noticeable melting point range suggests that there is still some impurity present or that the product is not a single isomer. *Anal.* Found: F, 55.7, 56.0; Cl, 20.0. Calcd. for $C_6F_{10}Cl_2$: F, 57.0; Cl, 21.3. The literature values reported for this compound are: b.p. 107.5–107.7°; m.p. 12–14°; n^{20}D 1.3413.[3]

The compound or compounds containing approximately twelve carbon atoms per molecule have thus far been obtained only in small amounts and have not been identified. The fraction does decolorize neutral permanganate and can be chlorinated photochemically, indicating olefinic character.

Some preliminary kinetic data indicate that, in general, the acid takes part in reactions at room temperature in the presence of Lewis-type bases both in aqueous and nonaqueous media. The decomposition in water may be considered as an example of this general type of reaction which the acid will undergo.

Acknowledgment.—We would like to thank Dr. H. M. Scholberg and Mr. E. A. Kauck of the Central Research Department of Minnesota Mining & Manufacturing Company for supplying the fluorocarbon acid.

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[3] V. V. Lindgren and E. T. McBee, U. S. Patent 2,480,081, August 23, 1949; *C. A.*, **44**, 2020*g* (1950).

FLUORINE LABORATORIES
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STATE COLLEGE, PENNA.
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Isolation of Tomatidine from the Roots of the Rutgers Tomato Plant

BY NORMAN G. BRINK AND KARL FOLKERS

Tomatidine, the nitrogenous aglycone of the antifungal agent tomatine, has been isolated directly from the roots of the Rutgers tomato plant (*Lycopersicum esculentum* (L.) Mill., horticultural variety "Rutgers").

The isolation of crystalline tomatine from the dry leaves of the Red Currant tomato, *L. pimpinellifolium*, was described by Fontaine, Irving, Ma, Poole and Doolittle.[1] The isolation of tomatine from the leaves of six species of wild tomato plants was reported by Kuhn, Löw and Gauhe[2] who cited yields of the crystalline product from the dried plant material which varied from 0.5 to 5%, the highest yield being obtained from *L. esculentum var. pruniforme.* They stated that tomatine could not be isolated from the commonly cultivated tomato plants; and that in those plants which did contain it, the amount of tomatine present decreased significantly in September and October.

Acid hydrolysis of crystalline tomatine gave xylose, galactose, two moles of glucose,[3] and a nitrogenous aglycone, tomatidine.[1,2] Recent work[4,5] has shown that tomatidine is a steroid secondary amine, for which the molecular formula $C_{27}H_{45}NO_2$ was proposed. Kuhn, Löw and Gauhe,[2] however, indicated formulas for tomatine and tomatidine containing two less hydrogen atoms.

We wish to report the isolation of tomatidine hydrochloride directly from the roots of the Rutgers tomato plant, a horticultural variety of *L. esculentum* (L.) Mill. developed by L. G. Schermerhorn at the New Jersey Agricultural Experiment Station, and distributed generally about 1934. The plants were gathered during the fall of the year, after the fruit had been picked, and only the washed and dried roots were used in the extraction. The extract was divided into a number of fractions, one of which gave a crystalline product in low yield (*ca.* 0.01%), which after purification was identified as tomatidine hydrochloride. The low yield may be explained partly by the isolation procedure, which included no deliberate acid hydrolytic step; and partly by the fact that the plants were gathered at the time when their tomatine content might be expected[2] to be low.

It is of interest that our analytical results on purified tomatidine hydrochloride are in agreement with the composition $C_{27}H_{45}NO_2$[4,5] rather than $C_{27}H_{43}NO_2$.[2]

Experimental[6]

In a typical extraction procedure, 1.36 kg. of dried root material was moistened with water and then extracted in a Soxhlet apparatus for 24 hours with 15 l. of methanol. The extraction was then continued for an additional three days, using fresh methanol. The combined methanolic solutions were concentrated *in vacuo* to a volume of 300 ml., and to this aqueous solution another 300 ml. of water was added, and the *p*H was adjusted to 8 with sodium hydroxide. After standing with occasional stirring for several days, the mixture was extracted with eight 1-l. portions of ether. The combined ethereal extracts were evaporated and the residue triturated with 2.5 l. of ether. After removal of solids, the ethereal solution was washed with eight 250-ml. portions of very dilute sodium hydroxide solution (*p*H 10); and then it was extracted with eight 250-ml. portions of 0.06 *N* hydrochloric acid. On standing in the cold, the acidic solution deposited crystalline material which was collected by filtration, washed with water, and dried. It weighed 183 mg.

The product, after two recrystallizations from ethanol melted at 275–280° (dec.); $[\alpha]^{25}$D $-8.8 \pm 2.1°$ (*c*, 0.455 in methanol).

Anal. Calcd. for $C_{27}H_{45}NO_2 \cdot HCl$: C, 71.73; H, 10.26; N, 3.10; Cl, 7.84. Calcd. for $C_{27}H_{43}NO_2 \cdot HCl$: C, 72.05; H, 9.86; N, 3.11; Cl, 7.88. Found: C, 71.76, 71.41; H, 10.26, 10.23; N, 3.50; Cl, 7.83.

