[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A Study of New Approaches to α-Halogenated Orthoesters

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The removal of the elements of an alkyl hypobromite from an α-bromoorthoester is at present the only general method that has been found for the preparation of substituted ketene acetals,[2] $RCH{=}C(OC_2H_5)_2$. An attempt to extend this method to the preparation of such a disubstituted ketene acetal as dimethylketene dimethylacetal, $(CH_3)_2C{=}C(OCH_3)_2$, was unsuccessful because the requisite methyl α-bromoorthoisobutyrate could not be prepared: alcoholysis of methyl α-bromoiminoisobutyrate hydrochloride yielded only the corresponding amide, and methyl orthoisobutyrate could not be brominated.[3]

The present paper reports an exploration of some new approaches to the synthesis of an orthoester of an α-haloisobutyric acid. The first of these involved the preparation and alcoholysis of certain N-substituted iminoesters of α-chloroisobutyric acid (III), which were obtained by the sequence of reactions, I to III

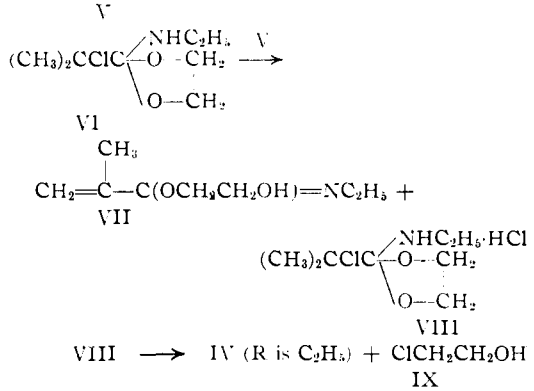
$$\underset{\text{I}}{(CH_3)_2CHCONHR} \xrightarrow{PCl_5} \underset{\text{II}}{(CH_3)_2CClC(Cl){=}NR} \xrightarrow{NaOR'} \underset{\text{III}}{(CH_3)_2CClC(OR'){=}NR} \xrightarrow{HCl} \underset{\text{IV}}{(CH_3)_2CClCONHR}$$

The iminoesters (III, R is CH_3; R′ is CH_3 or C_2H_5) were recovered unchanged after several hours of refluxing in methyl or ethyl alcohols. Since the free iminoesters did not undergo alcoholysis, attempts were made to prepare salts of III in order that these might be subjected to alcoholysis. However, III was converted directly to the amide (IV) when treated with dry hydrogen chloride in ether solution with no evidence of the formation of an intermediate hydrochloride.

In the hope that these results would be modified if the O–R′ bond of III were strengthened, the phenyl ester (III, R is C_2H_5; R′ is C_6H_5) was prepared. This ester is indeed more stable; it forms a homogeneous solution with ether containing dry hydrogen chloride (no salt formation) from which most of the ester may be recovered by evaporation of the ether. There is some cleavage of the phenoxy group as shown by the fact that a small amount of the iminochloride (II, R is C_2H_5) accompanies the recovered phenyl iminoester. When this phenyl iminoester is treated with hydrogen chloride in absolute alcohol, it is quantitatively converted to phenol and the amide (IV).

The hydroxyethyl iminoester V was prepared with the expectation that it would exist in the more basic cyclic form VI, which would form a hydrochloride that could be alcoholyzed to an orthoester. When the iminoester V, obtained from the reaction of II (R is C_2H_5) with the monosodium salt of ethylene glycol, was distilled the following products were obtained: IV (R is C_2H_5), ethylene chlorohydrin (IX), and a chlorine-free residue. The latter material had a wide boiling range and left considerable non-volatile residue each time it was distilled. These reaction products indicate that the ester V cyclizes to the more basic structure VI, which then dehydrochlorinates another molecule of V (or VI) to form the chlorine-free methiminoacrylate (VII) and the hydrochloride (VIII). Polymerization of VII accounts for the non-volatile residue, and pyrolysis of the hydrochloride (VIII) produces IV and IX.

