Preparation of Oxazolines.—Good yields of oxazolines from ethylene azidohydrin and aromatic aldehydes (all commercially available) resulted from the following procedure: To a mixture of 0.03 mole of the aromatic aldehyde in 50 ml. of benzene and 5 ml. of concentrated sulfuric acid, 2.6 g. (0.03 mole) of ethylene azidohydrin was added dropwise at a rate which kept the benzene gently boiling. After standing an additional five minutes with stirring, 50 ml. of ice-water was added. The water layer was separated and neutralized with sodium carbonate. The solid oxazolines were isolated by filtration, whereas the liquid phenyloxazoline was separated by ether extraction. The crude solid oxazoline was recrystallized from aqueous ethanol. Yields, physical constants and analytical data are in Table I.

Picrate derivatives (Table I) were prepared from ether solutions and recrystallized from ethanol and ethyl acetate.[21]

(21) Hydrolysis of oxazolines has long been known to lead to the formation of either β-hydroxyamides or β-aminoesters (R. H. Wiley and L. L. Bennet, Jr., *Chem. Revs.*, **44**, 447 (1949)). The latter generally are produced by the action of dilute acid upon an oxazoline. The ease with which this reaction may proceed was illustrated by the formation of the picrate of β-aminoethyl benzoate upon recrystallization of phenyloxazoline picrate from water. Apparently a similar transformation occurred in attempts to prepare and purify the picrate derivative of *p*-chlorophenyloxazoline.

The hydrochloride, m.p. 81°, of 2-phenyl-Δ^2-oxazoline[22] was prepared by bubbling anhydrous hydrogen chloride into an anhydrous ether solution of the amine.

Preparation of 2-Phenyl-Δ_2-dihydro-1,3-oxazine.—To a solution of 3.0 g. (0.03 mole) of benzaldehyde in 50 ml. of benzene and 5 ml. of concentrated sulfuric acid, 3.0 g. (0.03 mole) of 3-azido-1-propanol was added dropwise with stirring at a rate which kept the temperature at 80°. After standing five minutes with stirring, 50 ml. of ice-water was added. The water layer was separated, neutralized with sodium carbonate and extracted with ether. Evaporation of the ether left an oily residue. Distillation of this residue gave 3.5 g. (72%) of 2-phenyl-Δ_2-dihydro-1,3-oxazine, b.p. 115° (1.5 mm.).[23] The picrate, m.p. 151.5°,[24] was prepared in an ether solution.

Preparation of 5-Methyl-2-phenyl-Δ_2-oxazoline.—The above procedure was followed with the substitution of 1-azido-2-propanol for 1-azido-3-propanol. The product, 5-methyl-2-phenyl-Δ_2-oxazoline, b.p. 95° (0.5 mm.),[25] was obtained in 80% yield. Its picrate derivative, m.p. 166–167°,[25] was prepared from an ether solution.

(22) W. Wislicenus and H. Korber, *Ber.*, **35**, 164 (1902).
(23) T. Curtius and K. Thun, *J. prakt. Chem.*, **44**, 182 (1891).
(24) S. Gabriel, *Ber.*, **24**, 3214 (1891).
(25) S. Gabriel and T. Heyman, *ibid.*, **23**, 2479, 2499 (1890).

NEW ORLEANS 18, LA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF FORDHAM UNIVERSITY]

The Preparation and Structural Proof of Thiophene Amidone and Isoamidone

BY EDWARD A. SCHILDKNECHT AND ELLIS V. BROWN[1]

RECEIVED AUGUST 20, 1954

Heterocyclic analogs of amidone and isoamidone have been prepared in which the two phenyl groups have been replaced by two 2-thienyl groups. The structure of thiophene isoamidone has been proven, thus indicating the structure of the other isomer.

In view of the importance of amidone and isoamidone,[2] and the ever-present desire to obtain an analgesic of greater potency with the least number of side-effects, it seemed advisable to attempt the preparation of the thiophene analog of these two compounds. It was possible, on the basis of other investigations,[3] that these thiophene analogs might have greater analgesic activity, less toxicity or less tendency to cause addiction.

