4. Contrary to the assumption of Holden and Lapworth, the production of benzoylacetic enolate and α-methylcinnamic esters in the action of sodium enol methylmalonic ester on benzalacetophenone, has no theoretical connection with the formation of sodium enol α,β-dimethyl-γ-carbethoxyglutaric ester in the union of sodium enol methylmalonic and crotonic esters.

5. It has been shown that α-methyl-α-carbethoxy-β-phenyl-γ-benzoylbutyric ester, and α-carbethoxy-α,β-dimethylglutaric ester, do not form cyclobutanone structures when treated with sodium ethoxide or sodium, but undergo almost complete retrogression. These esters, or their enolates, therefore, cannot be intermediates in the addition reactions discussed above and for this reason alone the interpretations of Holden and Lapworth are untenable.

6. Certain difficulties arising from the assumptions of Holden and Lapworth have been discussed and it has been shown that the only explanation of the formation of the enolate of α,β-dimethyl-γ-carbethoxyglutaric ester from sodium enol methylmalonic ester, consistent with experiment and theory, is the migration of methyl during the addition process.

CAMBRIDGE, MASSACHUSETTS

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The Action of Bleaching Powder on Ketones and on Ethyl Acetoacetate

BY CHARLES D. HURD AND CHARLES L. THOMAS[1]

In contrast to the general familiarity of the reaction between acetone and bleaching powder, very little is known of the action of bleaching powder on other ketones. Three substances each containing a CH_3CO— group were selected for study, namely, ethyl methyl ketone, furfuralacetone and ethyl acetoacetate.

Ethyl methyl ketone was selected to see if the reaction would yield chloroform and calcium propionate or ethylidene chloride and calcium acetate. Only the first of these two possibilities was realized. This provides a convenient source of propionic acid. Furfuralacetone, similarly studied, was found to be an excellent starting material for furylacrylic acid. Since furfuralacetone is readily prepared from furfural and acetone this method for the synthesis of furylacrylic acid is preferable to the Perkin reaction[2] which employs furfural, acetic anhydride and potassium acetate as reagents.

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(1) Holder of a Quaker Oats Fellowship (1929–1930) administered through the Miner Laboratories, Chicago.

(2) Baeyer, *Ber.*, **10**, 357 (1877).

The general equation for this type of synthesis is

$$2RCOCH_3 + 6CaOCl_2 \longrightarrow (RCOO)_2Ca + 3CaCl_2 + 2Ca(OH)_2 + 2CHCl_3$$

In the cases mentioned above, R represents C_2H_5- and $C_4H_3O-CH=CH-$. Ethyl acetoacetate was studied to see if the enolic methylene hydrogens were the ones substituted by chlorine, in which case dichloroacetic acid would be anticipated, or if the methyl group would be attacked, giving chloroform, as in the former cases. The product formed was dichloroacetic acid and not chloroform. Therefore, the intermediate product was $CH_3COCCl_2COOC_2H_5$ and not $CCl_3COCH_2COOC_2H_5$.

Study was also made of the oxidation of furfuralacetone by nitric acid. Oxalic acid and ammonium tetroxalate were identified in the reaction products. This resembles the observation of Newbury and Orndorff[3] that ammonium tetroxalate was in the products from acetone and dilute nitric acid.

Experimental Part

Ethyl Methyl Ketone.—Three hundred grams of commercial bleaching powder (24% available chlorine) was made into a paste with 750 cc. of water at 15°. The temperature of the water must be above 10°, otherwise too viscous a paste results. This mixture was put into a 3-liter flask which was equipped with a dropping funnel, mercury-sealed stirrer and condenser. Then 25 cc. of ethyl methyl ketone was gradually introduced with stirring, care being taken to avoid frothing over. The mixture became quite warm and 10 cc. of chloroform, a 45% yield, distilled. The index of refraction, n^{20}_D, of the distillate was 1.4452; n^{20}_D of chloroform, 1.4458; n^{20}_D of ethylidene chloride, 1.4165.

The residue in the flask was neutralized with nitric acid. Then more nitric acid was added to liberate the propionic acid, purposely adding less than the calculated amount to avoid subsequent extraction of nitric acid. Even with an excess, however, ether extracts but insignificant quantities of nitric acid from a dilute aqueous solution.

