of derivatives studied. However, in the cases where data are available a few degrees of depression can be noted if exactly the same rate of heating is maintained for the original melting point and the mixed melting points. In one instance, it was obvious that no depression occurred between the semicarbazones of 2-acetyl-3,5-dimethylthiophene (VII) and 2-acetyl-4,5-dimethylthiophene (VIII) (see Table I).

Thus, from the data presented it seems logical to assume that the occurrence of isomorphism among thiophene compounds is no more prevalent than in other series of organic compounds. Surely if this tendency was a characteristic of thiophene compounds, as Steinkopf states, the occurrence of isomeric pairs failing to show mixture melting depression would have been much higher than two in approximately one hundred and twenty mixtures tested.

Experimental[5]

2,3-Dimethylthiophene[6] (b.p. 142.5° (760 mm.), $n^{20}\mathrm{D}$ 1.5194): The crude semicarbazone (315 g.) of 3-methyl-2-thiophenealdehyde[7] was converted to crude 2,3-dimethylthiophene (137.5 g.) according to the method of Shepard.[8] The crude product was washed with dilute orthophosphoric acid to remove ammonia, dried over solid potassium hydroxide and distilled through a 20-plate fractionating column. 2,5-Dimethylthiophene[9] (b.p. 136.4° (760 mm.) $n^{20}\mathrm{D}$ 1.5128), 2-ethyl-, 2-propyl- and 2-*n*-butylthiophenes were prepared likewise in 65–85% yield.

2,3,4-Trimethylthiophene[10] (b.p. 172.7° (760 mm.), $n^{20}\mathrm{D}$ 1.5208) and 2,3,5-trimethylthiophene[11] (b.p. 164.5° (760 mm.), $n^{20}\mathrm{D}$ 1.5112) were also prepared. The 2,3,4-isomer was obtained from the semicarbazone (m.p. 238–240° dec.) of 3,4-dimethyl-2-thiophenealdehyde[6,12] (m.p. 71.5–72°). Semicarbazones of both 2,5-dimethyl-3-thiophenealdehyde and 3,5-dimethyl-2-thiophenealdehyde yielded 2,3,5-trimethylthiophene.

2,4-Dimethylthiophene[13] (b.p. 140.7° (760 mm.), $n^{20}\mathrm{D}$ 1.5104): Method A: The method of Zelinsky[13] using α-methyllevulinic acid but with phosphorus pentasulfide instead of the trisulfide yielded this dimethylthiophene.

Method B: Two hundred and sixty grams of 85% 2-methyl-1,3-pentadiene[14] and 192 g. of sulfur were heated at 260° for two and a half hours in a one-liter Aminco rocking autoclave. The maximum pressure attained was 1700 p.s.i.g. After cooling to ambient temperatures a residual pressure of 250 p.s.i.g. of hydrogen sulfide was noted. This was vented and 349 g. of liquid organic residue was drained from the autoclave. This material was steam distilled from 1000 ml. of 20% sodium hydroxide solution to yield 128 g. of distillate. After drying over solid potassium hydroxide, distillation through a 10-plate fractionating column yielded 74.5 g. (26%) of 2,4-dimethylthiophene. A sample of this material converted step-wise into the oxime of 2-acetyl-3,5-dimethylthiophene gave no melting point depression with a sample of the same material obtained from method A.

2,5-Dimethylthiophene.—The method of Farrar and Levine[15] using acetonylacetone and phosphorus pentasulfide resulted in a 60–65% yield. However, it was considered advisable to decant the liquid organic layer directly into an excess of aqueous (20%) sodium hydroxide. Steam distillation yielded the crude product which was distilled through a 20-plate fractionating column after drying over potassium hydroxide. In addition to the 2,5-dimethylthiophene, a 4–5% yield of 2,5-dimethylfuran (b.p. 93.2–94° at 760 mm.) was also obtained. A sample of 2,5-dimethylthiophene obtained by this procedure was submitted to API project 48 and ultimately found by that group to have a m.p. of −62.638° (−62.57° calcd. for zero impurity) and a calculated purity of 99.8 mole per cent.[16]

Acetylations[17] were carried out in boiling benzene (30 ml.) using acetic anhydride (0.4 mole), a thiophene (0.2 mole) and orthophosphoric acid (85%, 4.0 g.). The vacuum distilled products were obtained in 88–94% yields.

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(5) All melting points and boiling points are corrected.

(6) W. J. King and F. F. Nord, *J. Org. Chem.*, **13**, 635 (1948), list b.p. 139.5–140.5°, $n^{20}\mathrm{D}$ 1.5188.

(7) H. D. Hartough and J. J. Dickert, THIS JOURNAL, **71**, 3922 (1949).

(8) A. F. Shepard, *ibid.*, **54**, 2951 (1932).

(9) Ref. 6 lists b.p. 135–136°, $n^{20}\mathrm{D}$ 1.5132.

(10) Ref. 2, p. 36 lists b.p. of 160–163°. This b.p. is also reported in V. Meyer, "Die Thiophenegruppe," Braunschweig, 1888, p. 60.