For this synthesis di-(2-thienyl)-acetonitrile was considered to be a useful intermediate; consequently, its preparation in good yields was investigated. Both stannic chloride and phosphorus pentoxide have been used as reagents in the condensation of mandelonitrile with benzene and its homologs.[4]

For the preparation of 2-benzylthiophene, zinc chloride has been used to condense benzyl alcohol with thiophene.[5] Our attempts to condense mandelonitrile with thiophene in the presence of stannic chloride, phosphorus pentoxide and zinc chloride have produced black tars.

(1) To whom inquiries concerning this paper should be sent. Present address: Chemistry Dept., Seton Hall University, South Orange, N. J.
(2) C. C. Scott and K. K. Chen, *J. Pharmacol. and Exptl. Therap.*, **87**, 63 (1946); N. B. Eddy, C. F. Touchberry and J. E. Lieberman, *ibid.*, **98**, 121 (1950).
(3) A. M. Lands, V. L. Nash and K. Z. Hooper, *ibid.*, **86**, 129 (1946).
(4) H. Michael and J. Jeanpretre, *Ber.*, **25**, 1615 (1892).
(5) W. Steinkopf and W. Hanske, *Ann.*, **541**, 238 (1939).

Many reports have been published[6] concerning the condensation of carbonyl compounds with rhodanine. Such products are useful intermediates for the synthesis of substituted acetonitriles. The condensation of 2-benzoylthiophene with rhodanine has been attempted with negative results. Almost a quantitative amount of ketone was recovered.

Carboxylic acids and esters have long been known as intermediates for the preparation of nitriles through the corresponding amides. Therefore the preparation of di-(2-thienyl)-acetic acid was investigated. This compound has been reported by Blicke and Tsao,[7] who have prepared it, in low yield, by a synthesis involving many steps; other routes therefore were investigated. Diphenyl-2-thienylacetic acid has been prepared by the condensation of benzilic acid with thiophene in glacial acetic acid using concentrated sulfuric acid.[8] The condensation of benzilic acid with benzene has been reported in the presence of stannic chloride.[9] Attempts to condense mandelic acid with thiophene in the presence of these two reagents failed to produce the desired product.

(6) P. L. Julian and B. M. Sturgis, THIS JOURNAL, **57**, 1126 (1935); F. Brown, C. Bradsher, S. McCallum and M. Potter, *J. Org. Chem.*, **15**, 174 (1950).
(7) F. Blicke and M. Tsao, THIS JOURNAL, **66**, 1645 (1944).
(8) J. Ancizar-Sordo and A. Bistrzycki, *Helv. Chim. Acta*, **14**, 141 (1931).
(9) A. Bistrzycki and L. Mauron, *Ber.*, **40**, 4060 (1907).

Grummitt, Buck and Egan[10] have prepared di-(*p*-chlorophenyl)-acetic acid by the hydrolysis of DDT with potassium hydroxide in diethylene glycol. Using a modification of their method, we have hydrolyzed 2,2-bis-(2-thienyl)-1,1,1-trichloroethane to the desired product in fair yields.

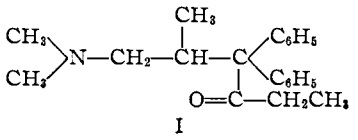
Three methods for the conversion of organic acids to amides were attempted. The first was the reaction of the acid with thionyl chloride and dropping the resulting acid chloride into cold ammonium hydroxide. A 68–75% yield of amide, m.p. 147–148°, resulted. The second method, a one-step synthesis, consisted in heating the organic acid with ammonium carbonate in acetic acid using the method of Kao and Ma.[11] In this reaction, a 79% yield of di-(2-thienyl)-methane was isolated from the residue. The third method consisted in esterification of di-(2-thienyl)-acetic acid with absolute ethyl alcohol saturated with dry hydrogen chloride, ethyl di-(2-thienyl)-acetate was produced in an 86% yield. The amide was then prepared in 89% yield by amination of the above ester with ammonium carbonate in methanol saturated with dry ammonia. Pure white crystals were obtained from this reaction as contrasted to the first method in which a purplish product was obtained. A mixed melting point with pure samples from both methods showed no depression.

A slight modification of the method of Sperber and co-workers[12] for the dehydration of amides was used to prepare di-(2-thienyl)-acetonitrile. A 76–83% yield of product melting at 50–51° and distilling at 184° at 2 mm. was obtained.

