the solution being treated each time with Darco, the white crystalline product melted at 53–54°.

Anal. Calcd. for $C_9H_8OBr_2$: C, 37.03; H, 2.74; Br, 54.75; mol. wt., 292. Found: C, 37.41; H, 3.08; Br, 54.69; mol. wt., 286.

The Benzal Derivative of 2,6-Dibromo-4-methylacetophenone.—The identity of the methyl ketone was confirmed by condensing it with benzaldehyde. About 6 g. of the crude ketone was mixed with 20 cc. of 10% sodium hydroxide solution, 10 cc. of 95% ethyl alcohol and 10 cc. of benzaldehyde. The mixture was shaken for twenty hours at room temperature. At the end of this period there was a yellow mixture of crystals and oil at the bottom of the flask. The entire mixture was shaken with ether which was then washed with bisulfite solution. The ether solution was washed with water, dried and evaporated giving a crystalline residue. After the crystals were washed with petroleum ether and recrystallized three times from ethyl alcohol they melted at 96–97°.

Anal. Calcd. for $C_{16}H_{12}OBr_2$: C, 50.57; H, 3.16; Br, 42.06; mol. wt., 380 Found: C, 51.06; H, 3.21; Br, 42.43; mol. wt., 379.

Summary

2,4,6-Trihalobenzoyl chlorides react with methylmagnesium halides to give the corresponding di-(2,4,6-trichlorobenzoyl)-methanes. Under suitable conditions the methyl ketone, undoubtedly an intermediate in the reaction, can be isolated.

The structure of the 1,3-diketones was proved by converting them to the corresponding mono- or dibromides and then regaining the original diketone by debromination.

2,6-Dibromo-4-methylacetophenone was obtained by the interaction of 2,6-dibromo-4-methylbenzoyl chloride and an excess of methylmagnesium iodide.

URBANA, ILLINOIS RECEIVED JUNE 17, 1938

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

Reformatsky Condensations Involving Vinylogs of Haloacetic Esters

BY REYNOLD C. FUSON, R. T. ARNOLD AND H. G. COOKE, JR.

The extension of the Reformatsky method to vinylogs of haloacetic esters was attempted with the hope of obtaining a method of synthesizing carotenoid chains. The general reaction sought was the following

$$XCH_2(CH{=}CH)_nCOOR \xrightarrow[Zn]{RCHO} R(CH{=}CH)_{n+1}COOR$$

Results obtained with ethyl γ-bromo- and γ-iodocrotonate show that the desired reaction takes place. The value of the method in synthetic work would appear to be conditioned by the availability of the γ-halocrotonates.

Ethyl γ-bromo- and γ-iodocrotonate react with benzaldehyde in the presence of zinc to give an oil which can be hydrolyzed to cinnamylideneacetic acid

$$XCH_2CH{=}CHCOOC_2H_5 \xrightarrow{C_6H_5CHO} C_6H_5(CH{=}CH)_2COOH$$

Cyclohexanone reacts similarly, giving the expected unsaturated ester, $C_6H_{11}(CH{=}CH)_2COOC_2H_5$.

Ethyl iodocrotonate also was condensed with *p*-chlorobenzaldehyde to give *p*-chlorocinnamylideneacetic acid. This acid was synthesized for comparison from *p*-chlorocinnamaldehyde and malonic acid.

It was of particular interest to compare the behavior of ethyl γ-iodocrotonate with that of the corresponding saturated ester, ethyl γ-iodobutyrate, to see what influence the vinylene linkage really had. The condensation reaction depends chiefly on the reactivity of the halogen atom which in turn is due presumably to the activating influence of the carbethoxy group. The transfer of this effect should be much more efficient in the vinylogs of haloacetic esters than in the corresponding saturated esters. This was found to be the case. Ethyl γ-iodobutyrate condenses with benzaldehyde in the presence of zinc to give the normal Reformatsky condensation but the reaction proceeds very slowly and the yields are almost negligible.

Experimental

The Condensation of Ethyl γ-Bromo- and γ-Iodocrotonate with Benzaldehyde.—Nineteen grams of ethyl γ-iodocrotonate[1] in 20 cc. of dry, peroxide-free butyl ether was added dropwise to a mixture of 16 g. of benzaldehyde, 30 cc. of butyl ether and 5.5 g. of zinc dust. The zinc dust was cleaned by treatment for a few seconds with dilute hydrochloric acid and subsequent washing with water, acetone and dry benzene. It was not allowed to stand in contact with the air. The mixture was refluxed, with stirring, for thirty-six hours, then decomposed with very

---

(1) Braun, THIS JOURNAL, 52, 3174 (1930).

dilute cold hydrochloric acid. Careful fractionation of the ether solution gave 2.3 g. of a viscous yellow oil; b. p. 162–165° (4 mm.).

The use of an equivalent amount of ethyl γ-bromocrotonate in the above process gave approximately 1 g. of the same high-boiling oil. Treatment of this oil with phenyl isocyanate in a closed, evacuated tube gave *sym*-diphenylurea. Oxidation with a sodium dichromate–sulfuric acid mixture converted the oil to benzoic acid.

The facts indicated that the oil was the expected hydroxy ester. Analysis showed, however, that it was impure, and it was subjected to *hydrolysis*. One cubic centimeter of the oil was added to a saturated solution of potassium hydroxide in ethyl alcohol and the mixture was allowed to stand overnight. Dilution with water followed by careful acidification with dilute sulfuric acid gave a solid which after recrystallization from benzene weighed 0.6 g. and melted at 165°. Admixture of a known sample of cinnamylideneacetic acid[2] did not depress the melting point.