(11) Ref. 6 lists b.p. 163–164°, $n^{20}\mathrm{D}$ 1.5131.

(12) A. W. Weston and R. J. Michaels, THIS JOURNAL, **72**, 1422 (1950).

(13) N. Zelinsky, *Ber.*, **20**, 2017, 2025 (1887), lists b.p. 137–138°.

(14) This material was obtained from Eastman Chemical Co. It contained 85% 2-methyl-1,3-pentadiene and 15% 4-methyl-1,3-pentadiene. Since the latter compound could not form a fully aromatic thiophene ring its presence was not considered harmful.

(15) M. W. Farrar and R. Levine, THIS JOURNAL, **72**, 4433 (1950).

(16) Private communication from J. S. Ball, U. S. Bureau of Mines, Laramie, Wyo.

(17) Method of H. D. Hartough and A. I. Kosak, THIS JOURNAL, **69**, 3093 (1947); see also U. S. Patent 2,458,520 (1949).

(18) W. Steinkopf and D. Jaffe, *Ann.*, **413**, 333 (1916).

(19) H. D. Hartough and L. Conley, THIS JOURNAL, **69**, 3096 (1947).

(20) W. Steinkopf and W. Nitsche, *Arch. Pharm. Ber.*, **278**, 360 (1940).

(21) E. Schleicher, *Ber.*, **18**, 3020 (1885).

(22) W. Steinkopf, H. Frommel and J. Leo, *Ann.*, **546**, 201 (1941).

(23) W. Steinkopf, *ibid.*, **428**, 144 (1921).

(24) N. Zelinsky, *Ber.*, **20**, 2019 (1887).

(25) F. Silberfarb, *J. Russ. Phys.-Chem. Soc.*, **45**, 1938 (1913).

(26) P. Chabrier, B. Tchoubar and S. LeTellier-Dupre, *Bull. soc. chim.*, 332 (1946).

(27) M. A. Youtz and P. P. Perkins, THIS JOURNAL, **51**, 3511 (1929).

Methyl 8,10-Hendecadienoate

BY L. HASKELBERG

Successive treatment of methyl 10-hendecenoate, $CH_2{=}CH(CH_2)_8COOCH_3$, with N-bromosuccinimide in presence of benzoyl peroxide[1] and with quinoline, gives in 50% yield methyl hendecadienoate.[2] Its ultraviolet spectrum (Fig. 1) shows an intense maximum at 2260 Å., as expected[3] for the 8,10-diene $CH_2{=}CHCH{=}CH(CH_2)_6COOCH_3$, which contains a *monosubstituted* butadiene system.

The infrared spectrum[4] is also in accordance with the formula of an 8,10-hendecadienoate; it shows peaks at 911 and 950 cm.$^{-1}$.[5] The bromo-ester formed from methyl hendecenoate and N-bromosuccinimide is accordingly methyl 9-bromo-10-hendecenoate, very probably in equilibrium with the tautomeric methyl 11-bromo-9-hendecenoate.[6]

In the ultraviolet spectrum of the doubly unsat-

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(1) Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

(2) The analogous reaction with the methyl esters of elaidinic and brassidinic acid has recently been described by Schmid and Lehmann (*ibid.*, **33**, 1494 (1950)). Their products showed an intense absorption band at 2300 Å. Compare also: Gensler, Behrmann and Thomas, THS JOURNAL, **73**, 1071 (1951).

(3) Woodward, *ibid.*, **64**, 72 (1942).

(4) Shreve, *et al.*, *Anal. Chem.*, **22**, 1498 (1950).

(5) Barnard and co-workers, *J. Chem. Soc.*, 915 (1950).

(6) Thanks are due to the Referee for drawing attention to this point.

urated methyl ester, there appear some—much less intense—bands between 2500 and 2800 Å. Whilst no definite statement can be made as to their origin, it is not impossible that they are due to traces of methyl hendeca*trien*oate. Such a substance could be formed by further allylic bromination of methyl 11-bromo-9-hendecenoate in the 8-position and subsequent elimination of two molecules of hydrogen bromide.

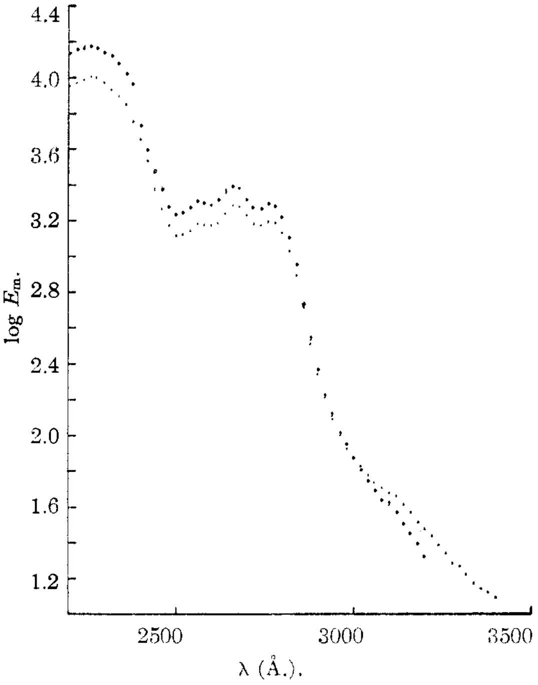

Fig. 1.—Methyl 8,10-hendecadienoate in isoöctane (+ + + + + +) and anhydrous ethyl alcohol(. . . . .).