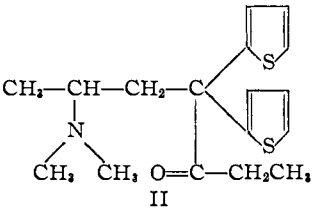
For the condensation of di-(2-thienyl)-acetonitrile with 1-dimethylamino-2-chloropropane, we have used lithium amide and obtained a 72% yield of a mixture of amino nitriles. They were then separated by fractional crystallization of their picrates. The first fraction had a melting point of 175–176° which was not altered by recrystallization. From the concentrated filtrate, there precipitated a picrate, which when recrystallized from alcohol melted at 139–140°. Upon treatment of the isolated picrates with dilute sodium hydroxide solution, oily products were obtained in both cases. From the picrate of the first fraction, there was obtained a product distilling at 159–160° at 2 mm. which was called thiophene preamidone I. From the second picrate, there was obtained a product distilling at 174–175° at 2 mm. which was called thiophene preamidone II. Both these compounds analyzed for the expected aminonitrile isomers.

These two isomers were then treated with ethylmagnesium bromide. From thiophene preamidone I, there was obtained an oil distilling at 184–185° at 2 mm. (thiophene amidone I). The hydrochloride of this compound analyzed for the ketone. From thiophene preamidone II, there was obtained a white, crystalline solid, thiophene amidone II, m.p. 106–108°. This product also analyzed for the ketone. It is interesting to note that both the aminonitriles in the thiophene series produced ketones upon hydrolysis of their Grignard complexes. This is in contrast to the phenyl series where a stable imine was obtained.

It was then decided to synthesize one of these isomers by an unequivocal route. The method of Sletzinger, Chamberlin and Tishler[13] for the synthesis of isoamidone (I) has been chosen because of its relatively high yields. By this route there was obtained a product distilling at 184° at 2 mm., corresponding to thiophene amidone I. This would then seem to indicate that thiophene amidone II has the structure represented in II.



I



II

Experimental

Di-(2-thienyl)-acetic Acid.—In a 2-l. round-bottomed, three-necked flask fitted with a Hershberg stirrer, an efficient reflux condenser and a thermometer was placed 125 g. (0.42 mole) of 2,2-bis-(2-thienyl)-1,1,1-trichloroethane[14] dissolved in 600 ml. of diethylene glycol. To this stirred solution was added 189 g. (3.37 moles) of potassium hydroxide in 110 ml. of water. This mixture was then stirred and refluxed for five hours at such a rate that the temperature remained at 128–134°. The reaction mixture then was cooled to room temperature, poured into cold water and filtered from the black solid. The filtrate was treated with charcoal, warmed on the steam-bath for about 15 minutes and filtered. The filtrate, about three liters, was then cooled to 0–5° and slowly acidified with 50% hydrochloric acid with stirring. The crude product was filtered, washed with water and dried at room temperature. It was then dissolved in benzene and the organic acid extracted from the benzene solution with 10% sodium bicarbonate solution. The aqueous layer was separated, cooled to 0° and precipitated with 50% hydrochloric acid to yield 68–75% of pure white product,[7] m.p. 93–94°.

Di-(2-thienyl)-acetamide (through the Acid Chloride).—In a flask fitted with a reflux condenser was placed 33.6 g. (0.15 mole) of di-(2-thienyl)-acetic acid and 178.5 g. (1.5 moles) of freshly distilled thionyl chloride. The reaction mixture was then gradually heated to reflux temperature and held there for 15 minutes. The excess thionyl chloride was removed under reduced pressure and finally by the successive addition and distillation of three 5-ml. portions of benzene.

The crude acid chloride obtained above was then added dropwise, with stirring, to 400 ml. of concentrated ammonium hydroxide cooled to 0°. The purplish precipitate was filtered, dried and recrystallized three times from alcohol using charcoal. In this manner, there was obtained 65–72% of pure di-(2-thienyl)-acetamide, m.p. 147–148°.

Anal. Calcd. for $C_{10}H_9S_2ON$: C, 53.81; H, 4.07. Found: C, 53.70; H, 4.18.