$$\underset{\text{V}}{(CH_3)_2CClC(OCH_2CH_2OH){=}NC_2H_5} \longrightarrow$$



$$\underset{\text{VII}}{CH_2{=}C(CH_3)C(OCH_2CH_2OH){=}NC_2H_5} + \underset{\text{VIII}}{(CH_3)_2CClC(NHC_2H_5{\cdot}HCl)(OCH_2)_2}$$

$$\text{VIII} \longrightarrow \text{IV (R is } C_2H_5) + \underset{\text{IX}}{ClCH_2CH_2OH}$$

The results of the experiments described above indicate that esters of α-chloroorthoisobutyric acid cannot be prepared from the corresponding N-alkyliminoesters.

The next approach to the preparation of an ester of this orthoacid involved the replacement of the halogens of chloretone (X) by alkoxy groups. It was found, however, that when chloretone was treated with three equivalents of sodium ethoxide in absolute alcohol, the product of the reaction was ethyl α-ethoxyisobutyrate[4] (XII), which was isolated in 72% yield. The mechanism by which this ester is formed undoubtedly involves the intermediate ethylene oxide[5] (XI) which is converted by alcoholysis to XII

(1) Wisconsin Alumni Research Foundation Research Assistant, 1944–1947.

(2) McElvain, *et al.*, THIS JOURNAL, **62**, 1482 (1940); **64**, 1966 (1942); **68**, 1922 (1946).

(3) Kent, Ph.D. Thesis, University of Wisconsin, 1944.

(4) The preparation of esters of α-alkoxyisobutyric acids from chloretone by this reaction is the subject of a recent patent (British Patent 578,082; *C. A.*, **41**, 2075 (1947)).

(5) Jacob (*Bull. soc. chim.* [5], **7**, 581 (1940)) postulated this intermediate to account for the formation of α-chloroisobutyryl chloride from the reaction of chloretone with dimethylaniline. Aston and Greenburg (THIS JOURNAL, **62**, 2590 (1940)) report the alcoholysis of the ethylene oxides, $(CH_3)_2C(\text{O})CR'$ to $(CH_3)_2COHC(OR)_2R'$.

$$(CH_3)_2COHCCl_3 \xrightarrow{NaOC_2H_5} (CH_3)_2C(OC_2H_5)COOC_2H_5$$

X → XI → XII

Other compounds derived from chloretone that were studied as possible sources of the desired orthoester were the acetate (XIII), 1,1,1-trichloro-2-methylpropene (XIV) and 1,1,1,2-tetrachloro-2-methylpropane (XV).

$(CH_3)_2C(OCOCH_3)CCl_3$ (XIII) $\quad CH_2{=}C(CH_3)CCl_3$ (XIV)

$(CH_3)_2CClCCl_3$ (XV)

When treated with three equivalents of sodium ethoxide in alcohol solution, the acetate XIII was converted to the α-ethoxyester XII in 55% yield, presumably through the same intermediate (XI) as was chloretone.

The propene XIV was prepared in 90% yield and free from the isomeric halide (XVI) by heating chloretone with an excess of thionyl chloride.[6] When treated with one equivalent of sodium ethoxide the propene XIV was converted, probably *via* the allylic halide XVI, to 1,1-dichloro-2-methyl-3-ethoxypropene-1[7] (XVII). However, with three equivalents of sodium ethoxide XIV was converted into a product that contained four ethoxyl groups. This compound is undoubtedly ethyl β-ethoxyorthoisobutyrate (XVIII) and results from the addition of alcohol to XVII either before or after the halogens are replaced by ethoxyl groups.

$$XIV \longrightarrow \underset{XVI}{ClCH_2C(CH_3){=}CCl_2} \xrightarrow{NaOC_2H_5} \underset{XVII}{C_2H_5OCH_2C(CH_3){=}CCl_2} \xrightarrow[C_2H_5OH]{2NaOC_2H_5} \underset{XVIII}{C_2H_5OCH_2CH(CH_3)C(OC_2H_5)_3}$$

The tetrachloropropane XV, which was prepared in 19% yield by the action of phosphorus pentachloride on chloretone, gave the same reaction products with sodium ethoxide as did XIV; in each reaction an additional equivalent of the ethoxide was required for the initial dehydrochlorination of XV to XIV. This behavior parallels that reported by Jacob[5] in which XV reacts with two equivalents of sodium acetate to form the acetate, $CH_3COOCH_2C(CH_3){=}CCl_2$, corresponding to the ether XVII.