Treatment of the recrystallized hydrochloride in methanolic solution with silver oxide, and recrystallization of the product from aqueous ethanol gave the free base, m.p. 204–205°. When this material was admixed with a sample of authentic tomatidine[7] for which we observed the m.p. 205–207°, no depression of the melting point occurred.

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[1] T. D. Fontaine, G. W. Irving, Jr., R. Ma, J. B. Poole and S. P. Doolittle, *Arch. Biochem.*, **18**, 467 (1948).

[2] R. Kuhn and I. Löw, *Ber.*, **81**, 552 (1948); R. Kuhn, I. Löw and A. Gauhe, *ibid.*, **83**, 448 (1950).

[3] R. M. Ma and T. D. Fontaine, *Arch. Biochem.*, **27**, 461 (1950).

[4] T. D. Fontaine, J. S. Ard and R. M. Ma, THIS JOURNAL, **73**, 878 (1951).

[5] Y. Sato, A. Katz and E. Mosettig, *ibid.*, **73**, 880 (1951).

[6] The authors wish to thank Mr. John Madas for technical assistance. They are indebted to Mr. Richard N. Boos and his associates for the microanalyses.

[7] Kindly furnished by Dr. T. D. Fontaine.

RESEARCH LABORATORIES
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Some Derivatives of 2- and 3-Methylthiophene

BY TOD W. CAMPBELL AND WARREN W. KAEDING

In view of recent reports by various workers on the halogenation of methylthiophenes with N-bromosuccinimide[1a,b,2] we feel that it would be worthwhile to record some of our experimental observations on this reaction, carried out prior to the ap-

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[1] (a) E. Campaigne and W. M. Le Suer, THIS JOURNAL, **70**, 415, 1555 (1948); (b) K. Dittmer, R. P. Martin, W. Herz and S. J. Cristol, *ibid.*, **71**, 1201 (1949).

[2] J. Le Cocq and Buu-Hoi, *Compt. rend.*, **224**, 658 (1947).

pearance of the above publications. Our results indicate that the reaction of one mole of N-bromosuccinimide, in the presence of benzoyl peroxide, with a mole of methylthiophene usually gives a mixture of roughly equal amounts of side-chain and nuclear bromination.[3] However, in several experiments, only nuclear brominated compounds could be isolated.[4] Since the original halogenation mixture was relatively clear and contained substantial amounts of the thenyl bromides, this was used without distillation to prepare a number of derivatives of 2- and 3-methylthiophenes. These are described in the experimental part.

Experimental

Reactions of 2-Methylthiophene with N-Bromosuccinimide.—One hundred and fifty grams of 2-methylthiophene[5] dissolved in 500 cc. of carbon tetrachloride was treated with 272 g. of N-bromosuccinimide and 1.0 g. of benzoyl peroxide. A vigorous exothermic reaction accompanied by the evolution of white fumes began. After the initial reaction subsided, the mixture was refluxed for 90 min. during which time the solid N-bromosuccinimide disappeared from the bottom of the flask.

After cooling to 10° the lachrymatory reaction mixture was filtered and distilled. The fraction boiling at 48–55° (3 mm.), was redistilled yielding 2-bromo-5-methylthiophene, b.p. 97° (67 mm.); yield 142 g. (53%). It formed a Grignard reagent which on carbonation gave 5-methylthiophene-2-carboxylic acid, m.p. 136°,[6] but would not react with piperidine.

The distillation residue consisted of 55 g. of a fuming, lachrymatory, viscous, black liquid which could not be distilled. It slowly evolved hydrogen bromide and became rock hard.

The Preparation of N-(2-Thenyl)-piperidine.—Fifty grams of 2-methylthiophene was slowly added, with constant stirring, to a mixture of 500 cc. of carbon tetrachloride, 1.2 g. of benzoyl peroxide and 105 g. of N-bromosuccinimide. The rate of addition was regulated so that the exothermic reaction maintained the temperature at 72–73°. After 60 minutes the heavy N-bromosuccinimide disappeared from the bottom of the flask. The reaction mixture was extremely lachrymatory. The solution was cooled and separated from the succinimide and added to three equivalents of piperidine in 100 cc. of carbon tetrachloride. Precipitation of piperidine hydrobromide occurred immediately, accompanied by the evolution of heat.

The reaction mixture was extracted with dilute mineral acid and the free amine was obtained by ether extraction after the addition of base. Under this treatment most of the excess piperidine remained in the water phase.

Distillation of the dried ether phase gave 54 g. (58%) of N-(2-thenyl)-piperidine, b.p. 139.5° (29 mm.); n^{25}D 1.5373. *Anal.* Calcd. for $C_{10}H_{15}NS$: C, 66.29; H, 8.34. Found: C, 66.55; H, 8.51.

Picrate, m.p. 147–148. *Anal.* Calcd. for $C_{16}H_{18}O_7N_4S$: C, 46.82; H, 4.42. Found: C, 47.31; H, 4.85.

