the acyl-oxygen or alkyl-oxygen bond. It was shown that polymerization of I is a competing reaction in most cases. In view of these results, it was of interest to investigate reactions of β-propiolactone which might occur at the carbonyl group such as those with Grignard reagents.

Addition of I to phenylmagnesium bromide in ether resulted in a mixture of products consisting mostly of β-bromopropionic acid (II). The neutral portion of the mixture contained phenyl vinyl ketone (III) in addition to some halogenated ketone. The expected β-hydroxypropiophenone (IV) was apparently too unstable to isolate.

Some polymerization of I occurred and the amount of polymer was increased considerably with reversal of the order of addition.

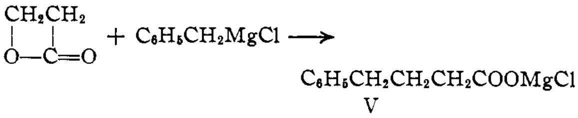


A study of the possible individual reactions was made. Addition of I to magnesium bromide dietherate in ether resulted in a vigorous reaction with immediate and complete precipitation of the magnesium salt II in almost quantitative yield. The insoluble reaction product was a salt rather than a complex of the type reported for ethylene oxide and magnesium bromide[2] because the addition of the filtered solid to a solution of thiourea in water and hydrochloric acid gave no β-isothioureidopropionic acid.[3] Addition of I to a solution of thiourea, magnesium bromide and hydrochloric acid gave only β-isothioureidopropionic acid, as the hydrochloride, rapidly and completely. Unless the solution is acid, β-isothioureidopropionic acid is formed slowly from magnesium β-bromopropionate and thiourea. The similarity of the infrared absorption curves for the solid salt and a sample of magnesium β-bromopropionate further confirmed the salt structure and the analysis showed it to be a normal salt. These experiments exclude the possibility of formation of the bromo acid by the reaction of I with magnesium bromide or hydrogen bromide during the decomposition with water.

Addition of I to diphenylmagnesium resulted in a mixture of products similar to the neutral fraction from the Grignard reaction. Phenyl vinyl ketone was isolated in poor yield and no β-bromopropionic acid was present.

With I and methylmagnesium iodide, the yields of β-halopropionic acid and vinyl ketone were similar to those with phenylmagnesium bromide.

Addition of I to benzylmagnesium chloride gave a mixture of about equal amounts of acidic and non-acidic products. The acidic portion consisted mostly of phenylbutyric acid (V) with a small amount of β-chloropropionic acid. The source of the chloro acid must have been from magnesium chloride. The phenylbutyric acid could have resulted from a direct salt type reaction of benzylmagnesium chloride with I or from a coupling type reaction[4] of benzylmagnesium chloride with magnesium β-chloropropionate. This latter reaction is unlikely, however, because attempts to carry it out gave negative results. Only a trace of phenylbutyric acid was isolated from the acid fraction. A considerable portion of neutral oil, part of which was toluene and dibenzyl, was formed.



Experimental

Reaction of I with Phenylmagnesium Bromide.—One mole (72 g.) of I in 70 ml. of anhydrous ether was added over a period of one and one-quarter hours to one mole of phenylmagnesium bromide in 400 ml. of ether at −6 to 0°. The Grignard complex was decomposed with ice cold sulfuric acid solution. The insoluble polymer of I (6.5 g., 9.6%) was filtered and the aqueous layer extracted with three 200-ml. portions of ether. The combined ether solutions were extracted with four 300-ml. portions of saturated sodium bicarbonate solution and dried over sodium sulfate. Following distillation of the ether, the product was distilled through a 6″ × 1″ column (packed with 1/2″ Berl saddles) giving the following fractions: 1, 90–112° (20 mm.), 7 g.; 2, 110–125° (18 mm.), 21 g.; 3, 140–195° (18 mm.), 15.5 g.; residue 30 g. All fractions gave a positive Beilstein halogen test. Fractions 1 and 2 consist mainly of vinyl phenyl ketone (21.2% yield) identified by its reaction with phenylhydrazine[5] to form 1,3-diphenyl-Δ²-pyrazoline, m. p. 151–153°.