(6) Jacob (ref. 5) and Price and Marshall (*J. Org. Chem.*, **8**, 532 (1943)) obtained the propene XIV in 15 and 43% yields, respectively, by heating chloretone with phosphoric anhydride in the presence of dimethylaniline. The main product obtained by Jacob was the isomeric halide, XVI, which was isolated in 57% yield.

(7) *Cf.* Kirrmann and Jacob, *Compt. rend.*, **203**, 1528 (1936); *Bull. soc. chim.*, [5] **7**, 588 (1940).

Experimental

N-Methylisobutyramide.—A solution of 320 g. (8 moles) of sodium hydroxide in one liter of water was added slowly to 278 g. (4 moles) of methylamine hydrochloride in 690 ml. of water. The resulting solution of methylamine was cooled in an ice-bath and, over a period of three hours, 424 g. (4 moles) of isobutyryl chloride was added at such a rate that the temperature remained below 10°. The mixture was allowed to come to room temperature, the amide layer decanted, and the aqueous layer extracted three times with 200-ml. portions of ether. The ether extracts and the product were combined and dried and the ether evaporated. Distillation at reduced pressure gave 303 g. (75%) of N-methylisobutyramide,[8] b. p. 120–121° (27 mm.): $n^{20}D$ 1.4350; d^{25}_4 0.953. The corresponding N-ethylamide,[9] prepared similarly, melted at 65–67°.

Ethyl α-Chloro-N-methyliminoisobutyrate.—To a stirred alcoholic solution of sodium ethoxide, prepared by dissolving 7.7 g. (0.33 mole) of sodium in 200 ml. of absolute alcohol, was added 51 g. (0.33 mole) of the α-chloro-N-methyliminoisobutyryl chloride prepared from N-methylisobutyramide by the method of v. Braun, *et al.*[9] Sodium chloride began to precipitate immediately and, after heating to 50° for three hours, 18.8 g. (97%) of the salt was filtered from the reaction. The alcoholic filtrate was distilled and 45 g. (84%) of ethyl α-chloro-N-methyliminoisobutyrate, b. p. 163–164° (760 mm.), 66–67° (21 mm.), $n^{20}D$ 1.4427, d^{25}_4 0.991, obtained.

Anal. Calcd. for $C_7H_{14}ClNO$: Cl, 21.7. Found: Cl, 21.8.

Ethyl α-chloro-N-ethyliminoisobutyrate, prepared similarly, boils at 60–61° (11 mm.), $n^{20}D$ 1.4385, d^{25}_4 0.960.

Anal. Calcd. for $C_8H_{16}ClNO$: N, 7.9. Found: N, 8.0.

A solution of 25 g. of the ethyl N-methyliminoester in 50 ml. of absolute alcohol was refluxed for five hours. After the alcohol was removed, the residue was distilled at reduced pressure and the ethyl α-chloro-N-methyliminoisobutyrate, b. p. 66–67° (21 mm.), $n^{20}D$ 1.4450, was recovered unchanged. After alcoholysis of 47 g. of this iminoester with 50 ml. of ethyl alcohol for a period of three days, the products recovered contained 7.8–8.6% nitrogen, showing that no appreciable alcoholysis had occurred.

Reaction of Ethyl α-Chloro-N-ethyliminoisobutyrate with Hydrogen Chloride.—Hydrogen chloride was allowed to bubble into an ether solution of 5 g. of the iminoester. After five minutes, the ether was evaporated and the residue distilled; 3.2 g. (80%) of α-chloro-N-ethylisobutyramide,[10] b. p. 83–84° (15 mm.), m. p. 40–42°, was obtained.