The acidified solution was made up to 2000 cc. with water. An aliquot portion of 500 cc. of this was extracted four times with ether for the organic acid and the extracts made up to 250 cc. Titration of an aliquot portion of 50 cc. of this ether solution with 0.2016 *N* alkali required 27.5 cc. This corresponds to a yield of 8.18 g. or 40.7% of the calculated amount of propionic acid.

The identity of propionic acid was confirmed by a Duclaux determination. For this purpose, a dilute solution of 110 cc. of the acid (in water) was distilled and ten 10-cc. distillates obtained therefrom. The cc. of 0.2016 *N* base to neutralize each in turn was: 7.72, 7.87, 7.51, 7.12, 6.57, 6.33, 5.79, 5.40, 5.26, 5.64. The ratio of each 10-cc. titration to the total 100 cc. value gave the series: 11.8, 23.9, 35.4, 46.4, 56.5, 66.3, 75.1, 83.4, 91.5, 100.0. These percentages practically coincide with the values obtained by Gillespie and Walters[4] for propionic acid. Acetic acid, in contrast, gives rise to a series beginning with 8 and continuing with approximate multiples of 8.

Furfuralacetone.—Furfuralacetone was prepared by the method of "Organic Syntheses."[5] In some experiments it was purified by vacuum distillation to separate it from

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(3) Newbury and Orndorff, *Am. Chem. J.*, **12**, 517 (1890).

(4) Gillespie and Walters, THIS JOURNAL, **39**, 2036 (1917).

(5) Leuck and Cejka, "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 42.

admixed difurfuralacetone. The purified product was collected at 110–112° (10 mm.); yield, 59–60%. In other experiments this tedious purification step was omitted. However, to ensure the removal of unused acetone the crude product was heated on a steam-bath for some hours. For purposes of calculation, it was assumed that this "crude furfuralacetone" contained 60% of furfuralacetone.

Furylacrylic Acid from Pure Furfuralacetone.—The details of this oxidation were identical with those previously described for ethyl methyl ketone, except that no dropping funnel was used. These quantities were involved: 300 g. of bleaching powder, made into a paste with 750 cc. of water at 15–20°; 37 g. of solid furfuralacetone; yield of chloroform, 18 g. or 55.5%. The reaction, as before, was exothermic and no external heat was applied. The paste in the flask was filtered and the filtrate acidified. The furylacrylic acid which separated was collected upon a filter. The filtrate from this operation was stirred up with the bleaching powder cake, boiled and refiltered. This filtrate gave more furylacrylic acid upon acidification. By repeating these steps, most of the furylacrylic acid was obtained in four such extractions. The yield was 33.5 g. or 89.5% of a product that melted at 139°.

Furylacrylic Acid from "Crude Furfuralacetone."—A larger run was made from the crude furfuralacetone mentioned above. A yield of 89.7% of furylacrylic acid was obtained on the basis of the furfuralacetone content. These quantities were taken: 1800 g. of bleaching powder (in 4.5 l. of water), 275 g. of crude furfuralacetone; yield of furylacrylic acid, 205 g. The assumption that none of the furylacrylic acid came from the difurfuralacetone in the crude ketone was justified since no furylacrylic acid was isolable in a test run with bleaching powder and difurfuralacetone.

Ethyl Acetoacetate.—The reaction between acetoacetic ester (52 g.) and bleaching powder (350 g. made into a paste with 1 liter of water) was exothermic but there was no odor of chloroform. The liquid was filtered after the heating effect had stopped and the filtrate was acidified and extracted with ether. The residue, after evaporating the ether, was a brown liquid with a strongly acid reaction and a sharp odor. The liquid was shown to be dichloroacetic acid by converting it into dichloroacetyl chloride with phosphorus trichloride and then treating it with aniline to produce dichloroacetanilide, m. p. 118°. The yield of the dichloroacetic acid was 31 g. or 60% of the calculated value.

