turned dull gray gradually. After 36 hours of stirring, a black precipitate was formed. Trimethylchlorosilane (2.0 g., 0.018 mole) dissolved in 20 ml. of ether was added rapidly to the reaction mixture. Fifteen minutes later it was hydrolyzed carefully (in a nitrogen atmosphere). Removal of ether from the sodium sulfate-dried ethereal solution left 4.9 g. (97%) of pale yellow crystals melting at 95–101°. Two recrystallizations from 95% ethanol yielded 3.4 g. (67%) of colorless needles melting at 107–108°.

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A New Synthesis of 2-Chloro-7-nitrofluorene[1]

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The synthesis of 2-chloro-7-nitrofluorene has been reported by Courtot[2,3] and more recently by Schulman.[4] These investigators chlorinated fluorene in chloroform or carbon tetrachloride at 0–5° without a catalyst for 18 to 30 hours. This was followed by nitration of the crude 2-chlorofluorene in glacial acetic acid.

This method of chlorination has yielded, in our hands, mixtures which contained large amounts of unreacted fluorene. The compounds melted from 87–92° but showed a chlorine content of only 4.09%. The theory requires a chlorine content of 17.45% for 2-chlorofluorene melting at 96°. Nitration of the chlorinated products resulted in mixtures of 2-nitrofluorene and 2-chloro-7-nitrofluorene melting from 140–160° which were very difficult to purify.

It has now been found that 2-chloro-7-nitrofluorene can also be prepared by the chlorination, for 35 minutes, of 2-nitrofluorene in monochlorobenzene using iodine as a catalyst. Pure 2-chloro-7-nitrofluorene was obtained in 56% yield. 2-Amino-7-chlorofluorene was likewise available from the 2-chloro-7-nitrofluorene by reduction with zinc dust and calcium chloride in ethanol.[5]

Experimental

Preparation of 2-Chloro-7-nitrofluorene.—A sample of 24.5 g. of 2-nitrofluorene (0.12 mole), m.p. 158°, was suspended in 300 cc. of monochlorobenzene in a 2 l. three-necked flask fitted with a mechanical stirrer, a reflux condenser and a gas inlet tube. The flask was submerged in a boiling water-bath and the suspension stirred vigorously. When all of the 2-nitrofluorene had dissolved 0.5 g. of iodine was added to the solution. Fourteen grams of dry chlorine (0.2 mole) was passed into the reaction mixture in the course of 20 minutes. Hydrogen chloride was observed to evolve from the solution. After the addition of chlorine had been completed carbon dioxide was passed through the chlorine generator and the reaction flask for 15 minutes. The reaction vessel was removed from the boiling water-bath and allowed to stand at room temperature for 16 hours. The crystalline mass which had precipitated from the reaction mixture was collected on a Buchner funnel and washed with 10 cc. of cold monochlorobenzene. The yellow product melted from 237–239°. The mixed melting point of the compound with an authentic sample of 2-chloro-7-nitrofluorene, m.p. 235–238° (nitrogen, found 5.71; nitrogen, calcd. 5.70) was 237–238°. Courtot and Vignati[3] reported a melting point of 237° for 2-chloro-7-nitrofluorene. After the material had been dried in air for three days it weighed 16.5 g. which represents a yield of 56%.

Preparation of 2-Amino-7-chlorofluorene.—The reduction of 16.5 g. of 2-chloro-7-nitrofluorene (0.068 mole), m.p. 237–239°, was carried out as described in reference 5 except that 0.5 g. of charcoal was included in the reaction mixture and the reaction time was 8 hours. The yield was 8.8 g. of 2-amino-7-chlorofluorene melting at 131.5–133.5°.

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[1] Our thanks are due to the Damon Runyon Memorial Fund for a grant that defrayed the cost of this work.

[2] Courtot, *Ann. chim.*, [10] **14**, 104 (1930).

[3] Courtot and Vignati, *Compt. rend.*, **184**, 1179 (1927).

[4] Schulman, *J. Org. Chem.*, **14**, 382 (1949).

[5] "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 448.