The m. p. of this product was unchanged when mixed with a sample of amide prepared by the hydrolysis of α-chloro-N-ethyliminoisobutyryl chloride.

α-Chloro-N-methylisobutyramide, which was obtained in a similar manner from the iminoester, boiled at 81–82° (18 mm.), $n^{20}D$ 1.4615, d^{25}_4 1.087.

Anal. Calcd. for $C_5H_{10}ClNO$: N, 10.3. Found: N, 10.5.

Phenyl α-Chloro-N-ethyliminoisobutyrate.—To a solution a 9.4 g. (0.1 mole) of phenol in 75 ml. of dioxane, 2.3 g. (0.1 mole) of sodium was added. The reaction mixture was stirred and refluxed until the sodium disappeared and then 16.7 g. (0.1 mole) of α-chloro-N-ethyliminoisobutyryl chloride was added. After stirring and refluxing this mixture for an hour, a quantitative yield of sodium chloride was filtered from the reaction. The dioxane was evaporated and the residue distilled at reduced pressure yielding 18.2 g. (81%) of phenyl α-chloro-N-ethyliminoisobutyrate, b. p. 114–115° (9 mm.), $n^{20}D$ 1.5100, d^{25}_4 1.047.

(8) Franchimont, *Chem. Zentr.*, **84**, II, 1960 (1913).

(9) v. Braun, Jostes and Munch, *Ann.*, **453**, 127 (1927).

(10) v. Braun, *et al.*, *Ber.*, **60**, 92 (1927).

Anal. Calcd. for $C_{12}H_{16}ClNO$: Cl, 15.8; N, 6.2. Found: Cl, 15.7; N, 6.2.

Hydrolysis of Phenyl α-Chloro-N-ethyliminoisobutyrate to Phenyl α-Chloroisobutyrate.—After 25 ml. of 10% hydrochloric acid was poured onto 7 g. of the phenyl iminoester and the mixture shaken (heat was evolved), the aqueous layer was extracted twice with ether and the ether dried and evaporated. Distillation of the residue gave 1.2 g. of forerun and then 4.7 g. (76%) of phenyl α-chloroisobutyrate, b. p. 111–112° (10 mm.), $n^{20}D$ 1.4988. Evaporation of the water left 2.3 g. (92%) of ethylamine hydrochloride, m. p. 106–107°.

Anal. Calcd. for $C_{10}H_{11}ClO_2$: Cl, 17.9. Found: Cl, 17.8.

Reaction of Phenyl α-Chloro-N-ethyliminoisobutyrate with Hydrogen Chloride in Ether.—Hydrogen chloride was bubbled into an ether solution of 4 g. (0.017 mole) of the iminoester until 0.61 g. (0.017 mole) had been absorbed. The liquid remained homogeneous. Distillation of the reaction mixture gave 0.5 g. of α-chloro-N-ethyliminoisobutyryl chloride, identified by its boiling point, 43–45° (13 mm.), and by its hydrolysis product, α-chloro-N-ethylisobutyramide, m. p. 38–40°, and 2.5 g. of unchanged phenyl α-chloro-N-ethyliminoisobutyrate.

Reaction of Phenyl α-Chloro-N-ethyliminoisobutyrate with Hydrogen Chloride in Absolute Alcohol.—To a solution of 7 g. (0.03 mole) of the phenyl iminoester in 25 ml. of absolute alcohol, a solution of 1.1 g. (0.03 mole) of hydrogen chloride in alcohol was added. After six hours at room temperature the alcohol was evaporated and the residue distilled at reduced pressure. The yield of product boiling at 83–84° (10 mm.), $n^{20}D$ 1.4950 was 5.8 g. This product contained 14.5% chlorine and 5.7% nitrogen (calcd. for a mixture of one mole amide and one mole phenol: Cl, 14.6; N, 5.8).

Extraction of a 2.5-g. sample of this product with cold 10% sodium hydroxide, followed by treatment of the alkaline extract with acid and then bromine water gave 2.6 g. (77%) of tribromophenol, m. p. 87–90°. Distillation of the remainder gave 1.5 g. (97%) of α-chloro-N-ethylisobutyramide.

