The filtrate from the first precipitate, on further standing for a few days, deposited an orange precipitate in small amount. Recrystallization from a mixture of acetic acid and pyridine afforded material of m.p. 300–301°; mixed m.p. with authentic derivative of pyruvaldehyde of m.p. 299°, 298–299°. Their infrared spectra were superimposable. These two products were obtained also from D-I itself, following the same procedure. Processing of the residue from the steam distillation did not yield any well defined products.

Degradation of D-I with Potassium Permanganate.—Compound D-I was suspended either in water buffered with magnesium salt, or acetone. Powdered potassium permanganate was added in small portions until color persisted. After removal of manganese dioxide the volatile materials were removed at reduced pressure and the residue was extracted with chloroform. Evaporation of the solvent left an acidic sirup. This was chromatographed on silica using chloroform–hexane as eluent.

In the course of several runs no well-reproducible results were obtained. The only material obtained in substantial amount from one run was D-I. In two other instances trace amounts of a solid, m.p. 134–139°, were obtained, the infrared spectrum of which showed most peaks of the non-pyrone moiety of the D-I to be intact. Most other fractions from chromatography turned out to be intractable sirups.

Reaction of D-I with Bromine and Alkali.—Compound D-I was treated at 0° with excess bromine in sodium hydroxide solution for 1 hr., then was stirred for 6 hr. at 25°. The mixture was acidified, volatile materials removed, and the residue was extracted with 2-propanol. On evaporation of solvent an amber sirup remained which darkened on exposure to air. The sirup formed a derivative with 2,4-dinitrophenylhydrazine reagent, m.p. 130–140°. Recrystallization from aqueous acetic acid gave material decomposing around 270°.

This derivative could be prepared more conveniently by treatment of the acidified solution after completion of the reaction with 2,4-dinitrophenylhydrazine reagent. The derivative was recrystallized from boiling bromobenzene. It decomposed around 285°.

Ozonolysis of D-I.—Compound D-I in acetic acid was treated with excess ozone (a transient yellow color appeared in the course of the reaction) and the ozonide was decomposed with zinc dust. After filtering off the zinc and removing the acetic acid at reduced pressure a yellow sirup was obtained which gave a weak ferric chloride test.

Attempted chromatography on silica failed to yield any crystalline fractions. Treatment of the sirup with excess 2,4-dinitrophenylhydrazine reagent gave rise to a transient yellow precipitate. Eventually an orange precipitate separated. It was difficult to recrystallize for it was so sparingly soluble in most solvents tried. Orange microcrystals were obtained from boiling bromobenzene, m.p. 290°.

Anal. Calcd. for $C_{23}H_{19}N_9O_{11}$: C, 46.23; H, 3.21; N, 21.10. Found: C, 45.99; H, 3.35; N, 21.10.

Reaction of D-I with Chromic Anhydride.—One gram of D-I was stirred in 25 cc. of acetic acid with 1.0 g. of chromic anhydride at room temperature for 22 hr. The green solution was diluted with 20 cc. of water and evaporated in an air stream. Two grams of a black-green sirup was obtained which crystallized on standing. This was soluble in water, methanol and 2-propanol, the solubility decreasing in that order. It did not melt when heated up to 300°, nor when heated with a bunsen flame at 15 mm. Standing with concentrated hydrochloric acid caused no change, but with concentrated alkali at room temperature chromic hydroxide precipitated. Separation of the hydroxide and acidification of the yellow mother liquor gave no crystalline material on concentration save sodium chloride.

Attempted Hydrogenation and Bromination of D-I.—Shaking of D-I with palladium-on-charcoal under hydrogen in a Parr apparatus for 24 hr. resulted in no uptake of hydrogen and the starting material was recovered unchanged. Similarly, stirring of a solution of D-I in dimethylformamide with excess of bromine for 24 hr. yielded only the starting material on processing.

EVANSTON, ILL.

