The above reaction was repeated and the sulfuric acid solution of the salt was examined by nmr. Proton nmr: δ 6.60 (s, broad, $A = 153$, NH_3^+) and 4.00 (d, q, $J_{HF} = 11.0$, $J_{NH-H} = 6.0$ Hz, $A = 102$, CH_2); fluorine nmr φ 101.0 (t, $J_{HF} = 10.4$ Hz).

Registry No. —2-Fluoro-2,2-dinitroethanol, 17003-75-7; (2-fluoro-2,2-dinitroethyl)methylamine, 30409-33-7, 30409-34-8 (HCl); (2-fluoro-2,2-dinitroethyl)dimethylamine, 30409-35-9, 30409-36-0 (HCl); (2-fluoro-2,2-dinitroethyl)aminoacetic acid, 30409-37-1; ethyl 2-fluoro-2,2-dinitroethylaminoacetate, 30409-38-2; (2-fluoro-2,2-dinitroethyl)aminoacetaldehyde diethyl acetal, 30409-39-3; (2-fluoro-2,2-dinitroethyl)aminosuccinic acid, 30476-99-4; 2-(2-fluoro-2,2-dinitroethylamino)ethanol, 30409-40-6; *N*-(2-fluoro-2,2-dinitroethyl)allylamine, 30409-41-7; *N*,*N*-bis(2-fluoro-2,2-dinitroethyl)allylamine, 30409-42-8; *N*,*N*′-bis(2-fluoro-2,2-dinitroethyl)-*N*,*N*′-bis(carbethoxymethyl)methylenediamine, 29925-43-7; *N*,*N*′-bis(2-fluoro-2,2-dinitroethyl)hydrazine, 30409-44-0; ethyl (2-fluoro-2,2-dinitroethyl)carbamate, 30409-45-1; methyl (2-fluoro-2,2-dinitroethyl)carbamate, 30409-46-2; isopropyl (2-fluoro-2,2-dinitroethyl)carbamate, 30409-47-3; 2-fluoro-2,2-dinitroethylammonium bisulfate, 30409-48-4.

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The Reaction of Ethyl β-Dimethylaminocrotonate and Benzoyl Isothiocyanate

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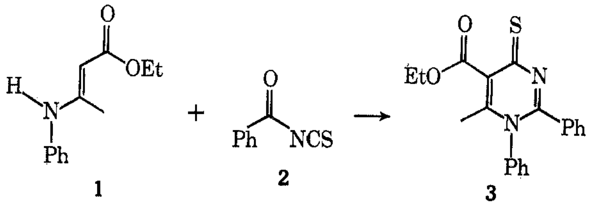
The reaction of ethyl β-dimethylaminocrotonate and benzoyl isothiocyanate in chloroform to yield ethyl 2-benzamido-5-benzoyl-4-dimethylamino-6-thioxonicotinate is described and the crystal structure analysis given. The intermediates leading to the product and the pathway of formation are discussed.

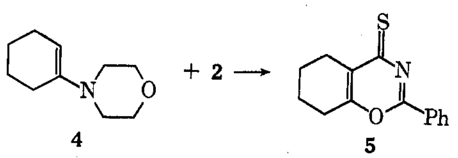
Part A

Enamines have been used to synthesize various carbocyclic and heterocyclic systems.[1] Our interest has been in the synthesis of pyrimidines[2] and tetrahydroquinazolines[3] by the interaction of an enamine with benzoyl isothiocyanate.

This paper is concerned with the novel product formed from the reaction of an α,β-unsaturated amino ester, ethyl dimethylaminocrotonate, with benzoyl isothiocyanate. We earlier observed that, when β-anilinocrotonate (**1**) and benzoyl isothiocyanate (**2**) were allowed to react, the thiopyrimidine **3** was obtained, whereas, when an enamine **4** derived from a secondary amine was allowed to react with **2**, the oxazinethione **5** resulted. It was, therefore, expected that the condensation of β-dimethylamino crotonate (**6**) with **2** would give rise to the analogous product **7** from which various N-substituted pyrimidines could be prepared (see Scheme I).



1 **2** **3**



4 **5**

When **6** was allowed to react with **2** in chloroform with warming on a steam bath, a yellow crystalline compound **11**, mp 233–235°, was obtained. Elemental analysis indicated that 2 equiv of **2** and 1 equiv of **6** had combined with the loss of hydrogen sulfide. The simplicity of the pmr (ester, dimethylamino, aromatic, and two exchangable protons) and the carbonyl region of the ir was in agreement with the assigned structure.