Reaction of α-Chloro-N-ethyliminoisobutyryl Chloride with the Monosodium Salt of Ethylene Glycol.—Sixty grams (0.36 mole) of the iminochloride was dropped slowly into a well-stirred suspension of 30 g. (0.36 mole) of the monosodium salt of ethylene glycol in 75 ml. of dioxane. The mixture was heated to 50° and stirred for twenty-four hours. The precipitated sodium chloride (quantitative yield) was filtered and the solvent evaporated from the filtrate. Fractionation of the residue at reduced pressures yielded 11 g. (20%) of α-chloro-N-ethylisobutyramide, m. p. 40–42°, 9 g. of ethylene chlorohydrin (caught in the cold trap) and 39 g. of higher boiling (55–105° (1 mm.)) material; 4 g. of non-distillable residue remained. Redistillation of this higher boiling material gave no definite fractions and produced considerable amount of non-volatile residue. Analysis of various samples of this high boiling material showed no appreciable chlorine content.

Reaction of Chloretone with Sodium Ethoxide.—To a well-stirred solution of sodium ethoxide, prepared from 27.3 (1.2 atoms) of sodium and 300 ml. of absolute alcohol, was added 70 g. (0.4 mole) of chloretone[11] slowly and with cooling, since the reaction proceeds rapidly with the evolution of considerable heat. Within one-half hour the mixture became neutral and the precipitated salt was filtered by suction, using a little Filter-cel. Concentration and distillation of the filtrate gave 52 g. (83%) of crude ethyl α-ethoxyisobutyrate,[12] boiling at 150–165°. Redistillation gave 45.1 g. (72%) of pure ester, b. p. 156–159°, $n^{20}D$ 1.4090, d^{25}_4 0.932, M_D 42.3 (calcd. 42.4), sapon. equiv. 156 (calcd. 160).

A small sample of the ester was saponified with sodium hydroxide and the resulting acid purified by distillation. The α-ethoxyisobutyric acid[13] so obtained boiled at 103–104° (17 mm.), $n^{20}D$ 1.4208, neut. equiv. 136 (calcd. 132) and contained 33.8% ethoxyl (calcd. 34.1%).

Reaction of Chloretone Acetate with Sodium Ethoxide.—Ten grams (0.05 mole) of chloretone acetate[14] was dropped slowly into a solution of sodium ethoxide, prepared from 3.2 g. (0.15 atom) of sodium and 40 ml. of absolute alcohol. Heat was evolved and a salt precipitated immediately. After refluxing an hour, the salt (6.8 g.) was filtered off; distillation of the filtrate yielded 4 g. (55%) of ethyl α-ethoxyisobutyrate, b. p. 156–159°.

1,1,1-Trichloro-2-methylpropene-2 (XIV).—A mixture of 42 g. of chloretone and 75 ml. of thionyl chloride was refluxed until evolution of the hydrogen chloride ceased (eight hours). Distillation of the residue after the excess thionyl chloride had been removed yielded 36 g. (93%) of XIV, b. p. 130–137°; if only two equivalents of thionyl chloride were used, the yield of this product dropped to 44% and a considerable amount of material, b. p. 156–158°, $n^{20}D$ 1.4472, was obtained. Refractionation of the crude XIV gave pure 1,1,1-trichloro-2-methylpropene-2,[6] b. p. 132–134°, $n^{20}D$ 1.4770, d^{25}_4 1.270, M_D 35.3 (34.8).

Ten grams of this compound and 0.1 g. of hydrogen chloride were heated in a glass bomb tube to 200° overnight. Distillation gave 2 g. of starting material, b. p. 130–135°, 4 g. of an intermediate cut and 1 g. of the pure allyic rearrangement isomer,[6] 1,1,3-trichloro-2-methylpropene-1, b. p. 154–156°; $n^{20}D$ 1.495.