Acylation Studies in the Thiophene and Furan Series.[1a] VIII. Mixed Melting Points of Some Homologous Acetylmethylthiophene Derivatives

BY HOWARD D. HARTOUGH[1b]

Steinkopf[2] has summarized the literature on the "isomorphic phenomena" exhibited by thiophene compounds. In this respect, Steinkopf creates the impression that mixed melting points cannot be relied upon in the thiophene series to distinguish between isomeric thiophene derivatives and cites many examples among the derivatives of halothiophenes to substantiate his postulation. The principal examples stressed[2] are the mixed melting points of the derivatives of the isomeric trichlorothiophenes studied by Steinkopf and Kohler.[3] They prepared some nineteen derivatives of 2,3,4-trichlorothiophene and of a compound *assumed* to be 2,3,5-trichlorothiophene and found that, in each case, the melting points of corresponding derivatives of these two materials were identical and the mixed melting point was the same. The investigators were able to distinguish between the isomeric derivatives by luminescence under light from a mercury-quartz lamp. This method appears spurious since the work of later investigators[4] showed that Steinkopf and Kohler were actually preparing derivatives of two individual samples of 2,3,4-trichlorothiophene.

Since Steinkopf's postulation[2] was felt to be misleading, the mixed melting points of the oximes, *p*-nitrophenylhydrazones, and semicarbazones of nine homologous acetylmethylthiophenes, 2-acetylthiophene and 2-acetyl-5-ethylthiophene have been determined. Among the oximes and *p*-nitrophenylhydrazones all nine acetylmethylthiophenes showed adequate mixed melting point depression. In one instance, the melting point of a mixture of the oximes of 2-acetyl-5-methylthiophene and 2-acetyl-5-ethylthiophene did not show depression. However, the semicarbazone and *p*-nitrophenylhydrazone derivatives showed adequate depression. These data are listed in Table I. The mixed melting point data on the semicarbazones are not complete since most of these materials decompose near their melting points. Thus mixture melting points normally are not so significant as in the other series

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[1] (a) Paper VII of this series, H. D. Hartough and A. I. Kosak, THIS JOURNAL, **70**, 867 (1948); (b) Hercules Experiment Station, Wilmington, Delaware.

[2] W. Steinkopf, "Die Chemie des Thiophens," Verlag von Theodor Steinkopf, Dresden and Leipzig, 1941, pp. 15–19.

[3] W. Steinkopf and W. Kohler, *Ann.*, **532**, 250 (1937).

[4] H. L. Coonradt, H. D. Hartough and G. C. Johnson, THIS JOURNAL, **70**, 2564 (1948), found that 2,3,4-trichlorothiophene arose from direct chlorination of thiophene. Steinkopf and Kohler[3] assumed this product to be 2,3,5-trichlorothiophene.

Table I

Melting Points and Mixed Melting Points of Ketone Derivatives of Acetylthiophene Homologs

Thiophene compound[a]		Ketone derivative[b]	M.p., °C.	Lit. m.p., °C.	Lit. Ref.	Mixed melting point data									
						I	II	III	IV	V	VI	VII	VIII	IX	X
I	2-Acetyl-[n]	O	112-113	112-113	17										
		N	182.5-183.5	181-182	18										
		S	191-192	191-192	19										
II	2-Acetyl-3-methyl-[n]	O	84.5-86	84.5-86	17	74-84									
		N	195-196	193.5-194	20	175-185									
		S	207-208	207-207.5	19										
III	2-Acetyl-4-methyl-[n]	O	132.5-134	132.5-134	17	95-117	81-108								
		N	181-182	[c]	[c]	154-162	165-169								
		S	219-220	219-220	19		202-207								
IV	2-Acetyl-5-methyl-[n]	O	124-125.5	124-125.5	17	86-109	77-104	99-119							
		N	209.5-210.5	206.5-207	20	167-173	175-181	167-174							
		S	215-217 (dec.)	215-217(dec.)	19		200-205	204-210							
V	2-Acetyl-5-ethyl-[o]	O	108.5-110	110	21	77-82	69-81	87-107	108-112						
		N	196.5-197.5	194-194.5	22	155-165	170-173	159-164	192-200						
		S	210-211.5	215	23				207-210						
VI	2-Acetyl-3,4-dimethyl-[p]	O	122-123	[d]	[d]	87-105	79-106	106-118	94-108	83-114					
		N	202-203	[c]	[e]	163-167	180-184	168-173	193-197	177-182					
		S	234-235 (dec.)	[f]	[f]										
VII	2-Acetyl-3,5-dimethyl-[q]	O	63.5-64.5	*ca.* 70	24	50-55	50-67	58-111	52-96	48-80	54-110				
		N	207-207.5	[g]	[g]	162-164	180-184	175-178	181-199	176-180	186-192				
		S	217-219.5	[h]	[h]						214-220.5				
VIII	2-Acetyl-4,5-dimethyl-[r]	O	143-144.5	[i]	[i]	93-116	83-119	109-118	106-119	99.5-129	105-112	61.5-114			
		N	207-208.5	204-205	20	158-170	173-180	170-174	183-191	178-182	187-190	182-187			
		S	238-240 (dec.)	245-245.5	20						227-231	223-228 (dec.)			
IX	2-Acetyl-3,4,5-trimethyl-[s]	O	126.5-127.5	[j]	[j]	87-111	81-107	99-108	95-100	85-115	96-107	60-111	111-116		
		N	197.5-198.5	[k]	[k]	158-175	173-178	169-171	178-188	171-175	158-164	182-185	192-195		
		S	239.5-241.5 (dec.)	[l]	[l]										
X	3-Acetyl-2,5-dimethyl-[t]	O	83.5-85	83	25	67-83	62-79	75-114	69-99	61.5-71.5	72-112	50-79	76-117	76-111	
		N	173-174	175-175.5	20	143-160	159-165	153-163	158-165	155-163	159-163	167-179	157.5-167	158-161	
		S	216-218	220	26						214-223	211-215	214-222		
XI	3-Acetyl-2,4,5-trimethyl-[u]	O	111.5-112.5	[m]	[m]	80-96	76-89	92-106	89-113	79-85	91-108	55-91	95-131	92-110	71-81
		N	156.5-157	157	27	134-139	147-169	140-152	150-177	144-150	147-164	150-157	145-148	147-152	137-162
		S	159-160	162.5-163	27										