The reaction pathway proceeds most likely through the addition of 2 equiv of benzoyl isothiocyanate to the α carbon of the crotonate with subsequent internal benzoyl displacement with loss of isothiocyanate or by the addition of 1 equiv of **2** to the α carbon with direct nucleophilic addition of benzoyl to carbon 4. Cyclization with loss of hydrogen sulfide gives **8a** which adds thiocyanate with ring opening and enamine reclosure to give **11** (see Scheme I). An alternate pathway that envisions the addition of benzoyl isocyanate to both the 2 and 4 positions of the aminocrotonate does not occur as has been observed in similar reactions.[4,5]

Methylation of **11** with 1 and 2 equiv of methyl iodide gave the mono- and dialkylated products **14** and **12**. Ethanolysis of **12** with sodium ethoxide yielded the debenzoylated product **13**, whereas treatment of **12** with sodium hydroxide under vigorous conditions yielded, after adjustment of the pH to 7, compound **15** devoid of the carbethoxy and benzoyl groups. Under similar treatment **14** gave **16** and **17**. Inspection of the pmr indicates that the NH of **15** which appears at δ 4.68 is shifted downfield to 7.3 when bonded to an α-carboethoxy group as in **13**. A similar downfield shift is found in **16** and **17** and is analogous to the

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[1] M. E. Kuehne in "Enamines Synthesis, Structure, and Reactions," A. G. Cook, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 8.

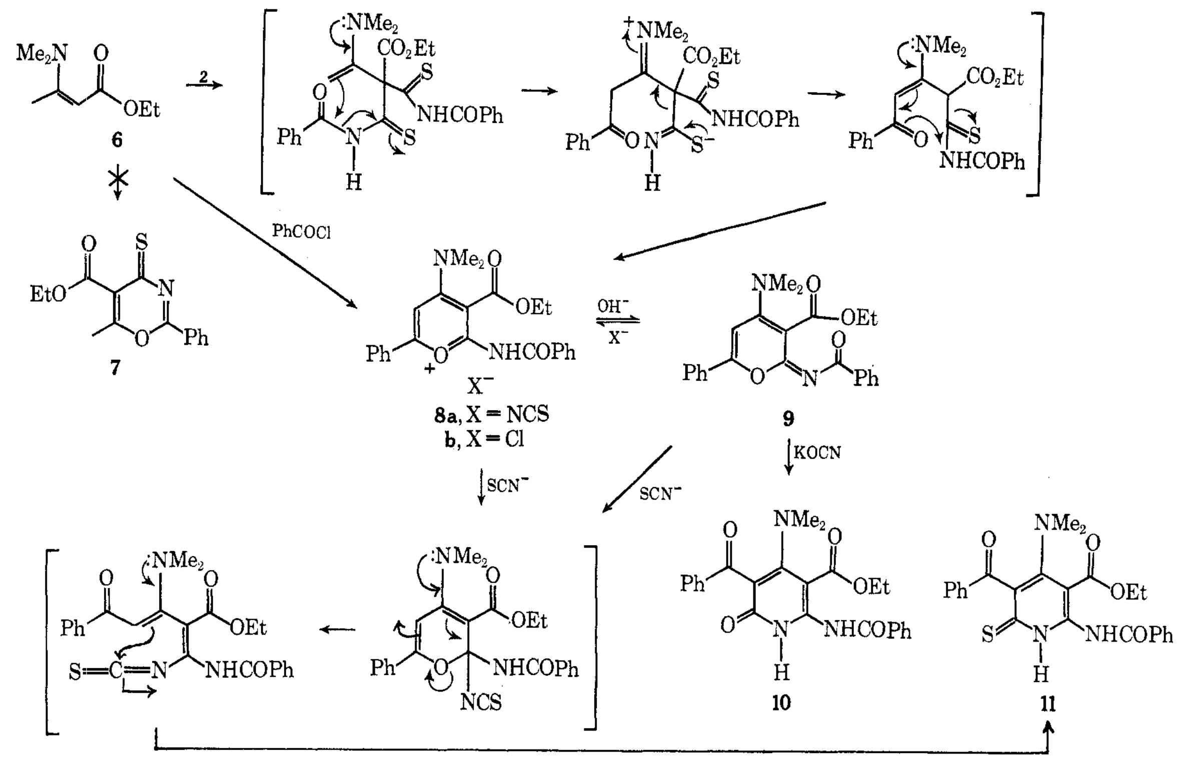
[2] G. deStevens, B. Smolinsky, and L. Dorfman, *J. Org. Chem.*, **29**, 1115 (1964).

[3] R. W. J. Carney, J. Wojthunski, and G. deStevens, *ibid.*, **29**, 2887 (1964).