Methiodide, m.p. 59°. *Anal.* Calcd. for $C_{11}H_{18}SNI$: C, 40.88; H, 5.61. Found: C, 41.11; H, 5.85.

The identical tertiary amine was obtained by treating 2-chloromethylthiophene (obtained from Arapahoe Chemical Co., Boulder, Colorado), with piperidine in carbon tetrachloride, as shown by mixed melting points of solid derivatives.

Independent Synthesis of N-(2-Thenyl)-piperidine.—One gram of thiophene-2-carboxylic acid was converted to the acid chloride with thionyl chloride. After removal of excess thionyl chloride, a benzene solution of piperidine (excess) was added, and the mixture allowed to stand for an hour. The solution was then washed with dilute acid, to remove piperidine, and dried. The solution of amide was added directly to a solution of 0.3 g. (excess) of lithium aluminum hydride (obtained from Metal Hydrides, Inc., Beverly, Mass.) in anhydrous ether. The amine was isolated as the picrate, m.p. 148–149°; yield 2.3 g. (77% based on thiophenecarboxylic acid). The melting point was not depressed by the admixture of the tertiary amine picrate obtained from 2-halomethylthiophene.

Reaction of 3-Methylthiophene with N-Bromosuccinimide. The halogenation experiments described above were repeated, using 3-methylthiophene.

Treatment of the halogenation mixture with piperidine before distillation, as for the 2-methyl derivative, gave a 49% yield of N-(3-thenyl)piperidine; b.p. 141° (29 mm.); n^{24}D 1.5373 (*cf.* 2-thenyl derivative).

Anal. Calcd. for $C_{10}H_{15}NS$: C, 66.29; H, 8.34. Found: C, 66.17; H, 8.42.

Picrate, m.p. 114–115°. *Anal.* Calcd. for $C_{16}H_{13}O_7N_4S$: C, 46.82; H, 4.42. Found: C, 46.80; H, 4.60.

The methiodide melted at 122–124°. *Anal.* Calcd. for $C_{11}H_{18}SNI$: C, 40.88; H, 5.61. Found: C, 41.41; H, 5.98.

Preparation of 3-Thenaldehyde.[1a]—Treatment of the halogenation mixture from 50 g. of 3-methylthiophene, as above, with 65 g. of hexamethylenetetramine for two hours with vigorous stirring gave a bulky precipitate, which was hydrolyzed by refluxing for three hours with 250 ml. of 50% ethanol. 3-Thiophenealdehyde was isolated by distillation; b.p. 78° (14 mm.), n^{23}D 1.5810; yield 26.5 g. (47%). The odor is similar to that of benzaldehyde. It formed a 2,4-dinitrophenylhydrazone, m.p. 235°.

Isolation of 3-Thenyl Bromide.[1a]—Direct distillation of the reaction mixture at 1 mm. gave a product which consisted of 3-thenyl bromide, plus substantial amounts of 2-bromo-3-methylthiophene.[1b] The mixture was redistilled, and the fraction, b.p. 66° (16 mm.), refractive index n^{22}D 1.5712, was taken to be 2-bromo-3-methylthiophene. A second fraction was isolated at 92° (16 mm.), n^{20}D 1.6048, which was intensely lachrymatory. It reacted instantly with piperidine to give N-thenylpiperidine, and thus was presumably 3-thenyl bromide. When pure it was quite stable; impure samples, darkened gradually, finally setting to a solid tarry mass after several days.

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(3) The experimental conditions were not strictly comparable to the prior investigators (ref. 1a) who obtained high yields of side-chain bromination by the use of smaller amounts of benzoyl peroxide catalyst.

(4) Similar results have been reported by other investigators (ref. 1b, footnote 8). Campaigne and Le Suer (ref. 1a) obtained only nuclear substitution in the absence of peroxide catalyst.

(5) Both 2- and 3-methylthiophene were obtained through the generosity of the Socony-Vacuum Oil Co.

(6) Confirming this melting point Rinkes, *Rec. trav. chim.*, **51** [4], 1141 (1932), and Hartough and Conley, THIS JOURNAL, **69**, 3096 (1947).

The Reaction of Aromatic Triazenes with Nitric Oxide

BY TOD W. CAMPBELL[1]

If a solution of an aromatic triazene, ArNH—N=NAr, in a hydrocarbon solvent is agitated in an atmosphere of pure nitric oxide, the nitric oxide is absorbed readily at a rate which increases with time, indicating a free radical reaction and possibly autocatalysis. If the absorption of nitric oxide in moles per mole of triazene is plotted against time, a curve similar to Fig. 1 is obtained. These curves are not reproducible, since repeating the experiment under identical conditions gives in each case a somewhat different absorption curve. The main difference is the position of the maximum with reference to the time axis. By examining the curve in Fig. 1, one can see that the reaction of a triazene with nitric oxide involves the absorption of more than two moles of nitric oxide, and probably three per mole of triazene, with the subsequent evolution of two moles of unidentified gas, probably nitrogen. The nature of the primary non-gaseous products was deduced from the following experiments: (1)

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(1) Western Regional Research Laboratory, Albany 6, California.