Anal. Calcd. for $C_{31}H_{34}O_6$: C, 74.10; H, 6.77. Found: C, 74.03; H, 6.39.

Diazotization Experiments.—To a solution of 1 ml. of *o*-toluidine in 3 ml. of concentrated hydrochloric acid was added 5 ml. of water. The solution was cooled to 0° and 1 g. of sodium nitrite dissolved in 5 ml. of water added. Two ml. portions of this cold diazonium solution were added, respectively, to dilute sodium hydroxide solutions of each of the condensation products (0.1 g.). The solutions were then made acid. The tests were negative in each case. Control experiments were run, using *p*-cresol under the same conditions. In this case, a red precipitate was obtained.

Summary

Indirect phenol–aldehyde condensations were carried out with completely and partially blocked phenols.

When *o,o'*-dimethylol-*p*-cresol, a completely blocked phenol, was condensed with phenols having two ortho positions available for condensation, such as *p*-cresol and *p*-bromophenol, high-melting crystalline condensation products resulted, the acetates of which analyzed for a 2:2 condensation and not for a 2:1 condensation as previously suggested.

For purposes of comparison, a 2:1 condensation product was actually formed by condensing the same phenolic dialcohol with a "blocked" phenol, 2,4-xylenol, unable to undergo cyclization. In contrast, the "linear" condensation product thus prepared proved to be a low-melting amorphous solid.

Thus, the analytical evidence presented in this paper does *not* support Koebner's postulations that phenol–aldehyde condensation products are of the linear type only, but rather favors a structural distinction between low-melting and high-melting types of condensation products. Thus, the lower-melting or "fusible" types appear to possess a "*linear*" structure, while for the high-melting types or "non-fusible" types, a "*cyclic*" structure appears to be in better harmony with actual analytical findings.

WASHINGTON SQUARE COLLEGE
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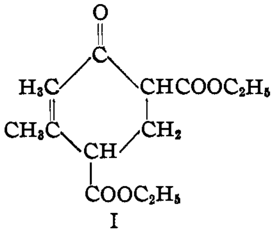
RECEIVED DECEMBER 22, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

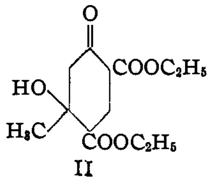
Alkylation of 3-Methyl-4-carbethoxy-2-cyclohexen-1-one (Hagemann's Ester) and Related Substances

BY LEE IRVIN SMITH AND GEORGE F. ROUAULT[1]

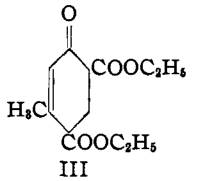
In studies in the vitamin E series, it was of interest to investigate the introduction of perhydrogeranyl and other groups into the molecules of substituted cyclohexenones. The so-called Hagemann's ester (3-methyl-4-carbethoxy-2-cyclohexen-1-one, IV) appeared to be a promising starting material, and accordingly a study of its preparation and properties was undertaken. Knoevenagel and Klages[2] studied the condensation of acetoacetic ester with formalin (or trioxymethylene). They found that the condensation proceeded to completion under the influence of basic catalysts, and that it involved the sequence I, II and III. Rabe and Rahm[3] found that the bis-acetoacetate I could be prepared without the use of a catalyst, but that a basic catalyst was necessary for conversion of I to the ketol II, which had been isolated previously, and which was readily converted (even by steam distillation) into III by loss of water.[4] When piperidine was used as the catalyst, considerable heat was evolved, and unless the reaction mixture was cooled efficiently, the direct product was the diester III.[4] Hagemann[5] first prepared the ester IV from aceto-



I



II



III

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[1] Abstracted from a thesis by G. F. Rouault, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, July, 1942.

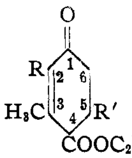
[2] Knoevenagel and Klages, *Ann.*, **281**, 94 (1894).