(Through the Ester).—Anhydrous hydrogen chloride was passed through a solution of 224 g. (1 mole) of di-(2-thienyl)-acetic acid and 750 ml. of absolute ethyl alcohol, with stirring, for three hours. The mixture was then allowed to stand overnight and the excess ethanol was distilled under

(10) O. Grummitt, A. Buck and R. Egan, *Org. Syntheses*, **26**, 21 (1946).

(11) C. Kao and Shao-Yuan Ma, *J. Chem. Soc.*, 443 (1931).

(12) N. Sperber, D. Papa, E. Schwenk, M. Sherlock and R. Fricano, THIS JOURNAL, **73**, 5755 (1951).

(13) M. Sletzinger, E. M. Chamberlin and M. Tishler, *ibid.*, **74**, 5619 (1952).

14) J. F. Freeman, J. R. Dove and E. D. Amstutz, *ibid.*, **70**, 3136 1948).

reduced pressure. The crude ester was taken up in ether, washed with water, 10% sodium bicarbonate solution and water. The ether solution was dried with anhydrous sodium sulfate, filtered and the ether removed by distillation. In this manner, 218 g. (86.4%) of ethyl di-(2-thienyl)-acetate,[15] b.p. 147° (2 mm.), 120° (0.8 mm.), was prepared.

Ammonia gas was bubbled into 120 ml. of 95% methyl alcohol until the solution was saturated. Then, 100 g. of ammonium carbonate was added to the solution, followed by 112 g. (0.5 mole) of ethyl di-(2-thienyl)-acetate. The flask then was loosely stoppered and allowed to stand for five days. The clear solution was poured, with stirring, into one liter of cold water resulting in the precipitation of fine white needles which were filtered, washed with water and dried. The di-(2-thienyl)-acetamide weighed 99.0 g. (89%) and melted at 147–148°.

A mixed melting point with the product from the acid chloride method showed no depression.

Di-(2-thienyl)-acetonitrile.—A mixture of 73.6 g. (0.33 mole) of di-(2-thienyl)-acetamide, 30 g. of dry sodium chloride and 500 ml. of dry ethylene dichloride was stirred for one-half hour. Subsequently, 43.6 g. (0.28 mole) of phosphorus oxychloride was added and the resulting mixture was refluxed for nine hours. After it had cooled to room temperature, it was decomposed with 10% sodium hydroxide solution. The organic layer was washed with water, dried with anhydrous sodium sulfate and filtered. The ethylene dichloride was distilled under reduced pressure and upon fractional distillation of the residue there resulted 51–56 g. (76–83%) of di-(2-thienyl)-acetonitrile, b.p. 184° (2 mm.), m.p. 50–51°.

Anal. Calcd. for $C_{10}H_7NS_2$: C, 58.50; H, 3.43. Found: C, 58.62; H, 3.22.

Alkylation of Di-(2-thienyl)-acetonitrile with 1-Dimethylamino-2-chloropropane.—To 1.3 g. (0.056 mole) of lithium amide suspended in 20 ml. of dry benzene was added 10.3 g. (0.05 mole) of di-(2-thienyl)-acetonitrile at 45–50°. The mixture was stirred for 1.5 hours at this temperature and cooled to room temperature. To this mixture 6.1 g. (0.05 mole) of 1-dimethylamino-2-chloropropane[16] was added dropwise with stirring. The reaction mixture was slowly heated to reflux over a period of two hours and then refluxed for six hours. It was then cooled, poured into cold water and separated. The benzene layer was washed with water and extracted with a 10% solution of hydrochloric acid. This acid solution was then made alkaline with a 10% sodium hydroxide solution at 0°. The oil which separated was extracted with ether and the ether layer dried over anhydrous sodium sulfate. The ether was removed by distillation and the residue distilled under reduced pressure. In this manner, there was obtained 14.0 g. (71.6%) of a mixture of 4-dimethylamino-2,2-di-(2-thienyl)-3-methylbutyronitrile and 4-dimethylamino-2,2-di-(2-thienyl)-valeronitrile, b.p. 141–159° (2 mm.).

The methiodide of this mixture, prepared in the usual manner, melted at 132–140°.

Anal. Calcd. for $C_{16}H_{21}N_2S_2I$: C, 44.44; H, 9.89. Found: C, 44.90; H, 5.09.