Furfuralacetone and Nitric Acid.—Cold, concd. nitric acid reacted on furfuralacetone with almost explosive violence. The reaction was very vigorous even when the acid was diluted with an equal volume of water. Hence the tests were limited to 1–2 g. samples. In this case, after the oxides of nitrogen had been expelled, the solution was concentrated. On cooling, crystals of oxalic acid dihydrate, m. p. 100–101°, separated. It gave the characteristically insoluble calcium oxalate.

In other experiments, 50 cc. of nitric acid was diluted with 200 cc. of water and warmed. Then 2 g. of powdered furfuralacetone was added while stirring was maintained. The red-colored oxides of nitrogen appeared momentarily. Then more furfuralacetone was added in small portions just large enough to keep the reaction going, the heat being removed when the reaction would proceed alone. The red color developed by each addition was allowed to disappear before another portion was added. This was continued until 20 g. of furfuralacetone had been added. Then the solution was evaporated to a volume of 35 cc. Upon cooling, crystals separated. These were filtered off and recrystallized from hot water. The crystals melted with decomposition at 128–130° and weighed 3.5 g. The substance was shown to be ammonium tetroxalate by titration with standard alkali and with potassium permanganate. It contained nitrogen, furthermore. Hence it could not have been furoic acid or maleic acid which also melt in this range but this was confirmed by mixed melting point depressions and by non-reaction of the compound with bromine.

Summary

Ethyl methyl ketone and bleaching powder react to give propionic acid and chloroform. Furfuralacetone gives furylacrylic acid and chloroform. Difurfuralacetone does not react to produce furylacrylic acid. Ethyl acetoacetate gives rise to dichloroacetic acid but no chloroform.

Oxalic acid and ammonium tetroxalate are among the reaction products of dilute nitric acid on furfuralacetone.

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Stereochemistry of Diphenyls. XXX.[1] Preparation and Resolution of 2,2'-Diiodo-4,4'-dicarboxydiphenyl

BY N. E. SEARLE[2] AND ROGER ADAMS

In an earlier paper[3] in this series it was pointed out that on the basis of the studies already completed on 2,2',6 and 2,2',6,6'-substituted diphenyls, there appeared to be no reason why certain 2,2'-disubstituted diphenyls should not be resolved provided the groups were large enough. Moreover, the fact that a disubstituted dinaphthyl[4] was successfully resolved, although such a compound is not entirely comparable to the disubstituted diphenyls, does indicate the likelihood of the existence of resolvable 2,2'-disubstituted diphenyls.

On account of the size of the sulfonic acid group as roughly estimated from the x-ray data available, it was predicted that a 2,2'-disulfonic acid derivative of a diphenyl might be resolved. Diphenyl-2,2'-disulfonic acid and 4,4'-diaminodiphenyl-2,2'-disulfonic acid were prepared, but attempts to resolve them resulted in failure. In the same communication it was pointed out that possibly the 2,2'-dibromo and probably the 2,2'-disubstituted diiododiphenyl should be resolvable. By the system of calculation previously used, based on x-ray data and using a value of 2.20 Å. for the C–I distance,[5] the interference on each side of the molecule should be approximately 0.12 Å.

A diiodo compound has finally been obtained, namely, 2,2'-diiodo-4,4'-dicarboxydiphenyl (IV). It readily formed dialkaloidal salts from which

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[1] For paper XXIX see Patterson and Adams, THIS JOURNAL, **55**, 1069 (1933).

[2] Submitted as part of a thesis for the degree of Doctor of Philosophy at the University of Illinois.

[3] Stanley and Adams, THIS JOURNAL, **52**, 4471 (1930).

[4] Stanley, *ibid.*, **53**, 3104 (1931); Meisenheimer and Beisswenger, *Ber.*, **65**, 32 (1932); Corbellini, *Atti. R. Accad. Lincei (Roma), Rend.*, [6] **13**, 702 (1931).

[5] In a previous paper the aromatic internuclear distance C–I was calculated as 2.06–2.35 Å. [see Neuburger, *Z. Krist*, **80**, 118 (1931)]. The iodine atom has been demonstrated to be a polarizable atom in that its electron shell is easily distorted so that an average of the two limiting values given above seems a satisfactory approximation.