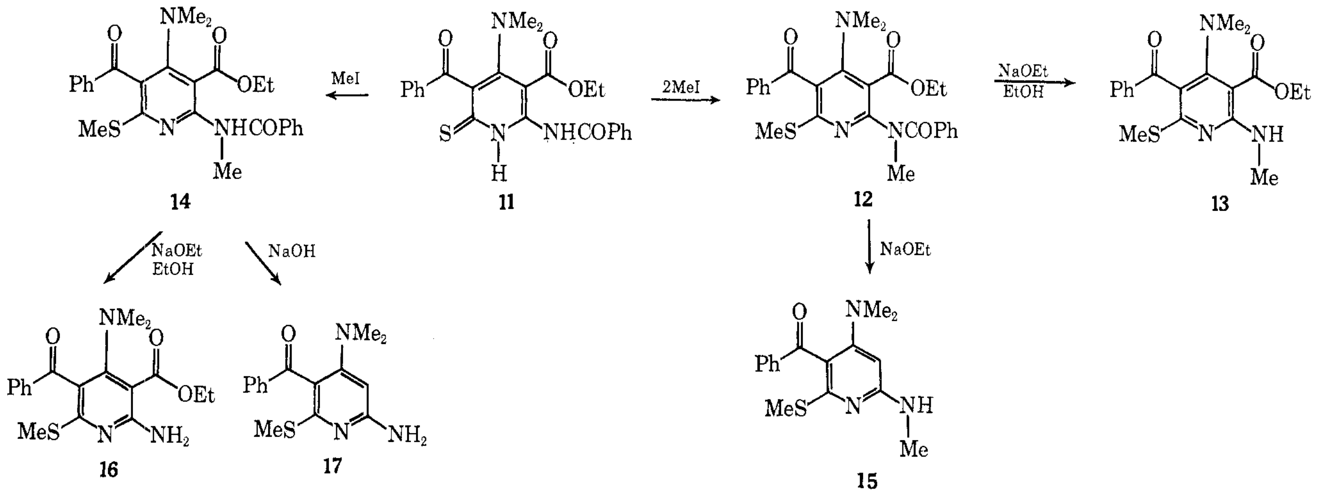
[4] W. M. Lauer and N. H. Cromwell, *J. Amer. Chem. Soc.*, **64**, 612 (1942).

[5] G. A. Berchtold, *J. Org. Chem.*, **26**, 3043 (1961); S. Hunig, K. Hubner and E. Benzing, *Ber.*, **95**, 926 (1962).

SCHEME I



SCHEME II



Shift in ethyl 2-aminonicotinate (NH, δ 6.7) and 2-aminopyridine (NH, δ 4.75).[6] See Scheme II.

In an attempt to isolate an intermediate whose formation would be relevant to the synthesis of **11**, compounds **2** and **6** in a 4:1 molar ratio were allowed to react at 5° in acetonitrile. The resulting yellow solid **8a** melted at 160–165°, whereupon it resolidified and again melted at 210–215°. The ir and elemental analysis agreed with this structure; however, on dissolving **8a** in chloroform for a pmr spectrum, it was readily converted to **11**. It seems likely that on heating **8a** above 165° or dissolution in chloroform a rearrangement spontaneously occurs leading to **11**.

At various times during the initial synthesis of **11**, a white crystalline hydrochloride **8b**, mp 194–196°, was obtained in addition to **11**. Although the salt **8b** was not soluble in most organic solvents, it could be recrystallized from acetonitrile. It was soluble in water and on treatment with dilute sodium hydroxide, a yellow color appeared which could be extracted with ether to yield **9**. Ir analysis of the original supply of benzoyl isothiocyanate indicated the presence of small amounts of benzoyl chloride, hence the chloride source. When equal molar amounts of **2**, **6**, and benzoyl chloride in benzene were combined a good yield of the hydrochloride **8b** was obtained. The addition of **9** to 6 *N* hydrochloric acid gave a white precipitate corresponding to **8b**.

A similar interconversion of **8a** and **9** was also observed. Reaction of **9** with potassium thiocyanate and *p*-touenesulfonic acid gave the thiocyanate salt **8a** while treatment of **8a** with sodium hydroxide gave **9**. Both **8a** and **9** were readily converted to **11** on the addition of thiocyanate. Potassium cyanate gave on reaction with **9** the hydroxyl derivative **10**. The addition

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[6] Varian Associates NMR Spectra Catalog, 1962, No. 431.

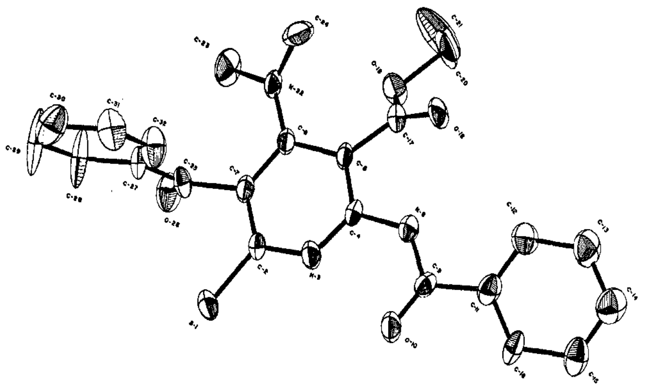

Figure 1.—Thermal ellipsoid plot of ethyl 2-benzamido-5-benzoyl-4-dimethylamino-6-thioxonicotinate.

