The solution was chilled in a freezing mixture, the crystals filtered with slight suction on a cold Büchner funnel with paper and the filtrate added to the next preparation; yield, 90–95%. It may contain dithiocyanate, from which it can be freed by sublimation; m. p. 76.1–76.6°; b. p. 127° (corr.) (by the Siwolliboff capillary tube method); sulfur, 27.5%; calcd., 27.6%. The molecular weight of the crude sulfide was determined by the freezing-point method in benzene: (1) 16.00 g. of solvent; 0.1423 g. of sample, depression 0.385°, molecular weight 115.5; (2) 0.2672 g. of sample, depression 0.719°, molecular weight 116.1, calcd. 116.19. Hence it contained no polymers.

Summary

Tetramethylethylene sulfide was prepared by the series of reactions acetone $\longrightarrow$ pinacone hydrate $\longrightarrow$ tetramethylethylene dibromide $\longrightarrow$ dithiocyanate $\longrightarrow$ sulfide, and some of its properties have been recorded.

WHITING, INDIANA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE STANDARD OIL COMPANY, INDIANA]

TRIMETHYL- AND TRIMETHYLETHYLTHIOPHENE

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Perhaps the most obvious method of preparing polyalkylthiophenes of known structure is by means of the reaction of phosphorus pentasulfide or phosphorus trisulfide on 1,4-dicarbonyl compounds. If the α-positions of the thiophene are to be substituted with alkyl groups, the carbonyl compound must be a diketone. The preparation of such compounds has proved to be extremely difficult. The only member thus far reported is 3,4-dimethylacetonylacetone prepared by Ciamician and Silber[1] by the action of light on methyl ethyl ketone and by Vladesco[2] by the action of sodium on methyl chloro-ethyl ketone. Willstätter and Clark[3] reported a large amount of work on attempts to produce such a diketone. While the action of iodine on sodium acetoacetic ester readily yields diacetylsuccinic ester, which is hydrolyzable to acetonylacetone with good yields, the attempt to carry out an analogous reaction with ethyl sodium acetoacetic ester has uniformly failed. Also the attempt to introduce alkyl groups into sodium diacetylsuccinic ester leads chiefly to ethers, and such of the desired compound as is produced readily loses one or more acetyl groups by hydrolysis or alcoholysis.[3] We have found that another variation of this synthesis gives negative results: the action of sodium on α-bromo-α-ethyl acetoacetic ester. An attempt to repeat the work of Vladesco where sodium is allowed to react with methyl chloro-ethyl ketone yielded no detectable amount of the desired diketone. Also the ethyl

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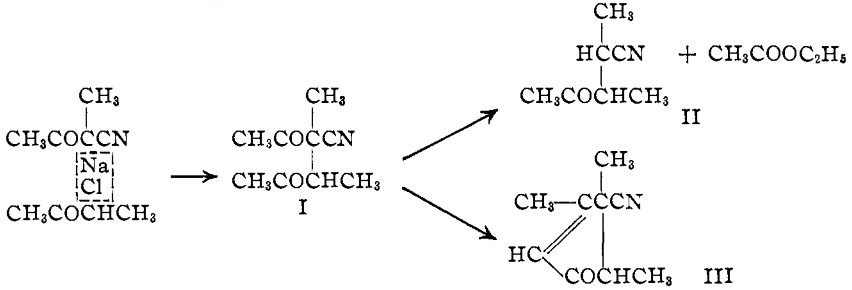
[1] Ciamician and Silber, *Ber.*, **45**, 1540 (1912).

[2] Vladesco, *Bull. soc. chim.*, [3] **6**, 809 (1891).

[3] Willstätter and Clark, *Ber.*, **47**, 291–310 (1914).

acetal of this ketone appeared to react with sodium but did not give the diketone acetal or the diketone.

The nitrile $CH_3COCHCNCH_3$,[4,5] prepared from methyl chloroethyl ketone and potassium cyanide, was converted into its sodium compound and this allowed to react with the chloroketone. The reaction yielded, besides unchanged nitrile, a substance b. p. 171° (760 mm.); b. p. 75° (25 mm.); d_4^{20} 0.957 (the first nitrile boils at 145°). It was colorless and had a strong odor. From its low boiling point it could hardly have been the expected diacetonitrile (I) but was perhaps the nitrile of α,β-dimethyl-levulinic acid (II) formed by the alcoholysis of one acetyl group from I, or perhaps a cyclic ketone-nitrile (III) formed from I by internal condensation. The ethyl ester of the acid corresponding to the nitrile (I) was shown to behave in this manner; but III would probably have had a higher boiling point than we observed since the corresponding ethyl ester according to Willstätter had a boiling point of 125–135° at 11 mm., and in general a nitrile of an acid has a boiling point very near that of the ethyl ester of that acid.