Anal. Calcd. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.95; H, 6.33; N, 12.67.

The sodium bicarbonate extracts were made strongly acid with concentrated sulfuric acid resulting in the separation of a colorless oil. The oil was extracted with three 150-ml. portions of ether and dried over sodium sulfate. Following distillation of the ether, the undistilled portion solidified giving 64 g. (43%) of a yellow crystalline solid. Two recrystallizations of the solid from hexane gave white

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[1] For paper VI of this series, see THIS JOURNAL, **71**, 661 (1949).

[2] Huston and Aggett, *J. Org. Chem.*, **6**, 123 (1941).

[3] Gresham, Jansen and Shaver, THIS JOURNAL, **70**, 1001 (1948).

[4] Fuson, *ibid.*, **48**, 2681 (1926).

[5] Kohler, *Am. Chem. J.*, **42**, 387 (1909).

crystalline plates, m. p. 60.5–61.5°. A mixture of the solid with a sample of β-bromopropionic acid, m. p. 60–61.5°, melted at 60–61.5°.

Anal. Calcd. for $C_3H_5O_2Br$: neut. eq., 152.9. Found: neut. eq., 153.5.

When an ether solution of phenylmagnesium bromide (1 *M* in 400 ml.) was added to 1 mole (72 g.) of I in 400 ml. of ether at −28 to −35°, the isolated products were as follows: polymer of I, 31 g. (43.1%); β-bromopropionic acid, 44 g. (28.7%); distilled neutral fractions, 1, 75–120° (0.4 mm.), 20 g.; 2, 110–165° (0.4–0.3 mm.), 18 g.; 3, 155–230° (0.3–0.4 mm.), 23.5 g.; residue, 10.5 g. All fractions gave a positive Beilstein halogen test.

β-Anilinopropiophenone can be prepared by the reaction of aniline with either vinyl phenyl ketone or β-halopropiophenone.[6] This derivative was obtained from fractions 1 and 2 as faintly yellow plates, m. p. 115–116°.

Anal. Calcd. for $C_{15}H_{15}ON$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.85; H, 6.71; N, 6.26.

Reaction of I with Magnesium Bromide Dietherate.—Addition of 36 g. (0.5 mole) of I to magnesium bromide dietherate[7] (0.5 mole) in 400 ml. of anhydrous ether resulted in the precipitation of a yellow solid. The solid was filtered, washed with 100 ml. of ether and dissolved in 400 ml. of water. The water solution was acidified and the resulting orange oil extracted with 3–150 ml. portions of ether and dried over sodium sulfate. Following distillation of the ether, the undistilled product solidified. Recrystallization from hexane gave 63.5 g. (83%) of β-bromopropionic acid, m. p. 59–60°.

Reaction of I with Thiourea, Hydrochloric Acid and Magnesium Bromide.—Addition of I to a water solution of equal molar quantities of thiourea, magnesium bromide and hydrochloric acid resulted in an exothermic reaction. Neutralization of the cooled solution with sodium hydroxide gave a 70% yield of a white crystalline solid. A mixture of the solid, m. p. 176–178°, with a sample of β-isothioureidopropionic acid, m. p. 178–179°, produced no depression of the melting point. A similar experiment using magnesium β-bromopropionate, thiourea and hydrochloric acid gave no β-isothioureidopropionic acid.