[3] Rabe and Rahm, *ibid.*, **332**, 10 (1904).

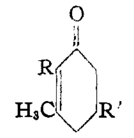
[4] Rabe and Elze, *ibid.*, **323**, 97 (1902).

[5] Hagemann, *Ber.*, **26**, 876 (1893).

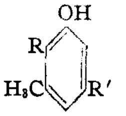
acetic ester and methylene iodide, but Bergmann and Weizmann[6] found that the diester III could be converted into IV by action of sodium ethoxide. Mannich and Fourneau[7] have also prepared IV, though in poor yield, by action of sodium ethoxide upon a mixture of acetoacetic ester and 4-dimethylamino-2-butanone.



IV, R = R′ = H
V, R = iso Pr.; R′ = H
VII, R = CH_3; R′ = H
IX, R = C_2H_5; R′ = H
XI, R = $C_{10}H_{21}$ (perhydrogenyl); R′ = H
XIII, R = H; R′ = CH_3



VI, R = iso Pr.; R′ = H
VIII, R = CH_3; R′ = H
X, R = C_2H_5; R′ = H
XII, R = $C_{10}H_{21}$; R′ = H
XIV, R = H; R′ = CH_3



XV, R = CH_3; R′ = H

Hagemann's ester, IV, can be alkylated by action of alkylating agents in the presence of bases, and it has been conclusively proved[8] that the alkyl group enters the 2-position and not the 4-position. These alkylated Hagemann's esters can be hydrolyzed and decarboxylated to 2-alkyl-3-methyl-2-cyclohexen-1-ones, VI, and such preparations of the esters V and VII, and of the cyclohexenones VI and VIII, have already been described in the literature.[9]

As stated in the introduction, the alkylated cyclohexenones obtained from Hagemann's ester appeared to be attractive substances for use as starting materials for preparation of a number of compounds of interest in connection with the chemistry and synthesis of vitamin E. Thus, introduction of various groups into the 2-position of Hagemann's ester could lead to a wide variety of substituted cyclohexenones, and if a good method for dehydrogenation of these could be found, many substituted phenols, and from them hydroquinones, could be prepared; moreover, introduction into Hagemann's ester of a perhydrogeranyl group, or other group made up of "isoprene" units, would give a cyclohexenone which might be converted into an "isoprenolog" of the starting material. Use of aldehydes other than formaldehyde in the initial condensation with acetoacetic ester would result in the introduction of a group into the 5-position of the cyclohexenone, and by substitution of other β-keto esters for acetoacetic ester, the groups in the 2- and 3-positions of the cyclohexenone could be varied. With these ideas in mind, the work described in this paper was undertaken. The synthesis has been completed to the phenol XV in one case, and to the cyclohexenone in three other cases (X, XII, XIV).

The best results were obtained by carrying out the preparation of Hagemann's ester IV in two steps. Condensation of acetoacetic ester with formaldehyde in the presence of piperidine gave directly the diester III, and this crude product was decarboxylated to IV by refluxing it with sodium ethoxide. Consistent yields of 40% of IV could be obtained by use of technical acetoacetic ester; when redistilled acetoacetic ester was used, the yield of IV was 50%, but this yield was the maximum ever obtained. The loss probably occurred during the conversion of III to IV, for although the crude diester III was a light yellow substance, the crude product IV obtained from it was red and contained considerable amounts of tarry material. The boiling point of the diester III was very high, even under 5 mm. pressure, and distillation of III was accompanied by considerable decomposition. Consequently the crude diester was used for conversion to IV. Attempts were made to improve the yield of IV, but none of these were successful. Use of 2 moles of sodium ethoxide, instead of one, for hydrolysis of III gave IV in only 10% yield; thorough drying of III by calcium chloride (instead of allowing it to stand for one hour over sodium sulfate), followed by refluxing with 1 mole of sodium ethoxide for three hours (instead of two hours), gave IV in 30% yield; thorough removal of piperidine from III by washing with dilute acid likewise did not result in an improved yield of IV; and hydrolysis of III by action of water alone at 200° gave 21% of IV, accompanied by 25% of 3-methylcyclohexenone. It appeared that hydrolysis of III was rather slow and, for good results, had to be carried out with bases; but the product IV was sensitive to bases and prolonged action of these substances had to be avoided. Action of acids upon III produced no better results; the product in these cases was 3-methyl-2-cyclohexen-1-one. When III was refluxed with sulfuric acid in water,

