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°.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

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

BY HELMUT R. GUTMANN AND FRANCIS E. RAY

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°.

CANCER RESEARCH LABORATORY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

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[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.