Fractional Crystallization of the Picrates.—To a solution of 25.5 g. (0.088 mole) of the aminonitriles prepared as above in 500 ml. of alcohol was added 20.4 g. (0.089 mole) of picric acid in 300 ml. of alcohol. After 15 minutes of heating this mixture on the steam-bath, with stirring, yellow crystals appeared. Heating was continued for a further 15 minutes when 1300 ml. of alcohol was added and the resulting mixture was refluxed for one hour or until all of the picrate redissolved. The mixture was cooled to room temperature and the resulting crystals were filtered and dried; they melted at 175–176°. Recrystallization failed to alter the melting point. From the filtrate was distilled 500 ml. of alcohol upon which more crystals precipitated and were separated; these melted at 173–174°. After recrystallization from alcohol they melted at 175–176°. The combined dried picrates of this first fraction weighed 19.2 g.

Anal. Calcd. for $C_{21}H_{21}N_5S_2O_7$: C, 48.54; H, 4.07; N, 13.67. Found: C, 48.12; H, 4.06; N, 13.30.

Further evaporation of the mother liquor from the original crystallization produced the second picrate fraction. It was filtered and dried and melted at 131–134°. Evaporation of the filtrate produced only a few oily crystals. The second picrate was recrystallized three times from alcohol or until a product with a constant melting point of 139–140° was obtained; it weighed 12.1 g.

Anal. Calcd. for $C_{21}H_{21}N_5S_2O_7$: C, 48.54; H, 4.07 Found: C, 48.86; H, 4.19.

Thiophene Preamidone I.—By the decomposition of 19.0 g. of the picrate melting at 175–176° with 70 ml. of a 5% sodium hydroxide solution, there was obtained 9.3 g. of thiophene preamidone I, b.p. 159–160° (2 mm.).

Thiophene Preamidone II.—By the decomposition of 12.0 g. of the picrate melting at 139–140° with 50 ml. of a 5% sodium hydroxide solution, there was obtained 6.3 g. of thiophene preamidone II, b.p. 174–175° (2 mm.).

Anal. Calcd. for $C_{15}H_{18}N_2S_2$: C, 62.02; H, 6.24; N, 9.64. Found: C, 62.53; H, 6.60; N, 9.46.

Thiophene Amidone I.—To an ethylmagnesium bromide–ether solution prepared from 0.88 g. (0.036 mole) of magnesium turnings, 4.4 g. (0.036 mole) of ethyl bromide and 10 ml. of anhydrous ether, there was added 5.4 g. (0.019 mole) of thiophene preamidone I in 10 ml. of dry xylene, dropwise with stirring. A reaction immediately ensued and after the addition, the mixture was heated on the steam-bath for three hours resulting in a gray precipitate. The hot mixture was then poured into 50 ml. of a 50% solution of hydrochloric acid causing a vigorous reaction. The reaction was then extracted with benzene and the cold acid solution was rendered alkaline with 20% sodium hydroxide. The resulting oil was extracted with ether, dried with anhydrous sodium sulfate and the ether removed by distillation. The residual oil was then distilled under reduced pressure. In this manner, 4.8 g. (78%) of thiophene amidone I was obtained, b.p. 184° (2 mm.).

The hydrochloride, m.p. 195–196°, which was prepared in the ordinary manner, analyzed for the hydrochloride of the ketone.

Anal. Calcd. for $C_{17}H_{24}ONS_2Cl$: C, 57.03; H, 6.75; N, 3.91. Found: C, 56.88; H, 6.77; N, 3.99.

Thiophene Amidone II.—This compound was prepared from thiophene preamidone II in the same manner as the above preparation of thiophene amidone I from thiophene preamidone I.

From 5.4 g. of thiophene preamidone II, there was obtained 3.2 g. (52.5%) of white needles of thiophene amidone II, m.p. 106–108°, which analyzed for the ketone structure.

Anal. Calcd. for $C_{17}H_{23}ONS_2$: C, 63.50; H, 7.21; N, 4.36; S, 19.95. Found: C, 63.48; H, 7.53; N, 4.40; S, 20.04.

The hydrochloride of this compound melted at 194–195°; a mixed melting point with the hydrochloride of thiophene amidone I melted at 151–170°.