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(6) Bergmann and Weizmann, *J. Org. Chem.*, **4**, 267 (1939).

(7) Mannich and Fourneau, *Ber.*, **71**, 2090 (1938).

(8) (a) Kötz and Anger, *ibid.*, **44**, 466 (1911); (b) Rabe and Pollack, **45**, 2926 (1912); (c) Kötz, Blendermann, Mahnert and Rosenbusch, *Ann.*, **400**, 77 (1913); (d) Dieckmann, *Ber.*, **45**, 2697 (1912).

(9) (a) Callenbach, *Ber.*, **30**, 639 (1897), (b) also refs. 6, 8a, b, c, d.

or in 60% acetic acid, the cyclohexenone was produced in yields of 24 and 44%, respectively.

Condensation of acetaldehyde with acetoacetic ester in the presence of piperidine produced the monoester XIII which was not purified but was directly hydrolyzed to the cyclohexenone XIV by the procedure of Knoevenagel and Klages.[2] However, the yield was only about 20 instead of the 83% of XIV as claimed by Knoevenagel and Klages.

Alkylation of Hagemann's ester IV was accomplished by action of alkyl halides upon IV in the presence of sodium ethoxide. Methylation with methyl iodide according to the procedure of Bergmann and Weizmann[6] gave a mixture of the ester VII (25% yield) and the dimethylcyclohexenone VIII (40% yield); decarboxylation of this ester VII gave VIII in 60% yield, so that the over-all yield of VIII from IV was 55%. Curiously, no conditions were found for methylation of IV which led to VII alone; Bergmann and Weizmann reported no difficulty in obtaining VII from IV. When methyl bromide was substituted for methyl iodide in the alkylation of IV, the exclusive product, formed in 50% yield, was the cyclohexenone VIII. On the other hand, ethylation of IV gave the ester IX in 55% yield, unaccompanied by the related cyclohexenone X. Likewise, alkylation of IV by perhydrogeranyl bromide gave the ester XI (50% yield) and none of the cyclohexenone XII. No explanation can be offered for this curious difference between the action of the methyl halides and that of the other halides in this alkylation; it may be that the higher alkyl compounds have a "semi-cyclic" double bond, and so are not strictly cyclohexenones, but this point was not investigated.

Hydrolysis and decarboxylation of the Hagemann's esters was accomplished by refluxing the esters with alcoholic potassium hydroxide. A substantial loss resulted from formation of tarry material by action of the base upon these esters, but again it was found that good results were obtained only by alkaline hydrolysis, and although prolonged action of the base had to be avoided, sufficient time had to be allowed for complete hydrolysis. The yields of alkylated cyclohexenones were 55–65%. Rabe and Pollack[8b] found that hydrolysis of VII by action of dilute sulfuric acid gave VIII which was contaminated by an unidentified by-product, and the unfavorable action of sulfuric acid upon the derivatives of IV was verified in this work. Thus, acid hydrolysis of IV produced 3-methylcyclohexenone in 24% yield, but no XII could be obtained from XI by action of dilute sulfuric acid for twenty-five hours, or by action of water alone at 200°.

Crystalline semicarbazones were obtained from the esters IV, IX and XI, and from the cyclohexenones VIII, X, XII, XIV and 3-methyl-2-cyclohexenone. The semicarbazones of XI and XII, however, crystallized only after the reaction mixtures stood for very long times in the refrigerator—three months and two weeks, respectively.