Reaction of I with Diphenylmagnesium.—One mole (72 g.) of I was added over a period of one-half hour at −25 to −32° to an ether solution of diphenylmagnesium prepared from 1 mole of phenylmagnesium bromide by dioxane precipitation. The addition complex was decomposed as described above and the insoluble solid (84 g., consisting largely of polymers of I) filtered. Distillation of the products gave the following fractions: 1, 27–95° (40–24 mm.), 5.5 g.; 2, 100–150° (23 mm.), 12 g.; 3, 140–158° (23 mm.), 5.5 g.; and residue, 4.5 g. Fraction 2, consisting largely of vinyl phenyl ketone, gave 1,3-diphenyl-Δ^2-pyrazoline,[5] m. p. 151–153°, on treatment with phenylhydrazine.

Reaction of I with Methylmagnesium Iodide.—One mole of I was added to an ether solution of methylmagnesium iodide (1 mole) at −10 to −13°. The Grignard complex was decomposed giving polymer of I (3 g., 4.2%), a neutral oil (13 g., b. p. 29–78° (25–28 mm.)) and β-iodopropionic acid (87 g., 43.5%). The neutral oil contained methyl vinyl ketone as identified by treating with phenylhydrazine to give 1-phenyl-3-methylpyrazoline,[8] m. p. 75.5–76.5°.

Reaction of I with Benzylmagnesium Chloride.—One mole of I was added to an ether solution of benzylmagnesium chloride (1 mole) at −12 to 0°. The Grignard complex was decomposed giving polymer of I (16.1 g., 22.4%) and neutral and acidic portions. Distillation of the neutral portion gave two fractions from which no identifiable product could be isolated. Distillation of the acidic portion gave 17.5 g. (16.1%) of β-chloropropionic acid, m. p. 35–38° and 53.2 g. (32.4%) of γ-phenylbutyric acid, m. p. 47–48°. A mixture of the β-chloropropionic acid with an authentic sample produced no depression of the melting point. The analytical data for the γ-phenylbutyric acid are as follows:

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37; neut. eq., 164.2. Found: C, 73.37; H, 7.46; neut. eq., 165.2.

Addition of an ether solution of benzylmagnesium chloride to a suspension of magnesium β-bromopropionate in ether gave a neutral fraction containing toluene and dibenzyl and an acid fraction containing a relatively large amount of β-bromopropionic acid but only a trace of γ-phenylbutyric acid.

Summary

Reactions of β-propiolactone with Grignard reagents give mixtures of beta-halopropionic acids and vinyl ketones. The possible individual reactions with the components of the Grignard reagent are described. With benzylmagnesium chloride, phenylbutyric acid is a major reaction product.

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[6] Collet, *Bull. soc. chim.*, [3] **17**, 80 (1897).

[7] Menschutkin, *Z. anorg. Chem.*, **49**, 34–35 (1906).

[8] Maire, *Bull. soc. chim.*, [4] **3**, 277–278 (1909).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Studies on the Mechanism of the von Braun Reaction

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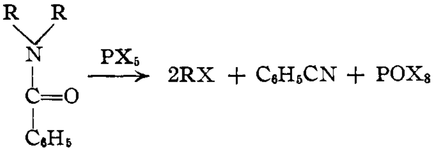
The reaction in which phosphorus pentahalide converts an N-substituted benzamide (I) to an alkyl halide or alkylene dihalide and benzonitrile has been termed the von Braun reaction.[1] Intermediates such as amido-halides, imido-halides, and compounds containing a nitrogen–phosphorus link have been postulated, but in no case has the existence of such intermediates been definitely established. In the belief that the von Braun reaction might belong to the general class of displacement reactions at a saturated carbon, where bimolecular or unimolecular nucleophilic substitution is possible,[2] we have made a study of several series of N-substituted benzamides to determine the effect of hindrance and the fate of asymmetry at the α_N-carbon.

I



$$R_2N{-}C(=O){-}C_6H_5 \xrightarrow{PX_5} 2RX + C_6H_5CN + POX_3$$

In the N,N-alkylene-substituted benzamide series, we have investigated the reaction of N-

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[1] For leading reference, see von Braun, *Ber.*, **37**, 3210 (1904).

[2] Hughes, *J. Chem. Soc.*, 968 (1946).