The attempt to prepare a ketone from which a tetra-alkyl thiophene could be prepared directly was then abandoned. α,β-Diacetyl butyric ester (IV) was then prepared from sodium acetoacetic ester and methyl chloro-ethyl ketone by means of a slight modification of the method of

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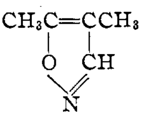
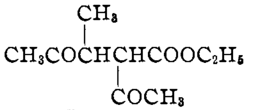
[4] Von Reymenant, *Bull. acad. roy. Belg.*, 724–742 (1900); *Chem. Centr.*, I, 95–96 (1901).

[5] There is doubt in the minds of the authors that the substance produced in the manner described is really a nitrile. If it is, it would be the nitrile of methylacetoacetic acid and should have a boiling point of 180–190° instead of 145° as it has. Its elementary composition is that represented by the formula. From its anomalous boiling point, its basic properties, the formation of addition compounds with mercuric chloride and with methyl iodide and its very slow reaction with sodium, it seems much more probable that it is the isomeric 4,5-dimethyl isoxazole, as shown. If so, a whole series of isoxazoles can readily be prepared in a similar manner with high yields. However, such an isoxazole would probably behave toward sodium or sodium ethylate as if it were the nitrile, forming the expected sodium derivative of methyl acetoacetonitrile and hence be suitable for the work here described. The authors wish to reserve this field for further work.

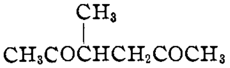


Willstätter and Clark. This ester was hydrolyzed by boiling for several hours with an excess of 20% potassium carbonate solution to the new diketone, 3-methylacetonylacetone (V).



$CH_3CO\overset{\overset{CH_3}{|}}{C}H\underset{\underset{COCH_3}{|}}{C}HCOOC_2H_5$

IV



$CH_3CO\overset{\overset{CH_3}{|}}{C}HCH_2COCH_3$

V

This ketone reacted readily with phosphorus pentasulfide in the cold, giving after purification 2,3,5-trimethylthiophene.

2,3,4-Trimethylthiophene, the only position isomer possible, has been prepared by Victor Meyer.[6] Our thiophene with isatin and sulfuric acid gives a brilliant brownish-red color but not blue or green. 2,5-Dimethylthiophene, where both α-positions also are substituted, does likewise[7] but the 2,3,4-compound gives a green color.

Our thiophene reacted readily with acetyl chloride and aluminum chloride giving 2,3,5-trimethyl-4-acetothienone. This ketone has an unpleasant penetrating odor similar to but much stronger than that of the thiophene itself. The ketone was reduced by the method of Clemmensen, giving 2,3,5-trimethyl-4-ethylthiophene.

This thiophene does not give the indophenine reaction. Both thiophenes dissolve in concentrated sulfuric acid with slight discoloration and a slight heat evolution. Both are reprecipitated on dilution though probably the trimethylthiophene is converted to a sulfonic acid to some extent. This inertness is in great contrast to the ready reaction of thiophene itself with sulfuric acid. Both thiophenes show the characteristic depression of the molecular refraction, while the trimethylacetothienone has a normal value.

The trimethylthiophene reacts readily with iodine in the presence of yellow mercuric oxide to give an iodo compound. This was only distillable in steam and was probably impure.

Experimental Part

Diethyldiacetosuccinic Ester.—α-Bromo-α-ethylacetoacetic ester was prepared according to the method of Macbeth.[8] The boiling point, however, is 100–102° at 11 mm. and not 106°. Four and two-tenths grams of sodium (calcd. 3.8 g.) was placed in 150 cc. of dry ether and 26.3 g. of ethylacetoacetic ester added and allowed to reflux for two hours with shaking. The solution was poured off the remaining sodium and mixed with 39.5 g. of α-bromo-α-ethylacetoacetic ester. The solution became warm, and sodium bromide precipitated in one to two minutes, after which the solution was refluxed for ten minutes. It stood for sixteen hours and although still slightly alkaline was treated with water, washed and dried with sodium sulfate. After evaporation of

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[6] Victor Meyer, "Die Thiophengruppe," Braunschweig, **1888**, pp. 59–60.

[7] Ref. 6, p. 53.

[8] Macbeth, *J. Chem. Soc.*, **123**, 1127 (1923).

ether, there remained 36 g. of a brown oil which did not crystallize. It gave no diketone (3,4-diethylacetonylacetone) when boiled with potassium carbonate solution.