All the dehydrogenation experiments were conducted upon 2,3-dimethyl-2-cyclohexen-1-one (VIII). No really satisfactory process was found for production of the phenol XV in good yield from VIII. Dehydrogenation by action of the palladium–charcoal catalyst "d" of Linstead, Michaelis and Thomas[10] at 200° for seventy-two hours produced the phenol in 55% yield. No by-products were isolated, although 90% of the cyclohexenone VIII disappeared during the reaction. Action of this catalyst upon the ethyl homolog IX produced nothing but tar—another curious difference between the methyl and ethyl compounds in this series. The following methods, all applied to the dehydrogenation of VIII, failed completely: action of chloranil and copper chromite catalyst in boiling xylene upon VIII, or its sodium derivative (prepared by action of sodamide upon VIII)[11]; fusion of VIII with potassium hydroxide; fusion of the sodium derivative of VIII with sodamide[12]; and air oxidation of the sodium derivative. An attempt was made to prepare the enol acetate of VIII in the hope that this might be dehydrogenated more readily, but the acetate could not be obtained. All of these procedures, including the last, gave unchanged material or else tars and high boiling products. Catalytic dehydrogenation under high pressure,[13] action of selenium dioxide,[14] action of sulfur or selenium, and action of bromine[15] were not tried.

Experimental Part[16,17]

3-Methyl-4-carbethoxy-2-cyclohexen-1-one (Hagemann's Ester, IV).—Piperidine (20 cc.) was added to a

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[10] Linstead, Michaelis and Thomas, *J. Chem. Soc.*, 1139 (1940).

[11] Nasarow, *Ber.*, **70**, 595 (1937).

[12] Orthner and Reichel, "Organische Chemisches Praktikum," Verlag Chemie, Berlin, 1929, p. 182.

[13] (a) Reeve and Adkins, THIS JOURNAL, **62**, 2874 (1940); (b) Adkins and Reid, **63**, 741 (1941).

[14] Dane and Schmitt, *Ann.*, **536**, 196 (1938).

[15] Kötz and Gotz, *ibid.*, **358**, 183 (1908); see also Ref. 2.

[16] Microanalyses by E. E. Renfrew and C. H. Stratton.

[17] Some of the preliminary experiments were carried out by J. W. Opie.

mixture of acetoacetic ester (520 g., 4 moles) and paraformaldehyde (60 g., 2 moles). The mixture soon became very hot, and it was necessary to plunge the flask into an ice-bath occasionally in order to control the reaction. After the vigorous reaction subsided (thirty minutes), the mixture was heated on the steam-bath for forty minutes. The yellow viscous oil (III) was separated from the supernatant water (about 18 cc.) and dried over sodium sulfate. The diester III was refluxed for two hours with a solution of sodium ethoxide (46 g. of sodium) in dry ethanol (1.6 l.). The solvent was removed by distillation from an oil-bath until the temperature of the *liquid* reached 120°; the residue was diluted with water (1 l.) and acetic acid (140 cc.) was added, with vigorous stirring. The lower layer of red oil (320 cc.) was removed and the aqueous layer was extracted with ether (500 cc.). The extract was combined with the red oil, the solvent was removed by distillation, and the residue (360 cc.) was fractionated through a short packed column. Hagemann's ester IV (182 g., 50%) boiled at 142–144° (15 mm.) and had $n^{20}\text{D}$ 1.4852. The ester formed a semicarbazone which melted at 165–167°.[18]