Cursory biological tests on thiophene amidone II hydrochloride, through the courtesy of Dr. John Lee of Hoffman-La Roche, Nutley, N. J., have shown it to have greater activity than Demerol and about the activity of amidone.

4-Dimethylamino-2,2-di-(2-thienyl)-3-methylbutyronitrile.—Di-(2-thienyl)-acetonitrile, 31.4 g. (0.15 mole), was dissolved in 250 ml. of dry toluene and added to a suspension of 6.3 g. (0.16 mole) of sodium amide in 60 ml. of dry toluene. The mixture was heated to 106° under nitrogen with stirring and kept at this temperature until the reaction was complete. The mixture was then cooled to 60°, and 37.2 g. (0.15 mole) of the *p*-toluenesulfonate of 1-chloro-2-propanol[12] was added slowly. The reaction mixture was then refluxed for 18 hours, cooled to room temperature and poured into water. The organic layer was washed with water, dried over anhydrous magnesium sulfate, the toluene removed under diminished pressure, and the intermediate distilled at 142–143° (0.5 mm.). To 28.1 g. (0.1 mole) of this product was added 17 g. (0.38 mole, 25 g.) of dimethylamine and 9.5 g. of copper sulfate. The mixture was heated in a sealed tube at 150° for 48 hours, cooled to room temperature and extracted with benzene. The benzene extract was washed with water and then extracted with 2.5 *N* hydrochloric acid. The acidic extracts were concentrated under reduced pressure. The resulting oil was then distilled under reduced pressure using a modified Claisen flask. In this manner was prepared 12.4 g. (45%) of 4-dimethylamino-2,2-di-(2-thienyl)-3-methylbutyronitrile, b.p. 159–160° (2 mm.). The picrate of this compound melted at

(15) F. Leonard and I. Ehrenthal, THIS JOURNAL, 73, 2216 (1951).

(16) E. M. Schultz and J. M. Sprague, *ibid.*, 70, 48 (1948).

175–176°. A mixed melting point with the picrate of thiophene preamidone I melted at 175–176°.

6-Dimethylamino-4,4-di-(2-thienyl)-5-methyl-3-hexanone.—To an ethylmagnesium bromide–ether solution prepared from 0.88 g. (0.036 mole) of magnesium turnings, 4.4 g. (0.036 mole) of ethyl bromide and 10 ml. of anhydrous ether, 5.4 g. (0.019 mole) of 4-dimethylamino-2,2-di-(2-thienyl)-3-methylbutyronitrile in 10 ml. of dry xylene was added dropwise with stirring. A reaction ensued after which the mixture was heated on the steam-bath for three hours resulting in a gray precipitate. The hot mixture was then poured into 50 ml. of 50% hydrochloric acid. A vigorous reaction resulted causing much of the xylene to distil. Benzene was then added to the mixture and the resulting organic layer was separated. The cold acid solution was made basic with a 20% sodium hydroxide solution and extracted with ether. The ether solution was dried over anhydrous sodium sulfate and the ether then removed by distillation. The resulting precipitate of white needles was filtered and dried. Upon recrystallization from petroleum ether (60–75°), there was obtained 2.9 g. (48%) of 6-dimethylamino-4,4-di-(2-thienyl)-5-methyl-3-hexanone, b.p. 184° (2 mm.). The hydrochloride melted at 195–196°. A mixed melting point with a sample of the hydrochloride of thiophene amidone I melted at 195–196°. A mixed melting point with a sample of the hydrochloride of thiophene amidone II melted at 153–176°.

Acknowledgment.—We are indebted to the Nepera Chemical Company, Inc., for a grant-in-aid of this work.

NEW YORK 58, NEW YORK

[CONTRIBUTION FROM THE CANCER RESEARCH LABORATORY OF THE UNIVERSITY OF FLORIDA]

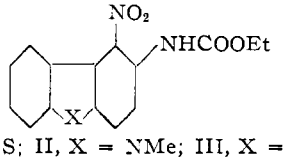
Preparation and Absorption Spectra of Analogous Dibenzothiophene, Dibenzoselenophene and Carbazole Compounds[1]

BY EUGENE SAWICKI

RECEIVED JUNE 11, 1954

The structure of 1,2- and 3,4-disubstituted dibenzoselenophene derivatives is proven by spectral comparison with the known iso-π-electronic dibenzothiophene and carbazole derivatives. Similarly a spectral proof of structure is given for 2-nitro-, 4-nitro-, 2,8-dinitro-, 2-acetyl-, 4-acetyl-, 2,8-diacetyl and 2(?),6-diacetyldibenzoselenophene. The spectra of these compounds, as well as those of 2- and 3-substituted azido and acylamino derivatives of dibenzothiophene, dibenzoselenophene and 9-methylcarbazole, are discussed.