3,4-Dimethylacetone.—Methyl α-chloro-ethyl ketone was prepared by passing chlorine into a stirred mixture of two parts of methyl ethyl ketone, two parts of water and one part of powdered calcium carbonate under a reflux and at 60–70° until the calcium carbonate was gone. Sodium was put in 200 cc. of dry ether and 128 g. (3 moles) of chloro ketone added. The mixture boiled spontaneously at first and was then heated until the reaction was complete (about one hour). The solution was filtered, washed, dried and fractionated. No diketone whatever was obtained, the product being unchanged chloro ketone and very high boiling products. Another trial, in which the sodium (as wire) was added during the course of the reaction, gave no better results. Heating of the chloro ketone with Kahlbaum's copper powder in a sealed tube at 150–160° gave no reaction. At 170–180° some decomposition occurred but no diketone was obtained.

Methyl chloro-ethyl ketone diethyl acetal was prepared by the method of Claisen[9] from 75 g. (3 moles) of absolute ethyl alcohol, 66.8 g. of chloro ketone and 102 g. of ethyl ortho-formate; yield, 70% in ten days' standing. The acetal showed b. p. 80–84° (36 mm.); d_4^{20} 0.9773; Cl, 19.3%; calcd. 19.6%. Without ammonium chloride as a catalyzer the yield was 39%. A shorter time of standing (four days) gave a 45% yield. Probably a longer period would increase the yield. Thirteen and seven-tenths grams of sodium wire (calcd. 11.7 g.) was placed in 300 cc. of dry ether with 93 g. of chloro acetal under a reflux condenser bearing a calcium chloride tube. The mixture was refluxed daily for five days, when the sodium was much disintegrated. The liquid was filtered, the residue washed once with dry ether and the combined filtrates were distilled, finally at reduced pressure; 32 g. of very pure acetal was recovered but no other products except ether.

3-Methylacetonylacetone.—α,β-Diacetylbutyric ester was prepared as described by Willstätter and Clark[3] except that a 100% excess of acetoacetic ester was used. This doubled the yield. We obtained 45–60% yields with 60–80% recovery of the excess acetoacetic ester.

Two hundred and six grams of ester was refluxed for six hours with a solution of 200 g. of potassium carbonate in 800 cc. of water. The mixture was diluted with ether, the upper layer separated and the water layer extracted with ether. The combined extracts were dried with potassium carbonate and after removal of ether in a bead column, fractionated at reduced pressure; yield 109 g. (83%); b. p. 68–74°; properties: b. p. 71° (10 mm.); d_4^{20} 0.9527; n_D^{20} 1.4260; b. p. (740 mm.) 195–196° (corr.) with some decomposition. It is soluble in all the usual organic solvents and miscible with water in all proportions. As prepared above it had a rather strong odor but after purification with sodium bisulfite (by shaking with saturated sodium bisulfite solution, extracting with ether, and heating the sodium bisulfite solution with sodium carbonate) it had a sweet and pleasant odor. In other respects the purified and unpurified ketones had practically identical properties.

The semicarbazone (di-semicarbazone), when crystallized from hot water, melted at 219–220° corr.

Anal. Subs., 0.0848: 23.5 cc. of N at 0° and 760 mm. Calcd.: N, 34.7. Found: N, 34.7.

The *p*-nitrophenylhydrazone (or possibly the 2,3,5-trimethyl-N-*p*-nitrophenyliminopyrrole) was recrystallized from toluene; m. p. 112–113° corr.

2,3,5-Trimethylthiophene.—Sixty-five to 70 g. of powdered phosphorus pentasul-

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[9] Claisen, *Ber.*, **40**, 3908 (1907).

fide in a flask with a reflux condenser was treated with 96 g. of 3-methylacetonylacetone, the mixture kept cool and not shaken for a few minutes (to avoid a too violent reaction), and then allowed to come to room temperature. Finally, it was heated to boiling for three to four hours with the addition of 10 g. of phosphorus pentasulfide after the first hour. The liquid was poured off the tarry residue, distilled, the distillate dried, refluxed over several portions of sodium and then sodium hydroxide, and fractionated. The yield was 35–40% of a colorless liquid with a durene-like odor; b. p. 163–165° corr. at 746 mm.; d_4^{20} 0.9753; n_D^{20} 1.5131; M_D^{20} 38.88, calcd. 39.50; sulfur calcd. 26.4, found 26.4. The sulfur was determined by analysis of a solution in naphtha by the Burton lamp method.

2,3,5-Trimethyl-4-acetothienone.—To 12 g. of powdered aluminum chloride in 50 g. of cold carbon disulfide in a flask with a reflux condenser was added a mixture of 10 g. of trimethylthiophene, 8 g. of acetyl chloride and 50 g. of carbon disulfide drop by drop during fifteen minutes. The mixture was allowed to stand for three to four hours in ice and water, then overnight at room temperature. The mixture was warmed for a few minutes, then cooled, decomposed with dilute sulfuric acid, diluted with ether, separated and the ether solution washed with dilute sulfuric acid, water, sodium carbonate and water; it then was dried and fractionated. The yield was 12.5 g. (93%); b. p. 245–250° corr. Other preparations gave 85–94% yields. The pure ketone boiled at 248–249° corr. (748 mm.); d_4^{20} 1.0891; n_D^{20} 1.5454; M_D^{20} 48.86, calcd. 48.75. *Anal.* (Parr oxygen bomb). Calcd.: S, 19.05. Found: S, 18.9. It formed no bisulfite compound.