3-Methyl-2-cyclohexen-1-one.—The crude diester III (380 g.) was refluxed for seventeen hours with water (3.3 l.) and sulfuric acid (740 cc.) and the mixture was distilled with steam. The distillate (4.5 l.) was saturated with potassium carbonate (about 5 lb.) and extracted with two 250-cc. portions of ether. The extracts were combined, the solvent was removed, and the residue was fractionated. 3-Methyl-2-cyclohexen-1-one (38 g., 24%) boiled at 75–77° (10 mm.). The semicarbazone melted at 199–201° (dec.).[19] The crude ester III (78 g.) was dissolved in a mixture of acetic acid (150 cc.), sulfuric acid (15 cc.), and water (100 cc.) and the solution was refluxed for five hours. The solution was neutralized by addition of sodium hydroxide (127 g. in 350 cc. of water) and was extracted with ether (300 cc.). The ether was removed and the residue, when fractionated, gave 3-methyl-2-cyclohexen-1-one (14.5 g., 44%) boiling at 95° (23 mm.) and Hagemann's ester IV (4.5 g., 8%) boiling at 163° (27 mm.).

2,3-Dimethyl-2-cyclohexen-1-one (VIII).—The ester IV (36 g.) was dissolved in sodium methoxide solution (4.6 g. of sodium, 120 cc. of methanol). The mixture was cooled (5°) and methyl iodide (29 g.) was added, after which the temperature was maintained at 20° for thirty minutes. The mixture was then refluxed for two hours, the methanol was removed by distillation, the residue was diluted with water (400 cc.), and extracted with three 100-cc. portions of ether. The combined extracts were washed with water, dried and the ether was removed. The residue, on fractionation, gave the ketone VIII (9.3 g., 37%) boiling at 90–96° (14 mm.) and the ester VII (6.7 g., 17%) boiling at 138–142° (12 mm.). The ester IV (91 g.) was dissolved in a solution of sodium ethoxide (13 g. of sodium, 200 cc. of dry ethanol) and the mixture was cooled (0°) and stirred while a solution of methyl bromide (47.5 g.) in dry ethanol (50 cc.) was rapidly (fifteen minutes) added. The temperature was maintained below 10°, and stirring was continued for two hours, and then alcohol was removed by distillation until the temperature of the liquid reached 116°. The residue was diluted with water (300 cc.) and extracted with three 100-cc. portions of ether. The solvent was removed from the combined extracts, and the red-brown residue (100 cc.) was dissolved in a solution of potassium hydroxide (24 g.) in alcohol (270 cc.) and the mixture was refluxed for eight hours. Alcohol was removed by distillation, and the residue was diluted with water (500 cc.) and extracted with ether (two 200-cc. portions). The ether was removed from the combined extracts and the residue was distilled through a short column packed with glass helices. The ketone VIII (30.2 g., 49%) boiled at 80–84° (9 mm.). A second fraction, boiling at about 139° (9 mm.), was unchanged ester IV. The semicarbazone of VIII, prepared in the usual way, and crystallized from dilute (30%) alcohol, sintered at 200–205° and melted at 222°.[20]

Anal. Calcd. for $C_9H_{15}ON_3$: C, 59.71; H, 8.28. Found: C, 59.91; H, 8.38.

2-Ethyl-3-methyl-4-carbethoxy-2-cyclohexen-1-one (IX).—The ester IV (36 g.) was dissolved in a solution of sodium ethoxide (4.6 g. of sodium, 120 cc. of dry ethanol) and alkylated with ethyl bromide (22 g.). The mixture was refluxed for three hours, the alcohol was removed by distillation, and the residue was diluted with water (200 cc.) and extracted with ether (two 100-cc. portions). The ether was removed, and the residue, when fractionated, gave the methylethylcyclohexenone X (7.4 g., 27%) boiling at 120–130° (9 mm.) and the ester IX (22.9 g., 55%) boiling at 141–143° (9 mm.). The semicarbazone of IX, recrystallized twice from dilute alcohol, melted at 160–164°.

Anal. Calcd. for $C_{13}H_{21}O_3N_3$: C, 58.44; H, 7.93. Found: C, 58.81; H, 8.05.