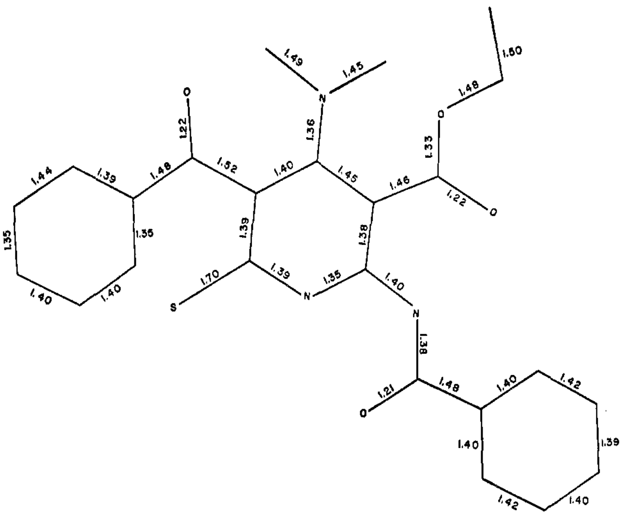

Figure 2.—Bond lengths are measured in ångströms.

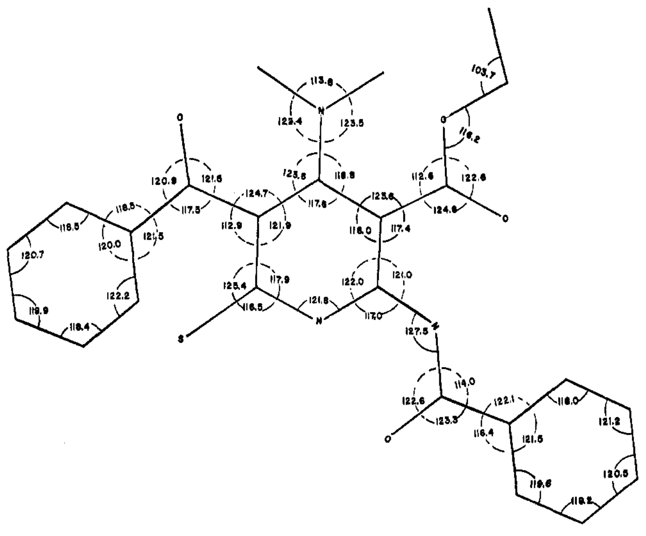

Figure 3.—Bond angles are measured in degrees.

of isothiocyanate ion (NCS^-) to the oxonium ring with subsequent ring opening and reclosure to yield **11** is analogous to numerous syntheses based on the addition of nucleophiles to triarylpyrylium salts.[7]

Finally, unequivocal proof that the addition and cyclization sequence had produced ethyl 2-benzamido-5-benzoyl-4-dimethylamino-6-thioxonicotinate (**11**) was obtained through single-crystal X-ray structure analysis. Suitable crystals were obtained in the form of elongated yellow platelets. The compound crystallizes in the monoclinic system with unit cell dimensions of $a = 14.67, b = 10.96, c = 13.82$ Å, $\beta = 95° \, 25'$, $Z = 4$. The space group was uniquely determined as $P2_1/a$ by the observed systematic extinctions of $0k0$ absent for k odd and $h0l$ absent for h odd. The structure was solved in a straightforward manner from visually estimated film data by applying the symbolic addition technique.[8] Using three origin-determining reflections together with one symbolic phase, it was possible to fix the signs of 290 reflections. The resulting E map showed the location of 22 of the 32 nonhydrogen atoms. The remaining atoms were located from a second map phased on the positions of the first 22 atoms. The resulting structure was then refined by full matrix least squares using anisotropic temperature factors to a conventional R value of 12.9% for 2067 observed reflections. A view of the molecule as it exits in the crystal is shown in Figure 1. Bond lengths and angles are summarized in Figures 2 and 3. The average estimated standard deviations of the bond lengths are of the order of 0.015 Å, those of the angles 1.0°. All values agree within 3 esd's with those commonly accepted.[9]

Part B

Experimental Section

Compound characterizations were performed with the following instrumentation: melting point, Thomas-Hoover melting point apparatus (uncorrected); infrared spectra, Perkin-Elmer Model 137 spectrophotometer; ultraviolet spectra, Cary Model 14 spectrophotometer (in ethanol); pmr spectra, Varian Associates A-60 spectrometer (in deuteriochloroform, except when noted, containing tetramethylsilane as internal standard, 50 ppm); mass spectra, Hitachi Perkin-Elmer RMU-6D, by Morgans-Schaffer Corp., Montreal, Canada, and AEI MS-902.

2-Benzamido-3-carbethoxy-4-dimethylamino-6-phenylpyrylium Isothiocyanate (8a).—A solution of 3.0 g (0.007 mol) of **9** in 65 ml of methylene chloride was combined with 1.4 g (0.014 mol) of potassium thiocyanate and 2.7 g (0.014 mol) of p-toluenesulfonic acid monohydrate. After being stirred in an ice bath for 3 hr, the white solid was filtered and washed with cold water and methylene chloride to give 0.8 g of **8a**: mp 160–165°, resolidified and melted at 210–215°; ir (Nujol) 2.98 (broad, NH), 4.87 (NCS), 5.78 (ester), 5.92 μ ($C_6H_5C{=}O$).