[CONTRIBUTION FROM OHIO STATE UNIVERSITY]

Reactions of Furan Compounds. XVI.[1] Conversion of Tetrahydro-2-methylenefuran Successively into Dihydromethylfuran, Cyclopropyl Methyl Ketone and Methyl Propenyl Ketone by Heat[2]

BY DOROTHY M. ATEN ARMITAGE AND CHRISTOPHER L. WILSON

RECEIVED NOVEMBER 10, 1958

In an extension of Paul's work,[4–6] pure tetrahydro-2-methylenefuran has been prepared in 89% yield by the dehydrobromination of tetrahydrofurfuryl bromide. The olefin isomerizes very easily either by heat or acids to 4,5-dihydro-2-methylfuran. At temperatures between 425 and 525° both compounds rearrange first to cyclopropyl methyl ketone and then to methyl propenyl ketone.

Tetrahydro-2-methylenefuran (I) could have been first made by Kirner[3] who attempted to make methyl tetrahydrofurfuryl ether by the reaction of the chloride and methanol using powdered potassium hydroxide. He described the formation of unsaturated material to which he tentatively gave formula I without, however, any data to support it. Later Paul[4] was somewhat more successful using the reaction of tetrahydrofurfuryl bromide (III) with potassium hydroxide and he proceeded[5] to study the isomerization of the material over alumina at 380°. He obtained a small amount of 2,3-dihydro-1,4-pyran. For reasons which will not be discussed here Paul had expected the pyran as a rearrangement product of tetrahydromethylenefuran, but he showed later[6] that the compound he started with was not I but its isomer II. He demonstrated the easy isomerization of I into II and was able to identify each by ozonolysis.

In the present work using Paul's method but in tetrahydrofurfuryl alcohol as medium, his yield of 50–55% has been raised to 89%.[6] The olefin, tetrahydro-2-methylenefuran (I), b.p. 98–99° (743-mm.), is stable in the presence of bases at ordinary temperature, but on heating or in the presence of

---

(1) Part XV, THIS JOURNAL, **73**, 4803 (1951).

(2) This work was generously supported by the Quaker Oats Co. and the text is taken from a Ph.D. thesis (D.M.A.A.), Ohio State University, 1951.

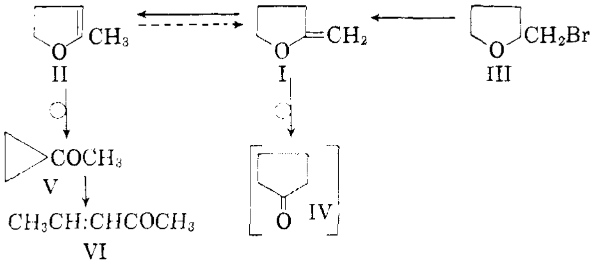
(3) W. R. Kirner, THIS JOURNAL, **52**, 3251 (1930).

(4) R. Paul, *Bull. soc. chim.*, [4] **53**, 417 (1933).

(5) R. Paul, *ibid.*, [5] **2**, 745 (1935).

(6) R. Paul and S. Tchelitcheff, *ibid.*, [5] **17**, 520 (1950). Recently M. F. Ansell and D. A. Thomas (*J. Chem. Soc.*, 1163 (1958)) have obtained 68% yield from tetrahydrofurfuryl chloride in diethylene glycol as solvent.

traces of acid it rearranges to isomeric II. It may be preserved at room temperature for months without change if kept over solid sodium hydroxide and sealed in glass previously washed in aqueous alkali and dried. It is also unchanged after heating to 105° for five days in the same vessel, but at 300° it is about one-half isomerized in 2.5 hours. In glass from which a drop of acetic acid has been evaporated the olefin is completely isomerized in three hours at 105°. Hydrolysis with very dilute (e.g. 0.01 N-hydrochloric acid) acids is extremely rapid and becomes quite violent with large amounts of material. The product of hydrolysis is the expected 3-acetylpropanol. It is so sensitive to heat that isomerization occurs on distillation and the boiling point drops from about 98° progressively to 83°. This is particularly true if slow fractionation is attempted and explains Paul's early troubles.[6] However, distillation was found to be safe if the entire apparatus is first washed with dilute sodium hydroxide and then thoroughly dried by a warm stream of air free from carbon dioxide. The purity of the product and its isomerization were checked by the use of characteristic infrared bands at 6.2, 7.8, 9.6 and 12.5 μ for tetrahydro-2-methylenefuran (I) and 7.2, 10.5 and 14.0 for dihydromethylfuran (II).