The semicarbazone, when recrystallized from acetone, melted at 157° corr.

The *p*-nitrophenylhydrazone was recrystallized from xylene; m. p. 162.5–163° corr. *Anal.* Subs., 0.2102: 24.0 cc. of nitrogen at 0° and 760 mm. Calcd.: N, 13.9. Found: N, 14.2.

The phenylhydrazone was an oil which did not crystallize.

2,3,5-Trimethyl-4-ethylthiophene.—The acetothienone was reduced by the method of Clemmensen,[10] using 80 g. of zinc to 400 cc. of 5% mercuric chloride solution, pouring off this solution after one hour, adding the ketone (21.7 g.) and then 40 cc. of 6 *N* hydrochloric acid and refluxing, with further additions of 40 cc. of hydrochloric acid every one to two hours for fourteen hours. The yield was 70–80% after deducting unchanged ketone (15–25% of the original ketone). This thiophene boiled at 204–206° corr. at 748 mm.; d_4^{20} 0.9609; n_D^{20} 1.5132; M_D^{20} 48.25, calcd. 48.75. *Anal.* Calcd.: S, 20.78. Found: S, 20.8. These thiophenes gave the characteristic depression of the molecular refraction: trimethylthiophene, M_D^{20} 38.88, calcd. 39.50; trimethylethylthiophene, M_D^{20} 48.25, calcd. 48.75; trimethylacetothienone M_D^{20} 48.86, calcd. 48.75. This latter is probably to be interpreted as a depression, since an acetyl group on an aromatic nucleus usually produces an exaltation of 0.5 to 1.0 unit.[11]

Some attempts were made to prepare the compound by preparing iodotrimethylthiophene and treating it with sodium and ethyl bromide, but these were unsuccessful. Trimethylthiophene reacts readily with iodine and yellow mercuric oxide to give an iodo compound (which could not be distilled except with steam) but this gave no considerable amount of the desired product when treated with sodium and ethyl bromide. However, tetramethylthiophene has been made in this way.[12] Perhaps the success of the latter preparation depended on the fact that the group entered the α-position instead of the β-position as in our case. The α-positions are much more reactive.

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[10] Clemmensen, *Ber.*, **46**, 1837 (1913); **47**, 51, 681 (1914).

[11] Brühl, *ibid.*, **40**, 1159 (1907); Auwers and Eisenlohr, *ibid.*, **43**, 806 (1910); Auwers and Kohlhaas, *J. prakt. Chem.*, **108**, 321–331 (1924).

[12] Zelinsky, *Ber.*, **21**, 1837 (1888).

Summary

Attempts to synthesize a 3,4-dialkylacetonylacetone have yielded negative results, but 3-methylacetonylacetone was prepared and from it 2,3,5-trimethylthiophene by the action of phosphorus pentasulfide. From this thiophene was prepared 2,3,5-trimethyl-4-acetothienone, which was reduced to 2,3,5-trimethyl-4-ethylthiophene.

WHITING, INDIANA

NEW BOOK

Dispersoidanalyse. Die Methoden der Teilchengrössenbestimmung und ihre theoretischen Gründlagen. (The Methods for the Determination of the Size of Colloidal Particles and the Theoretical Considerations Involved.) BY FRIEDRICH-VINCENZ v. HAHN, Hamburg. Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1928. xxiv + 553 pp. 165 figs. 15.5 × 23.5 cm. Price, unbound, M. 39; bound, M. 42.

This monograph is Volume III of a handbook describing single aspects of colloid science. It deals with a problem which practical men in many fields, as, for example, those interested in the study of soil or clay, or filter-passing bacteria, have to solve. The book provides an admirable summary of our present resources in this direction. It describes the various experimental methods hitherto developed: optical, mechanical (filtration and ultrafiltration), methods depending upon diffusion, or upon Stokes' Law, estimations of the surface of particles and other special methods. It incidentally brings together a large number of interesting observations. There are 165 figures, mainly of apparatus, and the monograph is provided with indexes of authors, of subjects and of substances occupying altogether 55 pages. This is a volume which will provide indispensable information or save any amount of time for all those who happen to be concerned with any of the aspects of this general problem. It is interesting to note that this thorough yet concise treatment of this special subject is almost twice as lengthy as Svedberg's general monograph recently reviewed.

JAMES W. MCBAIN