Anal. Calcd for $C_{24}H_{23}N_3O_4S$: C, 64.13; H, 5.16; N, 9.35; S, 7.13. Found: C, 63.80; H, 5.02; N, 9.18; S, 7.26.

A cooled solution of 7.85 g (0.05 mol) of **6** in 50 ml of acetonitrile was added to a cooled solution of 32.7 g (0.2 mol) of **2** in 75 ml of acetonitrile. After being stirred at 5° for 70 min the solid was filtered and washed with cold acetonitrile to give 1.0 g of **8a**. The filtrate was stirred for an additional 4 hr whereupon an additional 2.2 g of **8a** was obtained: mp 160–165°, resolidified and melted at 210–215°; mmp with above 155–160° (which resolidified and melted at 210–215°).

2-Benzamido-3-carbethoxy-4-dimethylamino-6-phenylpyrylium Chloride (8b).—A cold solution of 10 g (0.063 mol) of ethyl dimethylaminocrotonate in 50 ml of benzene was added to a cold mixture of 8.9 g (0.063 mol) of benzoyl chloride and 10.3 g (0.063 mol) of benzoyl isothiocyanate in 150 ml of benzene. The mixture was stirred 15 min and the solid filtered. The white solid was washed with cold benzene and recrystallized from acetonitrile to yield 8.7 g of **8b**: mp 194–196°; ir (Nujol) 5.79 (s, ester), 5.91 (s, C=O); λ_{max} 220 mμ sh (ε 16,320), 246–255°

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[7] K. Dimroth and K. H. Wolf in "Newer Methods of Preparative Organic Chemistry," Vol. 3, W. Foerst, Ed., Academic Press, New York, N. Y., 1964, p 357.

[8] J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

[9] L. E. Sutton, Ed., *Chem. Soc. Spec. Publ.*, **11**, Section B (1958).

plateau (16,570), 280 (30,170), 296 sh (25,630), 322 sh (20,500); pmr (CF_3CO_2H) δ 1.42 (t, 3, OCH_2CH_3), 3.47 (d, 6, NMe_2), 4.58 (q, 2, OCH_2CH_3), 7.4–8.2 (m, 11, aromatic), 11.38 (s, 1, NH exchangeable).

2-(3-Carbethoxy-4-dimethylamino-6-phenyl)pyranylidene Benzamide (9).—To 100 ml of 25% sodium hydroxide was added 10 g of **8b** and the solution was stirred for 1 hr. The solution immediately turned yellow and, after extraction with ether, drying, and concentration, yielded on crystallization from benzene–hexane 6.1 g of **9**: mp 108–110°; ir (Nujol) 5.81 (ester), 5.90 ($C_6H_5C{=}O$), 6.10 ($C{=}N$); λ_{max} 246 mμ (ε 21,820), 293 (33,760), 372 (19,940); pmr δ 1.32 (t, 3, OCH_2CH_3), 3.09 (s, 6, NMe_2), 4.35 (q, 2, OCH_2CH_3), 6.52 (s, 1, $=CH$), 7.2–8.4 (m, 10, aromatics).

Anal. Calcd for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68; N, 7.18. Found: C, 71.09; H, 5.72; N, 7.27.

Addition of 0.5 g of **8a** to 10 ml of 10% sodium hydroxide, followed by stirring for 2 hr, gave on extraction with ether, drying, and concentrationg 0.2 g of **9**, identical with the above.

Ethyl 2-Benzamide-5-benzoyl-4-dimethylamino-6-oxonicotinate (10).—To potassium cyanate (1.22 g, 0.015 mol) in 75 ml of chloroform was added 10 drops of 6 *N* hydrochloric acid. **9** (3 g, 0.0075 mol) was dissolved in 25 ml of chloroform and added dropwise with stirring over 1 hr. After being stirred overnight the reaction mixture was concentrated and the insoluble material washed with water. Recrystallization from ethanol yielded 1 g of **10**: mp 215–217°; ir (Nujol) 3.12 (s, NH, OH), 5.99 (s, ester), 6.13 μ (s, C_6H_5CO); λ_{max} 245 mμ (ε 32,870), 279 (31,760), 320 sh (13,026); pmr (CF_3CO_2H) δ 1.58 (t, 3, OCH_2CH_3), 3.15 (s, 6, NMe_2) 4.69 (q, 2, OCH_2CH_3), 7.33–8.34 (m, 10, Ar), 11.96 (s, 2, OH, NH).

Anal. Calcd for $C_{24}H_{23}N_3O_5$: C, 66.50; H, 5.35; N, 9.70. Found: C, 66.17; H, 5.53; N, 9.64.