Nitration of 2-carbethoxyaminodibenzothiophene has been shown to give the 1-nitro derivative I,[2] while nitration of the analogous 3-carbethoxyamino-9-methylcarbazole was found to give the 4-nitro derivative II.[3]



I, X = S; II, X = NMe; III, X = Se

The nitration of 2-carbethoxyaminodibenzoselenophene gives a nitro derivative whose spectrum[4] is similar to that of 2-carbethoxyamino-1-nitrodibenzothiophene[2] and 3-carbethoxyamino-4-nitro-9-methylcarbazole.[3] The derived nitroamines of the above compounds are closely similar spectrally, Fig. 1, as are the derived nitroamine hydrochlorides and piaselenoles. On the basis of the similarity of the spectral curves it is concluded that the nitration of 2-carbethoxyaminodibenzoselenophene gives the 1-nitro compound III. From these spectral curves, and additional spectral data in the literature,[2–7] it would seem that analogous dibenzothiophene, dibenzoselenophene and carbazole derivatives have fairly similar absorption spectra. This is of value in proof of structure studies and could be of great value in theoretical molecular spectroscopy work.

In Fig. 1, the longest wave length band in all three compounds is an *o*-nitroaniline band; in the carbazole derivative the effect of the ring nitrogen is to push this band further into the visible.

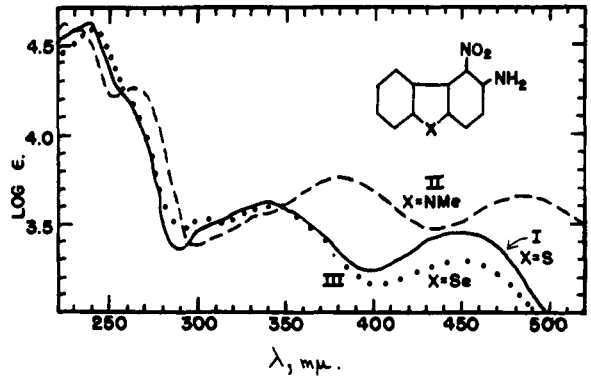


Fig. 1.—I, 2-Amino-1-nitrodibenzothiophene[2] (——); II, 3-amino-4-nitro-9-methylcarbazole[3] (– – –); III, 2-amino-1-nitrodibenzoselenophene (. . . .).

A comparison of the melting points illustrates further the remarkable resemblance among these substances. Compounds I, II and III melt within a range of 189 ± 5°, at 189–190°, 184–185° and 194°, respectively. In the nitroamines derived from I, II and III the melting points have a range of 156 ± 10°, at 165–166°, 145–146° and 154–155°, respectively, while in the piaselenoles derived from I, II and III the melting points have a range of 180 ± 4°; at 176–177°, 180–181° and 184°, respectively.

The nitration of 2-*p*-tosylaminodibenzoselenophene followed by deacylation gave a mixture of nitroamines out of which one main product, m.p. 247–248.5°, was isolated. The absorption spectrum of this derivative is closely similar to the spec-

(1) This investigation was supported by research grants from the Damon Runyon Memorial Fund and Grant C-1066 from the National Cancer Institute, National Institutes of Health, Public Health Service.

(2) E. Sawicki, *J. Org. Chem.*, **19**, 608 (1954).

(3) E. Sawicki, THIS JOURNAL, **76**, 664 (1954).

(4) The ultraviolet absorption spectra of all compounds in this paper are available from the author.

(5) E. Sawicki and F. E. Ray, THIS JOURNAL, **74**, 4120 (1952).

(6) E. Sawicki and F. E. Ray, *J. Org. Chem.*, **18**, 946 (1953).

(7) E. Sawicki, *ibid.*, **18**, 1492 (1953).