2-Ethyl-3-methyl-2-cyclohexen-1-one (X).—The ester IX (22 g.) was refluxed for eight hours with a solution of potassium hydroxide (6 g.) in alcohol (60 cc.). Alcohol was removed by distillation and the residue was diluted with water and extracted with ether. The cyclohexenone X (9 g., 62%) boiled at 82–85° (9 mm.). The semicarbazone of X, crystallized from aqueous alcohol, melted at 190–194°.

Anal. Calcd. for $C_{10}H_{17}ON_3$: C, 61.44; H, 8.73. Found: C, 61.74; H, 8.64.

2-Perhydrogeranyl-3-methyl-4-carbethoxy-2-cyclohexen-1-one (XI).—The ester IV (18.2 g.) was dissolved in a solution of sodium ethoxide (2.3 g. of sodium, 80 cc. of dry ethanol), perhydrogeranyl bromide[21] (22.1 g.) was added, and the mixture was refluxed for twelve hours. The alcohol was removed by distillation under reduced pressure, and the residue was washed successively with water, dilute sulfuric acid, and finally with water. The residue, on fractionation, gave the ester XI (15.7 g., 49%) boiling at 182° (4 mm.).

Anal. Calcd. for $C_{20}H_{34}O_3$: C, 74.48; H, 10.63. Found: C, 74.48; H, 10.57. The semicarbazone, after crystallization from aqueous alcohol (long standing in the refrigerator), melted at 85.5–87°. *Anal.* Calcd. for $C_{21}H_{37}O_3N_3$: C, 66.45; H, 9.83. Found: C, 66.65; H, 9.66.

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[18] Rabe and Rahm, *Ber.*, **38**, 971 (1905), give the m. p. as 169°.

[19] The melting points given in the literature range from 198 to 201°; (a) Vorländer and Gärtner, *Ann.*, **304**, 23 (1899); (b) Simonsen and Storey, *J. Chem. Soc.*, **95**, 2112 (1909); (c) Fargher and Perkin, *ibid.*, **105**, 1362 (1914); (d) Bluman and Zeitschel, *Ber.*, **46**, 1190 (1913); (e) Harries, *ibid.*, **47**, 790 (1914).

[20] Ref. 8c, p. 83, gives the m. p. as 225°.

[21] Smith, Ungnade, Austin, Prichard and Opie, *J. Org. Chem.*, **4**, 336 (1939).

2-Perhydrogeranyl-3-methyl-2-cyclohexen-1-one (XII).—The above ester XI (15.7 g.) was refluxed for eight hours with a solution of potassium hydroxide (5 g.) in ethanol (50 cc.). The alcohol was removed by distillation and the residue was diluted with water and extracted with ether. Removal of the ether and fractionation of the residue gave the ketone XII (6.6 g., 54%) boiling at 153–155° (3 mm.). The semicarbazone, after three crystallizations from aqueous alcohol (long standing in the refrigerator), melted at 93–95°.

Anal. Calcd. for $C_{18}H_{33}ON_3$: C, 70.31; H, 10.82. Found: C, 70.19; H, 10.57.

3,5-Dimethyl-2-cyclohexen-1-one (XIV).—Piperidine (13 g.) was added to a mixture of acetoacetic ester (520 g.) and acetaldehyde (88 g.). After the reaction (slow refluxing) had subsided (four hours), water (2 l.) and sulfuric acid (500 cc.) were added, and the mixture was refluxed for twenty-two hours. The cooled mixture was extracted with three 600-cc. portions of ether, the solvent was removed from the combined extracts, and the residue was fractionated. The products were the ketone XIV (47 g., 19%) boiling at 81° (9 mm.), 3,5-dimethyl-4-carbethoxy-2-cyclohexen-1-one (XIII, 23 g., 6%) boiling at 146° (12 mm.), and a little 3,5-dimethyl-4,6-dicarbethoxy-2-cyclohexen-1-one boiling at 205° (11 mm.). The semicarbazone of the ketone XIV, after crystallization from dilute alcohol, melted at 177–180.5°.[22]