Ethyl 2-Benzamido-5-benzoyl-4-dimethylamino-6-thioxonicotinate (11).—A solution of 15.7 g (0.1 mol) of ethyl dimethylaminocrotonate (**6**) in 75 ml of chloroform was added dropwise over 20 min to 32.6 g (0.2 mol) of benzoyl isothiocyanate (**2**) in 75 ml of chloroform with stirring in an ice bath. The mixture was then warmed on a steam bath for 30 min. The resulting solid was filtered and recrystallized from acetonitrile to give 14.5 g of **11** as yellow prisms: mp 233–235; ir (Nujol) 3.12 (m, NH), 6.00 (s, ester), 6.19 μ (s, C_6H_5CO); λ_{max} 257 mμ (ε 3440), 304 (2515), 372 (1670); pmr δ 1.40 (t, 3, OCH_2CH_3), 2.76 (s, 6, NMe_2), 4.48 (q, 2, OCH_2CH_3), 7.40–8.40 (m, 10, aromatic), 12.14 (s, 1, NH, slowly exchanged with D_2O), 13.3 (s, 1, SH rapidly exchanged).

Anal. Calcd for $C_{24}H_{23}N_3O_4S$: C, 64.13; H, 5.16; N, 9.35. Found: C, 64.02; H, 5.15; N, 9.23.

To a mixture of 0.46 g of *p*-toluenesulfonic acid and 0.12 g of potassium thiocyanate in 75 ml of chloroform was added 0.5 g (0.0012 mol) of **9** dissolved in 75 ml of chloroform. After refluxing for 4 hr the solvent was removed under reduced pressure and the residue crystallized from acetonitrile to give 200 mg of **11**, identical with the above.

Ethyl 5-Benzoyl-4-dimethylamino-2-(*N*-methylbenzamido)-6-methylthionicotinate (12).—To a solution of 18.0 g (0.04 mol) of **11** in 500 ml of dimethylformamide and 100 ml of toluene was added 4.2 g (0.088 mol) of 50% sodium hydride–mineral oil over 1 hr with stirring and cooling. To the light yellow solution 23.0 g (0.16 mol) of methyl iodide was added dropwise at which time the solution became red-orange and then the color gradually disappeared on stirring overnight. Water was added, and the solution was concentrated, extracted with ether, dried, and evaporated to yield 20.9 g of **12**. Crystallization from benzene–hexane gave 17 g of pure **12**: mp 146–148°; ir (Nujol) 5.81 (s, ester), 6.03 μ (s, C_6H_5CO); λ_{max} 263 mμ (ε 3060); pmr δ 1.37 (t, 3, OCH_2CH_3), 2.28 (s, 3, SMe), 2.45 (s, 6, NMe_2), 3.45 (s, 3, NMe), 4.34 (q, 2, OCH_2CH_3), 7.2–7.7 (m, 10, aromatic).

Anal. Calcd for $C_{26}H_{27}N_3O_4S$: C, 65.39; H, 5.70; N, 8.80. Found: C, 65.58; H, 5.77; N, 8.74.

Ethyl 5-Benzoyl-4-dimethylamino-2-methylamino-5-methylthionicotinate (13).—A solution of 5.0 g (0.011 mol) of **12** and sodium ethoxide (from 1.0 g of sodium) in 500 ml of ethanol was refluxed for 12 hr. The solvent was removed under reduced pressure, and water was added and extracted with ether. Drying, concentrating, and crystallization of the ether extract from hexane gave, 1.12 g of **13**: mp 128--130; ir (Nujol) 3.96 (NH), 5.98 (ester), 6.09 μ ($C{=}O$); λ_{max} 258 mμ (ε 35,250), 315 (14,600), 344 sh (10,670); pmr δ 1.32 (t, 3, OCH_2CH_3), 2.46 (s, 9, NMe_2, SMe), 3.08 (d, 3, NMe), 4.28 (q, 2, OCH_2CH_3), 7.2–7.8 (m, 6, NH, aromatics).

Anal. Calcd for $C_{19}H_{23}N_3O_3S$: C, 61.11; H, 6.21; N, 11.25; S, 8.59. Found: C, 61.17; H, 6.49; N, 11.31; S, 8.54.

Ethyl 5-Benzoyl-4-dimethylamino-2-(*N*-methylbenzamido)-6-methylthionicotinate (14).—To a solution of 18.0 g (0.04 mol) **11** in 500 ml of dimethylformamide and 100 ml of toluene was added 1.9 g (0.04 mol) of 50% sodium hydride–mineral oil with stirring and cooling. After addition of 5.8 g (0.04 mol) of methyl iodide the reaction mixture was stirred overnight and worked up as above. Recrystallization from benzene–hexane yielded 14.3 g of **14**: mp 142–144°; ir (Nujol) 3.10 (m, NH), 6.01 μ (s, $C{=}O$), λ_{max} 261 mμ (ε 3500); pmr δ 1.33 (t, 3, OCH_2CH_3), 2.53 (s, 3, SMe), 2.58 (s, 6, NMe_2), 4.55 (q, 2, OCH_2CH_3), 7.2–8.2 (m, 10, aromatic), 9.0 (s, 1, NH).