[a] Physical properties are listed in the footnotes. [b] O = oxime; N = *p*-nitrophenylhydrazone; S = semicarbazone. [c] Not listed. *Anal.* Calcd. for $C_{13}H_{13}N_3O_2S$: N, 15.27. Found: N, 15.08. [d] Calcd. for $C_8H_{11}NOS$: N, 8.28. Found: N, 8.31. [e] Calcd. for $C_{14}H_{15}N_3O_2S$: N, 14.53. Found: N, 14.53. [f] Calcd. for $C_9H_{13}N_3OS$: N, 20.0. Found: N, 20.2. [g] Calcd. for $C_{14}H_{15}N_3O_2S$: N, 14.53. Found: N, 14.62. [h] Calcd. for $C_9H_{13}N_3OS$: N, 20.0. Found: N, 20.1. [i] Calcd. for $C_8H_{11}NOS$: N, 8.28. Found: N, 8.40. [j] Calcd. for $C_9H_{13}NOS$: N, 7.65. Found: N, 7.57. [k] Calcd. for $C_{15}H_{17}N_3O_2S$: N, 13.86. Found: N, 13.97. [l] Calcd. for $C_{10}H_{15}N_3OS$: N, 18.67. Found: N, 18.82. [m] Calcd. for $C_9H_{13}NOS$: N, 7.65. Found: N, 7.67. [n] Physical constants reported in ref. 17. [o] B.p. 67° (0.20 mm.), $n^{20}D$ 1.5516. Ref. 24 lists b.p. 121–123° (13 mm.). [p] B.p. 61.5° (0.15 mm.), $n^{20}D$ 1.5602. *Anal.* Calcd. for $C_8H_{10}OS$: S, 20.8. Found: S, 20.9. [q] B.p. 61° (0.15 mm.), $n^{20}D$ 1.5568. Ref. 26 lists uncor. b.p. 226–228°. [r] B.p. 76° (0.20 mm.), $n^{20}D$ 1.5618. Ref. 22 lists b.p. 131–133° (17 mm.). [s] B.p. 76° (0.15 mm.), $n^{20}D$ 1.5632. *Anal.* Calcd. for $C_9H_{12}OS$: S, 19.05. Found: S, 19.03. [t] B.p. 62° (0.25 mm.), $n^{20}D$ 1.5452. Ref. 15 lists b.p. 109–110° (14 mm.). [u] B.p. 80° (0.30 mm.), $n^{20}D$ 1.5454. Ref. 27 lists b.p. 248–249°, $n^{20}D$ 1.5454.

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}_{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}_{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}_{D} 1.5208) and 2,3,5-trimethylthiophene[11] (b.p. 164.5° (760 mm.), n^{20}_{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}_{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.

Acknowledgment.—The interest and encouragement of F. P. Richter and R. C. Hansford during the course of this work were greatly appreciated.

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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}_{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}_{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}_{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).

SOCONY-VACUUM LABORATORIES
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PAULSBORO, NEW JERSEY
RECEIVED APRIL 20, 1951

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.