2,3-Dimethylphenol (XV).—2,3-Dimethyl-2-cyclohexen-1-one (VIII, 2.0 g.) was heated at 200° with palladium-charcoal catalyst "d"[10] (0.22 g.) for seventy-two hours. The cooled mixture was diluted with petroleum ether (70 cc., b. p., 30–60°), filtered, and the filtrate was extracted with three 10-cc. portions of sodium hydroxide solution (17%). The combined extracts were acidified with hydrochloric acid and the phenol XV (1.04 g., 53%) was removed and crystallized from petroleum ether (b. p. 30–60°). The phenol melted at 71.5–72.5°, alone or when mixed with an authentic specimen.[23]

Summary

1. Hagemann's ester, 3-methyl-4-carbethoxy-2-cyclohexen-1-one (IV) has been alkylated in the 2-position with methyl, ethyl and perhydrogeranyl halides and the resulting substances have been converted into 2-alkyl-3-methyl-2-cyclohexen-1-ones.

2. Dehydrogenation of 2,3-dimethyl-2-cyclohexen-1-one (VIII) by action of a palladium catalyst gave 2,3-dimethylphenol in 53% yield; the dehydrogenation was attempted by other methods, but none of these attempts was successful.

3. By substitution of acetaldehyde for formaldehyde in the initial condensation, 3,5-dimethyl-2-cyclohexen-1-one has been prepared and it appears that this synthesis of cyclohexenones is general and may be varied widely by suitable choice of starting materials.

MINNEAPOLIS, MINNESOTA RECEIVED DECEMBER 5, 1942

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[22] The melting points given in the literature range from 178° to 180°; (a) Knoevenagel, *Ann.*, **297**, 165 (1897); (b) Mazurewitsch, *Chem. Zentr.*, **85**, I, 1653 (1914); (c) Baeyer and Piccard, *Ann.*, **407**, 342 (1915).

[23] Smith and Opie, *J. Org. Chem.*, **6**, 431 (1941).

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

Arsenicals Derived from Acetophenone

BY ROBERT L. CLARK[1] AND CLIFF S. HAMILTON

In an effort to obtain compounds of value in the treatment of spirochaetal and trypanosomal diseases, the synthesis of omega-hydroxy and omega-amino derivatives of 4-arsonoacetophenone was undertaken.

4-Arsonoacetophenone was converted to ω-chloro-4-arsonoacetophenone by the method of Sergeev and Kudryashev.[2] The product obtained in this investigation melted at 208–209°, whereas they reported a melting point of 189°. When ω-chloro-4-arsonoacetophenone was refluxed with potassium formate in a medium of methyl alcohol, ω-hydroxy-4-arsonoacetophenone resulted. In the same manner, secondary amines treated with ω-chloro-4-arsonoacetophenone to yield omega-amino derivatives.

When phenylhydrazine was treated with ω-chloro-4-arsonoacetophenone a product was obtained which contained no halogen. Hoogeveen[3] reported that similar reactions formed derivatives of 1,2-diazacyclobutene-2. The arsenic analysis indicated that such a type of compound was prepared in this investigation. Other derivatives involving the carbonyl group of ω-hydroxy- and ω-chloro-4-arsonoacetophenone were prepared by familiar procedures.

ω-Hydroxy-4-arsonoacetophenone was reduced with sulfur dioxide to give the corresponding arsine oxide.

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[1] Parke, Davis and Company Fellow; present address, Merck and Company, Rahway, N. J.

[2] Sergeev and Kudryashev, *J. Gen. Chem.*, (U. S. S. R.) **7**, 1488 (1937).

[3] Hoogeveen, *Rec. trav. chim.*, **50**, 669 (1931).