Reaction of 1,1,1-Trichloro-2-methylpropene-2 with Sodium Ethoxide. (a) With One Mole of Sodium Ethoxide.—When 10 g. of the trichloro-olefin was allowed to react with one equivalent of sodium ethoxide in refluxing alcohol, 4.6 g. of 1,1-dichloro-2-methyl-3-ethoxypropene-1,[7] b. p. 165–166°; $n^{20}D$ 1.4600, was isolated.

(b) With Three Moles of Sodium Ethoxide.—Ten grams (0.063 mole) of the trichloro-olefin was placed in a glass-lined bomb and a solution of sodium ethoxide, prepared from 4.35 g. (0.19 atom) of sodium and a minimum of absolute alcohol, was added. The bomb was heated at 190° overnight. Although the resulting reaction mixture was basic, 9.9 g. (90%) of sodium chloride was filtered off. Distillation of the residue at atmospheric pressure gave 10 g. of material boiling at 194–200°. A fraction of this material, boiling at 100–110° (24 mm.), $n^{20}D$ 1.4310, contained 74.5% ethoxyl indicating the presence of four ethoxyl groups (calcd. for $C_4H_6(OC_2H_5)_4$: 77.0%). This ethoxyl content indicates that this product is ethyl β-ethoxyorthoisobutyrate.

1,1,1,2-Tetrachloro-2-methylpropane (XV).—In a flask, fitted with a reflux condenser, 167 g. (0.94 mole) of chloretone and 300 g. (1.44 mole) of phosphorus pentachloride were mixed and heated until solution was effected. After twelve hours at 80°, the solution was cooled and the excess phosphorus pentachloride allowed to crystallize, after which it was filtered off and washed with benzene. The filtrate was fractionated through a ten-plate Fenske column. Phosphorus oxychloride first was collected at 104–106° and amounted to 128 g. (84%); the next fraction consisted of 56.5 g. of material, b. p. 154–160°, which corresponds in properties to the hexachlorodi-*t*-butyl ether, $(CCl_3C(CH_3)_2)_2O$, reported by Willgerodt and Dürr.[15] At 160° the distillate solidified and distillation was no longer possible using the column. The residue was transferred to an apparatus for distillation of solids, and the distillation continued. The distillate so obtained contained an appreciable amount of liquid impurity which was separated from the solid by absorption on a porous plate. 1,1,1,2-Tetrachloro-2-methylpropane prepared in this manner melted at 163–168° and boiled within the same range; the yield amounted to 34 g. (19%). This compound is very irritating to the eyes and nose.

This tetrachloro compound gave reaction products similar to those obtained with the trichloropropene, XIV, when treated, in each case, with an additional

(11) Fishburn and Watson, *J. Am. Pharm. Assoc.*, **28**, 491 (1939).
(12) Bischoff, *Ber.*, **32**, 1758 (1899).
(13) Blaise and Picard, *Compt. rend.*, **152**, 447 (1911).
(14) Aldrich, THIS JOURNAL, **37**, 2720 (1915).
(15) Willgerodt and Dürr, *Ber.*, **20**, 540 (1887).

equivalent of sodium ethoxide, which served to convert XV to XIV.

Summary

Ethyl and phenyl α-chloro-N-alkyliminoisobutyrates have been prepared and subjected to alcoholysis. The free iminoesters remain unchanged in this reaction. Hydrogen chloride converts the ethyl esters to the corresponding amides, but the phenyl ester is relatively unaffected by this reagent. Neither of these esters form hydrochlorides. The β-hydroxyethyl N-ethyliminoester appears to cyclize to a more basic structure, $(CH_3)_2CClC(NHC_2H_5)OCH_2CH_2O$, which dehydrochlorinates a portion of the original iminoester. The resulting hydrochloride of this iminoester then decomposes into α-chloro-N-ethylisobutyramide and ethylene chlorohydrin.

Both chloretone and its acetate are converted to ethyl α-ethoxyisobutyrate by sodium ethoxide.