The purity of the tetrahydromethylenefuran obtained was shown to depend on the source of the tetrahydrofurfuryl bromide used in its preparation. The best specimen, shown to be free from any recognizable impurity by the simplicity of its infrared spectrum, was produced from bromide made by reaction of tetrahydrofurfuryl tosylate with lithium bromide in acetone. That made from bromide made in the conventional way from alcohol and phosphorus tribromide in pyridine contained a little 2.3-dihydro-1,4-pyran. That from bromide resulting from the direct reaction of alcohol and hydrogen bromide contained several per cent. of dihydropyran.

Using an excess of hydrogen bromide the reaction with tetrahydrofurfuryl alcohol proved to be a very convenient way to make tetrahydrofurfuryl bromide. The yield was about 62% and the chief by-product was 1,5-dibromo-2-pentanol which could be separated by distillation. The presence of dihydropyran in the tetrahydromethylenefuran made from this distilled bromide was shown by the existence of characteristic infrared bands at 9.3, 12.0 and 13.8 μ. Dihydropyran could not be separated by fractionation owing to extensive isomerization of the methylene compound to dihydromethylfuran, b.p. 82–83°, which is rather near the b.p. for the pyran, 86–87°. It was possible, however, to separate a sample of pure dihydropyran by making use of the much more rapid hydrolysis of the methylene compound by 0.01 *N* aqueous hydrochloric acid. Dihydropyran was identified by its boiling point and the formation of the dinitrophenylhydrazone of 5-hydroxypentanal with Brady reagent.

It was found that the methylene derivative I contained less dihydropyran if the starting bromide was itself made at about 80° rather than about 120 to 140°. This suggests that the dihydropyran results from an impurity in the bromide rather than from an alternative mode of dehydrobromination as once proposed by Paul.[5] Such an impurity must be isomeric with tetrahydrofurfuryl bromide and it is believed that 3-bromotetrahydropyran best fits the facts. It probably forms by acid-catalyzed cyclization of 2-bromo-1,5-pentanediol, a primary fission product of the alcohol.

Isomerization of tetrahydromethylenefuran (I) to dihydromethylfuran (II) was almost complete at 325, 375 and 400°. At 425° carbonyl compounds began to appear in the products. At all temperatures, however, the spectrum still contained weak bands at 6.2, 9.6 and 12.5 μ characteristic of methylene compound. Dihydromethylfuran at the same temperatures also gave material with the same weak bands. This indicates the existence of an observable equilibrium between I and II corresponding with about 2% of the methylene isomer. As the temperature was raised further more carbonyl material formed and at 450 and 475° the product was essentially cyclopropyl methyl ketone (V). This product is the expected result of Claisen rearrangement of II just as 1,2-dihydrofuran has been shown to give cyclopropane carboxaldehyde.[7]

At still higher temperatures, those from 475 to 525° the cyclopropyl methyl ketone was further converted into methyl propenyl ketone (VI). This step was confirmed by starting with the cyclopropyl ketone and getting the same product in about the same yield.

Over the range 425 to 525° it was shown that the nature and the amount of the products was about the same whether the starting product was tetrahydromethylenefuran or dihydromethylfuran. Using infrared methods the conversion of dihydromethylfuran (II) into the two ketones over this temperature range was followed. The results are summarized in Fig. 1.