Anal. Calcd for $C_{25}H_{25}N_3O_4S$: C, 64.78; H, 5.44; N, 9.07. Found: C, 64.49; H, 5.40; N, 8.91.

4-Dimethylamino-6-methylamino-2-methylthio-3-pyridyl Phenyl Ketone (15).—A solution of 8.0 g (0.0115 mol) of **12**, 65 ml of 50% sodium hydroxide, and 700 ml of ethanol was refluxed for 8 hr and let stand overnight. The ethanol was removed under reduced pressure. Water was added, the pH was adjusted to 7, and the solution extracted with ether. Drying and solvent removal gave, on crystallization from methanol, 4 g of **15**: mp 157–159°; ir (Nujol) 2.97 (m, NH), 6.15 μ (s, $C_6H_5C{=}O$); λ_{max} 249 mμ (ε 42,130), 288 sh (8660), 360 (5410); pmr δ 2.40 (s, 3, SMe), 2.62 (s, 6, NMe_2), 2.97 (d, 3, NMe), 4.68 (s, 1, NH), 5.49 (s, 1, $HC{=}$), 7.2–7.9 (m, 5, aromatic).

Ethyl 2-Amino-5-benzoyl-4-dimethylamino-6-methylthionicotinate (16).—A solution of 1.0 g (0.002 mol) of **14** and sodium ethoxide (from 0.1 g of sodium) in 100 ml of ethanol was refluxed for 8 hr. The solvent was removed under reduced pressure, and water was added and extracted with ether. Drying, concentration, and crystallization of the ether extract from benzene–hexane gave 0.5 g of **16**: mp 115–118°; ir (Nujol) 2.79, 2.97 (NH), 5.98 (ester), 6.07 μ ($C{=}O$); λ_{max} 254 mμ (ε 33,810), 308 (14,560); pmr δ 1.33 (t, 3, OCH_2CH_3), 2.43 (s, 3, SMe), 2.50 (s, 6, NMe_2), 4.33 (q, 2, OCH_2CH_3), 6.17 (s, 2, NH_2), 7.2–8.0 (m, s, aromatic).

Anal. Calcd for $C_{18}H_{21}N_3O_3S$: C, 60.16; H, 5.89; N, 11.69. Found: C, 60.41; H, 6.13; N, 11.57.

6-Amino-4-dimethylamino-2-methylthio-3-pyridyl Phenyl Ketone (17).—A solution of 5.0 g of **14**, 35 ml of 50% sodium hydroxide, and 200 ml of ethanol was refluxed for 12 hr. The ethanol was removed, and the pH was adjusted to 7 with dilute hydrochloric acid and then extracted with ether. The extract was dried and concentrated, and the residue was crystallized from ethanol to give 4.1 g of **17**: mp 172–175°; ir (Nujol) 2.90, 2.99, 3.11 (NH_2), 6.15 μ ($C_6H_5C{=}O$); λ_{max} 206 mμ (ε 21,150), 247 (43,280), 354 (3790); pmr δ 2.38 (s, 3, SMe), 2.59 (s, 6, NMe_2), 4.59 (s, 2, NH_2), 5.66 (s, 1, $=CH$), 7.2–7.9 (m, 5, aromatics).

Anal. Calcd for $C_{15}H_{17}N_3OS$: C, 62.70; H, 5.96; N, 14.63. Found: C, 62.65; H, 5.89; N, 14.50.

Crystal Structure Analysis of Ethyl 2-Benzamido-5-benzoyl-4-dimethylamino-6-thioxonicotinate (11).—Crystal data for $C_{24}H_{23}N_3O_4S$, mol wt 449.54, are monoclinic, $a = 14.67$, $b = 10.96$, $c = 13.82$ Å, $\beta = 95° 25'$, $U = 2212$ Å^3, $Z = 4$; space group $P2_1/a$ $(C_{2n}{}^5)$ $F_{000} = 1044$; absorption coefficient for X-rays ($\lambda = 1.5418$ Å) 15.74 cm^{-1}.

Elongated yellow platelets of **11** were obtained and mounted parallel to the axis of elongation. All data were taken using nickel-filtered Cu K radiation ($\lambda = 1.5418$ Å). Unit cell dimensions were evaluated from oscillation and precession photographs. Weisenberg equiinclination photographs of levels $0kl$–$12kl$ and $h0l$ were obtained, and the intensities of the reflections were estimated visually by comparison to a calibrated strip. After merging of the data 2067 independent reflections were obtained. Systematic extinctions of the type $h0l$ absent for h odd and $0k0$ absent for k odd uniquely fixed the space group as $P2_1/a$. The intensities thus derived were corrected for Lorentz and polarization effects. No absorption corrections were made due to the small size of the crystal.