The spectra have been measured by Y. Hirshberg and S. Pinchas, respectively.

Experimental

Methyl 9-Bromo-10-hendecenoate.—When a trace of benzoyl peroxide was added to the mixture of 19.8 g. (0.1 mole) of methyl 10-hendecenoate,[7] 19.5 g. (0.1 mole) of N-bromosuccinimide and 100 cc. of carbon tetrachloride, a strongly exothermic reaction took place after an induction period of a few minutes. The reaction was completed by refluxing the mixture for two hours. The succinimide formed was removed by filtration (8 g.) and the solution distilled *in vacuo*. A small quantity of starting material (b.p. 86–90° (0.05 mm.)) was recovered. The bromo-ester distilled at 110° at 0.05 mm. with slight decomposition; it formed a viscous liquid which did not crystallize even at low temperature (−20°). *Anal.* Calcd. for $C_{12}H_{21}O_2Br$: Br, 28.8. Found: Br, 28.1.

Methyl 8,10-Hendecadienoate.—The bromo-ester was heated for two hours with an equal weight of quinoline at 120–130°. The reaction product was cooled, treated with a slight excess of dilute hydrochloric acid and extracted with ether. The ethereal layer was washed with water, sodium bicarbonate solution and water, dried and distilled; b.p. 80° at 0.5 mm.; yield 8.9 g. (50%); d^{25}_4 0.898; n^{25}_D 1.4542; mol. refr., calcd. 58.34 (without exaltation); found, 59.17. *Anal.* Calcd. for $C_{12}H_{20}O_2$: C, 73.5; H, 10.2. Found: C, 73.4; H, 10.2.

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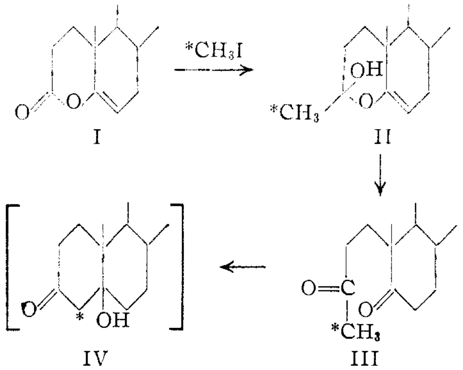
(7) Komppa, *Ber.*, **34**, 895 (1901).

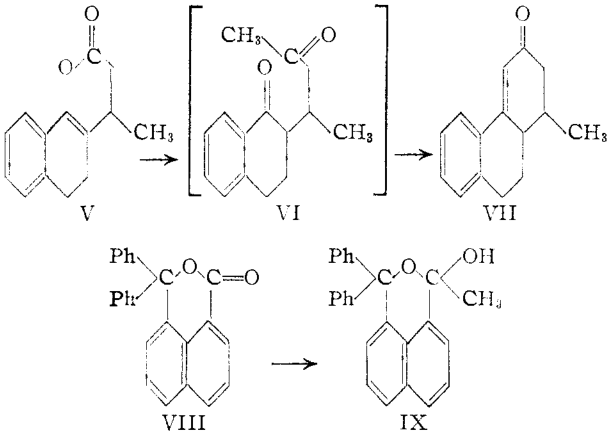
Steroids. IX. An Improved Method of Preparation of Cholestenone-4-C^{14} [1]

BY R. D. H. HEARD AND P. ZIEGLER[2]

Two methods of preparation of cholestenone-3-C^{14} and -4-C^{14} have been described by Turner.[3] As neither procedure proved fully satisfactory in a preparative sense, particularly as regards over-all yield from $C^{14}O_2$, a convenient route to the readily cyclizable methyl diketone III was sought.



A promising approach to III arose from the observation of Belleau,[4] in studies on total synthesis in the doisynolic acid series, that the enol-lactone V with methylmagnesium iodide gave predominantly the α,β-unsaturated ketone VII, after acid hydrolysis. The reaction was assumed to proceed through the intermediate 1,5-diketone VI. On the other hand, with certain other unsaturated lactones, such as coumarin[5] and VIII[6], the end products are the corresponding hemiacetals (*viz.* IX).



The enol-lactone I, with only 1.0 to 1.2 molar proportions of methylmagnesium iodide, was found to give a high yield (70–80%) of product finally identified as the hemiacetal II which separated readily in excellently defined crystalline state but which exhibited a broad melting point range (165–175°) which could not be sharpened with the usual puri-

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(2) Contributed in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Turner, THIS JOURNAL, **72**, 579 (1950).

(4) Belleau, Thesis, McGill University, 1950.

(5) Willstätter, *et al.*, *Ber.*, **57**, 1938, 1945 (1924).

(6) Geissman and Morris, THIS JOURNAL, **63**, 1111 (1941).