At still higher temperatures extensive decomposition resulted. Above 450° in addition to the products already mentioned, acetone and two other products which were not identified were formed to the extent of a few per cent. The following compounds were, however, shown to be absent by searching the infrared spectra: dihydropyran, cyclopentanone, crotonaldehyde and allyl methyl ketone. It should be pointed out that if tetrahydromethylenefuran (I) undergoes Claisen rearrangement in the manner of other vinyl ethers it would give cyclopentanone (IV).[7] The absence of this product indicates that isomerization to dihydromethylfuran is much faster than Claisen rearrangement under all the conditions.

---

(7) C. L. Wilson, THIS JOURNAL, **69**, 3002 (1947).

Unlike the conversion of I into II that of II into V appeared to be irreversible.[8]

Experimental

Tetrahydrofurfuryl Bromide. From Alcohol and Phosphorus Tribromide.[9]—Using 4 moles of alcohol and adding the tribromide (4 × 0.36 mole) at −10 to −5° over a 3-hour period rather than using one mole and adding bromide (0.36 mole) at −5 to −3° over a 4-hour period of the reference gave a 70% yield, b.p. 65–67° (20 mm.).

From the Tosylate and Lithium Bromide.—Tetrahydrofurfuryl alcohol (49 ml., 0.5 mole), *p*-toluenesulfonyl chloride (95 g., 0.5 mole) and sodium hydroxide (40 g., 1.0 mole) were stirred in water (100 ml.) at 100°. The oily layer was separated, the aqueous layer extracted with ether and the combined organic material dried over sodium sulfate. The ether was removed to give 70% of crude liquid tosylate. This material (81.5 g., 0.3 mole) and lithium bromide (43.5 g., 0.5 mole) were dissolved in acetone (100 ml.), allowed to stand at 20° for 12 hours, refluxed for one hour and filtered. Water was added and the mixture extracted with ether. Distillation gave tetrahydrofurfuryl bromide (11.5 g., 23%), b.p. 67° (20 mm.).

Tetrahydrofurfuryl Alcohol and Hydrogen Bromide.—The yields of bromide from various experiments varied between 45 and 62%. The higher figures were obtained by the following procedure. The alcohol (205 g., 2.0 moles) was treated with hydrogen bromide at 70–80° and allowed to stand for 72 hours. The amount of hydrogen bromide added was between 1.1 and 1.2 moles. Then a further 2.1 to 2.2 moles were added keeping the mixture at 80°. The product was washed with water and distilled to give (a) b.p. 60–66° (18 mm.) (about 200 to 210 g.) and (b) b.p. 70–122° (9 mm.) (about 105 g.). The second material was essentially all 1,5-dibromo-2-pentanol.[10] A very slightly lower yield resulted when 1.8 moles of hydrogen bromide was added to each mole of alcohol during a 4-hour period while the temperature rose from 80 to 90°. The tetrahydrofurfuryl bromide was distilled; b.p. 168–172° (743 mm.) with some decomposition, 64–66° (18 mm.).

Tetrahydro-2-methylenefuran. Sodium Hydroxide in Tetrahydrofurfuryl Alcohol.—Sodium hydroxide (50 g.) was dissolved in tetrahydrofurfuryl alcohol (195 g.), a mixture of tetrahydrofurfuryl alcohol (51 g.) and the bromide (100 g.) added at 30° and the mixture stirred for 8 hours. Volatile material was then removed up to a temperature of 135° taken in the reaction mass. The distillate was dried over anhydrous potassium carbonate and rapidly fractionated through a 12″ column packed with stainless steel gauze and which had previously been washed with sodium hydroxide solution and dried. The pure product (56%) had b.p. 96–99° (743 mm.).

Powdered Potassium Hydroxide Alone.—Powdered potassium hydroxide (60 g., 1.07 moles) was added to tetrahydrofurfuryl bromide (42.5 g., 0.39 mole) at 0°. The mixture was kept at this temperature for one hour, then heated, the volatile material caught over solid sodium hydroxide and then rapidly fractionated to give 12 g. (55.3%), b.p. 97–99° (743 mm.).