The Condensation of Ethyl γ-Iodocrotonate with *p*-Chlorobenzaldehyde.—Fourteen grams of pure *p*-chlorobenzaldehyde and 6 g. of clean zinc dust were placed in a 500-cc., round-bottomed, three-necked flask containing 50 cc. of dry benzene and equipped with two efficient reflux condensers. The solution was heated to boiling and a solution of 20 g. of ethyl γ-iodocrotonate in 20 cc. of dry benzene was added dropwise. The reaction was highly exothermic, and an ice-bath was used to keep the ebullition from becoming too vigorous. After the addition was complete the mixture was refluxed for ten hours and decomposed with dilute hydrochloric acid and ice. The benzene layer gave 8.7 g. of a yellow oil; b. p. 180–185° (4 mm.). As in the case of benzaldehyde, analysis of this ester indicated that it was partially dehydrated.

***p*-Chlorocinnamylideneacetic Acid.**—One gram of the yellow oil was dissolved in 30 cc. of saturated alcoholic potassium hydroxide solution and allowed to stand overnight at room temperature. The mixture was diluted with water and acidified with dilute sulfuric acid. The precipitated *p*-chlorocinnamylideneacetic acid was recrystallized from ethanol, m. p. 251° (corr.), with decomposition.

Anal. Calcd. for $C_{11}H_9O_2Cl$: C, 63.30; H, 4.30. Found: C, 63.24; H, 4.45.

For comparison this acid was synthesized from *p*-chlorocinnamaldehyde and malonic acid by a method similar to that used by Dutt[2] for the synthesis of cinnamylideneacetic acid. To a solution of 7 g. of the aldehyde and 6 g. of the acid in 30 cc. of pyridine was added 3 cc. of piperidine, and the mixture refluxed for twenty hours. It was then poured into 250 cc. of dilute sulfuric acid and the dark gray precipitate was recrystallized first from glacial acetic acid and then repeatedly from 95% ethyl alcohol. The *p*-chlorocinnamylideneacetic acid formed in white flakes melting at 251° (corr.), with decomposition. No depression of melting point was noted when this acid was mixed with that prepared by the Reformatsky method. The methyl ester (from methyl alcohol) melted at 132° (corr.).

Anal. Calcd. for $C_{12}H_{11}O_2Cl$: C, 63.60; H, 4.90. Found: C, 64.32; H, 4.91.

The Condensation of Ethyl γ-Iodocrotonate with Cyclohexanone.—Fifteen grams of ethyl γ-iodocrotonate in 10 cc. of dry benzene was added dropwise to 50 cc. of benzene containing 12 g. of cyclohexanone and 4 g. of clean zinc dust. The mixture was refluxed for eight hours after the initial vigorous reaction had subsided and then decomposed with dilute sulfuric acid. Fractionation of the dried benzene solution produced 6.2 g. of the ethyl ester; it is a colorless oil boiling at 143–148° (8 mm.). Bromine and permanganate tests for unsaturation were positive.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.23; H, 9.48. Found: C, 74.28; H, 9.28.

Ethyl γ-Iodobutyrate.—Ethyl γ-chlorobutyrate prepared according to the method of Henry[3] was converted into the iodo ester by treatment with sodium iodide. A mixture of 127 g. of the chloro ester, 450 cc. of acetone and 127 g. of sodium iodide was shaken for three hours at 27°. Only 30 g. of sodium chloride separated. The mixture was then refluxed for two hours, filtered and the filtrate poured into 1 liter of ether. The ether solution was washed with water containing about 1% of sodium thiosulfate. Fractionation of the ether layer gave 130.6 g. or 63.5% of the theoretical amount of the iodo ester. The ester boiled at 84–85° (4 mm.).

Anal. Calcd. for $C_6H_{11}O_2I$: C, 29.75; H, 4.55. Found: C, 29.61; H, 4.61.

The Condensation of Ethyl γ-Iodobutyrate with *p*-Chlorobenzaldehyde.—To a boiling mixture of 75 cc. of benzene, 17.5 g. of *p*-chlorobenzaldehyde, and 8 g. of clean zinc was added dropwise a solution of 30 g. of ethyl γ-iodobutyrate in 30 cc. of benzene. The mixture was refluxed for twenty-four hours, cooled, decomposed with water and filtered through bone charcoal. The benzene layer yielded 10.3 g. of *p*-chlorobenzaldehyde, 4.3 g. of ethyl γ-iodobutyrate, 0.7 g. of a liquid boiling at 195–200° (3 mm.) (m. p. 122–123°) and some tarry products. The compound melting at 122–123° (from ethanol) had the composition of the expected unsaturated ester.

Anal. Calcd. for $C_{13}H_{15}O_2Cl$: C, 65.41; H, 6.29. Found: C, 65.26; H, 6.37.

Summary

The Reformatsky condensation has been extended to vinylogs of haloacetic esters. Ethyl γ-bromo- and γ-iodocrotonate have been condensed with benzaldehyde to give cinnamylideneacetic acid. *p*-Chlorocinnamylideneacetic acid has been made from *p*-chlorobenzaldehyde in a similar manner. Ethyl γ-iodobutyrate undergoes this type of condensation only with difficulty and in very low yield.

URBANA, ILLINOIS RECEIVED JUNE 18, 1938

---

(2) Dutt, *J. Ind. Chem. Soc.*, **1**, 297 (1924–25).

(3) Henry, *Bull. soc. chim.*, **45**, 341 (1886).