The structure was solved by employing the symbolic addition method.[8] The following initial assignments were made.

h	*k*	*l*	Phase
8	5	6	+
6	4	9	+
11	2	2	+
6	1	3	A

Utilizing this starting set and the Σ_2 relation, it was possible to fix the signs of 290 reflections with $E > 1.30$. An E map computed for these 290 reflections clearly showed the positions of 22 atoms. Structure factors based upon these positions were then calculated and the resulting phases used with the observed structure amplitudes to yield an electron density map which revealed the 10 remaining nonhydrogen atoms. At this point a conventional R of 26.6% was obtained. The structure was refined by full matrix least-squares techniques using a weighting scheme of the type suggested by Hughes.[10] All atoms were assigned anisotropic temperature factors. A final value for R of 12.9 was obtained using all 2067 observed reflections.

A copy of the final atomic parameters together with the observed and calculated structure factors can be obtained on request from R. T. P. Calculations were performed using the X-Ray 67 System of programs developed by Dr. James Stewart of the University of Maryland, together with the programs FAME and MAGIC by Fleisher, Dewar, and Stone, for the application of the symbolic addition procedure.

Registry No.—**2**, 532-55-8; **6**, 14205-42-6; **8a**, 30378-32-6; **8b**, 30428-03-6; **9**, 30428-04-7; **10**, 30428-05-8; **11**, 30428-06-9; **12**, 30428-07-0; **13**, 30428-08-1; **14**, 30428-09-2; **15**, 30428-10-5; **16**, 30428-11-6; **17**, 30428-12-7.

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Synthesis of a *dl* Polymer and an Active (+) Polymer Containing the 2,4,5,7-Tetranitrofluorenylideneaminooxysuccinic Moiety. Chromatographic Studies[1]

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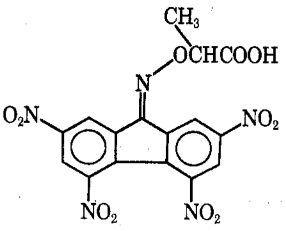
dl-Di-β-hydroxyethyl 2,4,5,7-tetranitrofluorenylideneaminooxysuccinate (6) was synthesized by the steps shown in Scheme I. Treatment with terephthalyl chloride yielded a solid polymer which was comparable to Woelm neutral alumina (grade I) in the separation of 6- and 10-methylbenz[*a*]anthracene by column chromatography. An optically active polymer was similarly prepared from (+)-6 but was ineffective in separating 2-butyl 1-naphthyl ether and hexahelicene into active forms in the range used, 3 g of polymer to 0.1 g of substrate.

α-(2,4,5,7-Tetranitro-9-fluorenylideneaminooxy)propionic acid (TAPA, **1**) was synthesized to provide a reagent suitable for resolution by complex formation of compounds lacking functional groups which would allow for resolution by standard method.[3] The resolution of hexahelicene (**2**) by TAPA was successful,[4] but very small amounts of optically pure **2** were obtained after considerable effort.

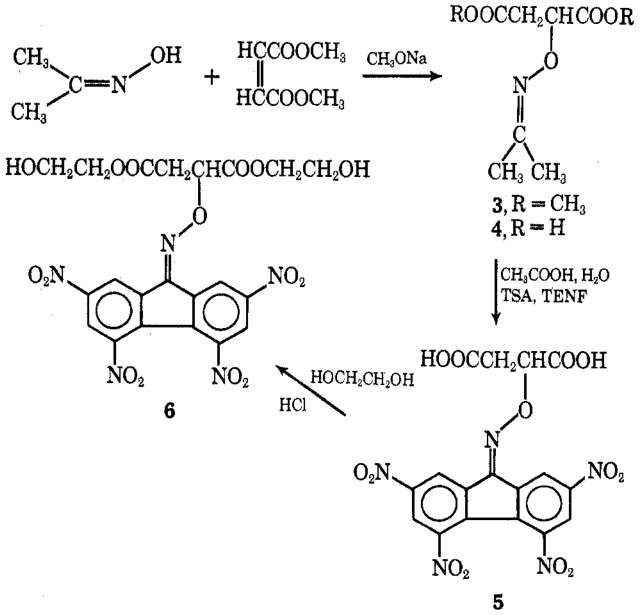
The object of the present study was to prepare a polymer containing the 2,4,5,7-tetranitrofluorene nucleus which might prove superior to alumina for the chromatographic separation of polynuclear hydrocarbons and to prepare an optically active polymer which might prove useful as a solid phase for column chromatographic resolution of **2** or other compounds[3] which have been resolved by the use of TAPA.[5]



1

An optically inactive diol suitable for formation of a polyester polymer was prepared as shown in Scheme I.

SCHEME I



The base-catalyzed reaction of acetone oxime with dimethyl maleate produced dimethyl isopropylideneaminoxysuccinate (**3**) in 50% yield. Acid-catalyzed (toluenesulfonic acid, TSA) ketone exchange with 2,4,5,7-tetranitrofluorenone (TENF) in aqueous acetic acid proceeded in high yield to 2,4,5,7-tetranitrofluorenylideneaminooxysuccinic acid (**5**) which was esterified to the bis-2-hydroxyethyl ester **6**, the glycol

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(2) Author to whom correspondence should be addressed.

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