Powdered Potassium Hydroxide in Tetrahydrofurfuryl Alcohol.—A mixture of the alcohol (30 ml.) and the bromide (50 g.) was cooled in an ice-bath and powdered potassium hydroxide (25 g.) added in portions of 5 g. keeping the temperature between 10 and 35°. After standing overnight, volatile material was removed by heating and collected over potassium carbonate. Tetrahydromethylenefuran was then redistilled as before to give 23 g. (89%), b.p. 98–99° (743 mm.). The dinitrophenylhydrazone of 3-acetylpropanol had m.p. 145–147°, mixed m.p. with authentic material (m.p. 146–147°) was 146–147°.

4,5-Dihydro-2-methylfuran (II).[11]—α-Acetobutyrolactone (128 g., 1.0 mole) was warmed with phosphoric acid (5%, 150 ml.) for three hours at 105–110° and then one hour at 110–115°. The cooled mixture was neutralized with sodium hydroxide (20%), potassium carbonate added to salt out an upper layer and the whole extracted with ether. Distillation gave 3-acetylpropanol (91 g., 89%), b.p. 73–74° (5 mm.). The keto-alcohol (240 g., 2.34 moles) was heated to between 210 and 290° with stearic acid (0.1 g.)[12] and the volatile material dried over potassium carbonate and distilled to give dihydromethylfuran (171 g., 86%), b.p. 79.3–80.0° (746 mm.).

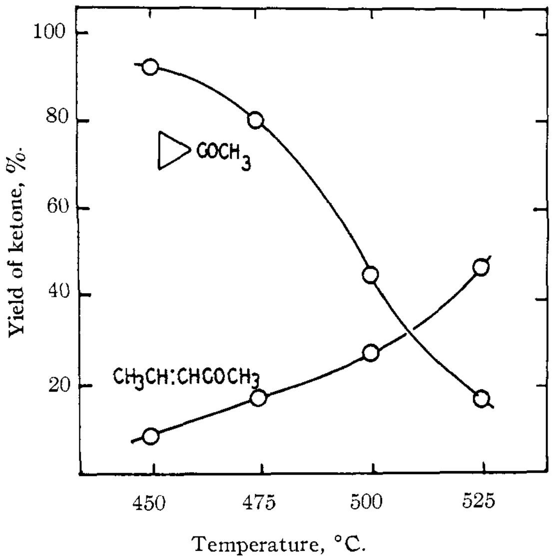


Fig. 1.—Pyrolysis of 4,5-dihydro-2-methylfuran: input, dihydromethylfuran, 30 g./hr.; nitrogen, 2.6 l/hr.; yield calculated on consumed furan.

Pyrolyses.—The apparatus consisted of an electrically heated Pyrex tube, 85 cm. by 4.5 cm. diameter filled with Pyrex chips so that the free space was 650 ml. Liquid was dripped into the upper end of the tube held vertically along with nitrogen as a carrier gas at 2.6 liters per hour unless otherwise indicated. Products were caught in traps at −78° and then distilled. Tetrahydromethylenefuran introduced at 40 g./hour gave at 325, 375 and 400° material which after drying over potassium carbonate had an infrared spectrum identical with that of dihydromethylfuran except for additional weak bands at 6.2, 9.6 and 12.5 μ characteristic of unchanged material. At 425° pyrolysis of both tetrahydromethylene- and dihydromethyl-furan gave products which after standing over potassium carbonate and distilling had identical spectra. Again each was analogous to the spectrum of pure dihydromethyl compound with the additional peaks mentioned above. Dihydromethylfuran was introduced into the tube at 30 g./hour, at 450, 475, 500 and 525°. Spectra of the product were taken on a Beckman IR2 instrument, and using a slit of 0.6 mm. the bands at 9.17 and 9.73 were used to estimate cyclopropyl methyl ketone and that at 6.14 to estimate methyl propenyl ketone. Artificial mixtures were used as standards. The results are in Fig. 1.