The preparation of 1,1,1-trichloro-2-methylpropene-2 and 1,1,1,2-tetrachloro-2-methylpropane from chloretone are described. The latter compound is converted to the former by alcoholic sodium ethoxide, after which the trichloropropene reacts with this reagent to give 1,1-dichloro-2-methyl-3-ethoxypropene-1 or ethyl β-ethoxyorthoisobutyrate, depending on the amount of the ethoxide employed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

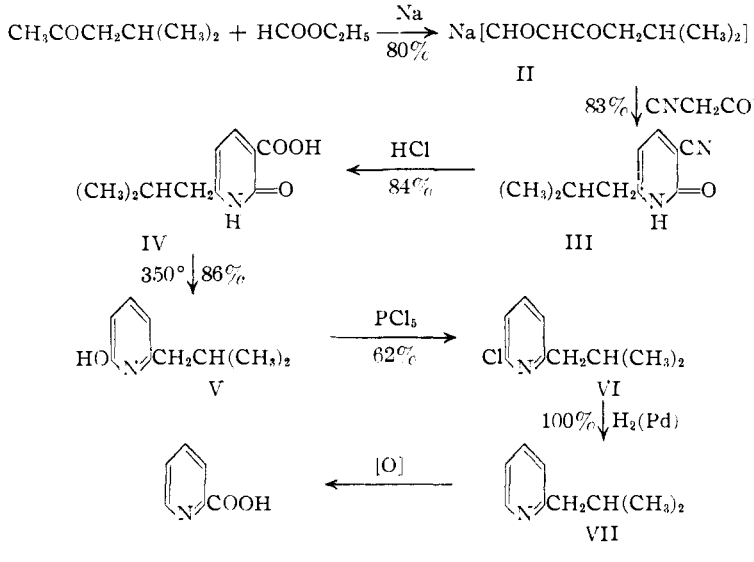
Condensations of Unsymmetrical Ketones. I. Condensations with Ethyl Formate

BY RAYMOND P. MARIELLA

It has been shown independently by Tracy and Elderfield,[1] and Joshi, Kaushal and Deshapande[2] that ethyl formate condenses with an unsymmetrical ketone, methyl ethyl ketone, to give I.

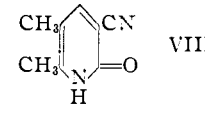
$$CH_3COC(CH_3)=CHOH \quad I$$

The present work was undertaken to determine whether methyl alkyl ketones, in general, are attacked by ethyl formate at the methylene group. Methyl isobutyl ketone was chosen as another example and the series of compounds shown on the accompanying flow sheet was developed.



The cyanopyridone (III), formed in the condensation of the sodium salt of the hydroxymethylene ketone (II) with cyanoacetamide, was converted into the acid (IV) by refluxing with concentrated hydrochloric acid, and then decarboxylated to the pyridol (V) by heating to 350°. This pyridol was converted into the corresponding chloropyridine (VI) with phosphorus pentachloride, and then reduced to 2-isobutylpyridine (VII) with palladium as the catalyst. Oxidation of VII with alkaline permanganate gave picolinic acid, thus proving the initial condensation occurred at the methyl group. The yields on all steps were good, and in no case was a bad mixture encountered.

Also in the present work, the sodium salt of I was prepared and condensed with cyanoacetamide to give the pyridone (VIII).[3] The modification of using the sodium salt instead of the free hydroxymethylene ketone greatly increased the over-all yield of the pyridone.[2]



VIII

Although ethyl formate condenses with methyl ethyl ketone at the methylene group, in the case of a β-substituted aryl or alkyl methyl ethyl ketone, such as methyl β-phenylethyl ketone and methyl isobutyl ketone, the methyl group is the point of attack. Moreover, in the condensation of ethyl oxa-

(1) Tracy and Elderfield, *J. Org. Chem.*, **6**, 63 (1941). See this reference for a review of the literature on this subject.

(2) Joshi, Kaushal and Deshapande, *J. Indian Chem. Soc.*, **18**, 479 (1941).

(3) In the only other attempt to use the sodium salt in this preparation, Barat, *J. Indian Chem. Soc.*, **8**, 801 (1931), reported the salt too hygroscopic to be used.