A large amount (125 g.) of dihydromethylfuran was passed through the tube at 500° and the product fractionated through a column packed with stainless steel gauze. About twenty fractions were collected and infrared curves made from each. Dinitrophenylhydrazones were prepared from those fractions which were indicated as pure. The results showed clearly the presence of acetone, b.p. 52–56°; two compounds not identified, b.p. below 100°, but only a few per cent. of each; cyclopropyl methyl ketone, b.p. 107.8–110.0°, dinitrophenylhydrazone, m.p. 147.8–149.2°, mixed m.p. with authentic material (147.6–149.2°) 147.8–149.2°; methyl propenyl ketone, b.p. 120–122°, dinitrophenylhydrazone, m.p. 154.6–155.6°, mixed m.p. with authentic material (m.p. 154.6–155.5°) 154.6–155.5°.

---

(8) Confirmed by H. Normant, private communication.

(9) *Org. Syntheses*, **23**, 88 (1943); Coll. Vol. III, p. 793.

(10) C. L. Wilson, *J. Chem. Soc.*, 48 (1945).

(11) I. L. Knunyantz, G. V. Chelintzev and E. D. Osetrova, *Compt. rend. acad. sci. (U.S.S.R.)(NS)*, **1**, 312 (1934); *C. A.*, **28**, 4382 (1934).

(12) L. P. Kyrides and F. B. Zienty, THIS JOURNAL, **68**, 1385 (1946). L. E. Schniepp, H. H. Geller and R. W. von Korff, *ibid.*, **69**, 674 (1947).

Cyclopropyl methyl ketone was pyrolyzed at 525° at a rate of 45 g./hour. The product contained acetone, an unidentified material, b.p. 69.6–75°, unchanged ketone and methyl propenyl ketone.

Using infrared methods search was made for cyclopentanone, crotonaldehyde and allyl methyl ketone but no trace was found.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

Reactions of Furan Compounds. XVII. Pyrolysis of Tetrahydrofurfuryl Esters to Methyl Propenyl Ketone[1]

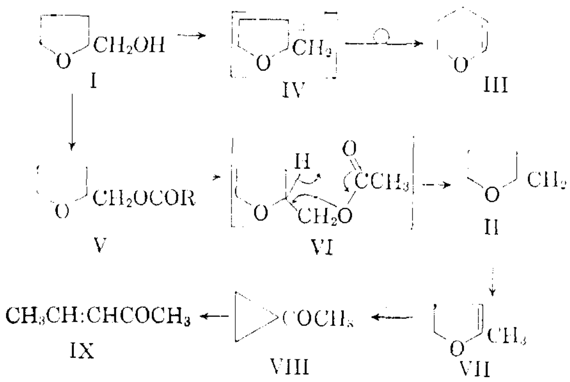
BY GEORGE J. BAUMGARTNER AND CHRISTOPHER L. WILSON

RECEIVED NOVEMBER 10, 1958

Tetrahydrofurfuryl acetate, propionate, formate, benzoate and oxalate have been pyrolyzed at between 450 and 580°. The main product was methyl propenyl ketone in yields as high as 51%. A mechanism for the reaction is proposed.

Dehydration of tetrahydrofurfuryl alcohol (I) in the vapor phase gives not tetrahydromethylenefuran (II) but 2,3-dihydro-1,4-pyran (III) and it is generally believed that the reaction involves the rearrangement of an intermediate (adsorbed) cation (IV).[2] Paul[3] thought that tetrahydromethylenefuran (II) was intermediate in this reaction and attempted to prove his point by passing the compound over alumina at 380°. He did obtain a small amount of the pyran, but it is now clear[4] that what Paul thought was tetrahydromethylenefuran was in fact dihydromethylfuran (VII) and the dihydropyran he obtained was present in his starting material.

The pyrolysis of alcohol esters as a means of making olefins was pioneered by Krafft[5] and has been extensively studied by others.[6,7] In general, the method gives unrearranged olefins although isomerization may result as a secondary reaction catalyzed by carbonaceous deposits.[7] Tetrahydrofurfuryl esters (V) on pyrolysis should, therefore, give tetrahydromethylenefuran (II) as primary product. Since this olefin is very sensitive to heat and acids and rearranges very rapidly to dihydromethylfuran (VII) which in turn isomerizes if the temperature is above about 400°[4] successively to cyclopropyl methyl ketone (VIII) and methyl propenyl ketone (IX), the ultimate product from ester pyrolysis should be the last of this series since the esters mostly decompose only above this temperature. Actually the acetate, propionate, formate, benzoate and oxalate had to be heated to above 450° before splitting and the only important product in all cases was methyl propenyl ketone (IX). The best results were obtained from the acetate and propionate and the yield of ketone rose to 51%. The method can be the basis for a preparative route to the ketone. Propionate is preferred to acetate since it is easier to separate the products of pyrolysis. It has already been shown that better results are obtained the lower the dissociation constant of the eliminated acid.[8] This would explain the inferior results obtained from the benzoate, formate and oxalate.



Unlike the dehydration of an alcohol which seems to go through positively charged intermediates, the pyrolysis of an ester is usually a homogeneous reaction involving neutral or cyclic intermediates such as VI.[9] This accounts for observed *cis* elimination.[8]

In the pyrolysis of esters other minor side reactions have been observed from time to time. Occasionally acyl–oxygen scission to two molecules of carbonyl compound occurs. In the present work small amounts of formaldehyde, acetone, acetaldehyde, butyraldehyde and valeraldehyde were identified in the products from tetrahydrofurfuryl acetate. Each of these substances other than acetone could arise by acyl–oxygen scission followed by further reactions of the primary products. Other known modes of decomposition involve splitting to alcohol and ketene, and decarboxylation. No evidence for these alternative reactions was obtained, but amongst the by-products methylfuran was identified. This compound probably

---

(1) This work is taken from the Ph.D. thesis of G. J. Baumgartner, University of Notre Dame, 1955.

(2) R. Paul, *Compt. rend.*, **96**, 1409 (1933); *Bull. soc. chim.*, [4] **53**, 1489 (1933); L. E. Schniepp and H. H. Geller, THIS JOURNAL, **68**, 1646 (1946); C. L. Wilson, British Patent 569,625 (to Revertex Ltd., June 1, 1945); *Nature*, **157**, 846 (1946); THIS JOURNAL, **69**, 3004 (1947); C. H. Kline and J. Turkevitch, *ibid.*, **67**, 498 (1945); H. P. Thomas and C. L. Wilson, *ibid.*, **73**, 4803 (1951).

(3) R. Paul, *Bull. soc. chim.*, [5] **2**, 745 (1935).

(4) D. M. Aten Armitage and C. L. Wilson, THIS JOURNAL, **81**, 2437 (1959).

(5) F. Krafft, *Ber.*, **16**, 3018 (1883); **19**, 2227 (1886).

(6) J. P. Wibaut and A. J. van Pelt, Jr., *Rec. trav. chim.*, **57**, 1055 (1938); **60**, 55 (1941); P. L. Cramer and M. J. Mulligan, THIS JOURNAL, **58**, 373 (1936); F. C. Whitmore and H. S. Rothrock, *ibid.*, **55**, 1106 (1933).

(7) J. P. W. Houtman, J. van Steenis and P. M. Heertjes, *Rec. trav. chim.*, **65**, 781 (1946); W. J. Bailey and J. Rosenberg, THIS JOURNAL, **77**, 73 (1955).

(8) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

(9) W. J. Bailey and R. Barclay, Jr., *ibid.*, **21**, 328 (1956).