Distillation of 3.6 g. of the crude mixture afforded the following fractions: (1) b.p. 25° (30 mm.), 0.15 g.; (2) b.p. 24° (0.15 mm.), 0.8 g.; (3) 24–26° (0.15 mm.), 1.7 g.; (4) 26° (0.15 mm.), 0.5 g.; and residue, 0.4 g., viscous oil.

The fractions were characterized by g.l.c. and n.m.r. spectroscopy. Fraction 1 consisted of 70% of 3-propenethiol and 30% of its dimer V; fraction 2 consisted of 87% of 1,3-propanedithiol and 13% of 3-propenethiol; fraction 4 consisted mainly of 1,3-propanedithiol; the residue showed a S–H band at 3.94 μ in the infrared. The n.m.r. spectrum in CS_2 showed the following characteristic signals: multiplet, δ = 1.88 (center methylene group of —$CH_2CH_2CH_2$—), and multiplet, 2.78 p.p.m. (methylene groups attached to sulfur in S—$CH_2CH_2CH_2$—S).

Preparation of Trimethylene Disulfide "Dimer."[19]—To a solution of 10.8 g. (0.1 mole) of 1,3-propanedithiol, and 100 mg. (0.0013 mole) of *t*-butyl amine in 50 ml. of methanol, 10 g. (0.11 mole) of *t*-butyl hydroperoxide was added within 30 min. The mixture was stirred overnight and the white precipitate (9.6 g., 90%) was filtered off. Recrystallization from benzene yielded a compound, melting at 77–78° (lit.[23] m.p. 77–78°). N.m.r. (in CS_2) gave a multiplet, δ = 2.09, and a triplet, 2.77 p.p.m.

Addition of Hydrogen Sulfide to Diallyl Sulfide.—A mixture of 10.7 g. (0.983 mole) of diallyl sulfide, 17 g. (0.5 mole) of hydrogen sulfide, and 100 mg. (0.006 mole) AIBN was irradiated by ultraviolet light at −70° for 41 hr. When the unchanged hydrogen sulfide and diallyl sulfide were removed, 12.3 g. of a pale yellow liquid remained, consisting of 60% of V, 31% of VII, and three minor, unidentified components (according to g.l.c.). Distillation of this mixture afforded the following fractions: (1) b.p. ~25° (1 mm.), 1.3 g.; (2) b.p. 25–47° (0.3 mm.), 0.8 g.; (3) b.p. 44–46° (0.3 mm.), 3.2 g.; (4) b.p. 46–96° (0.3 mm.), 1.8 g.; (5) b.p. 96–98° (0.3 mm.), 1.7 g.; and (6) b.p. 98–102° (0.3 mm.), 0.3 g. Fraction 3 was the 3-propenethiol dimer V. N.m.r. (neat) gave a triplet, δ = 1.52 (J = 8 c.p.s.) (S—H); multiplet, 1.70 (J = 6.5 c.p.s.) (S–CCH_2C–S); multiplet, 2.60 (—S—CH_2—C—CH_2S—); doublet, 3.11 (J = 6.5 c.p.s.) (CH_2 of S—CH_2—CH═); multiplet, 5.08 (J = 9, 17, and 6.5 c.p.s.) (═CH_2); and a multiplet, 5.83 p.p.m. (═CH—).

Anal. Calcd. for $C_6H_{12}S_2$: C, 48.59; H, 8.16; S, 43.25. Found: C, 48.61; H, 8.39; S, 43.28.

Fraction 5 was the dithiol VII (lit.[21] b.p. 138–140° at 6 mm.). N.m.r. (in $CDCl_3$) gave a triplet, δ = 1.49 (J = 8 c.p.s.) (S—H); multiplet, 1.86 (J = 6.5 c.p.s.) (S—C—CH_2—C—S); and a multiplet, 2.66 p.p.m. (S—CH_2—C—CH_2S).

Trithioacetone (X) was prepared in 50% yield,[27] b.p. 59–61° (0.25 mm.). N.m.r. (neat) gave a singlet, δ = 1.70 p.p.m.

Preparation of 1,3-Bis(allylmercapto)propane (XI).—Diallyl sulfide (34.2 g., 0.33 mole) and 7.4 g. of freshly distilled 3-propenethiol, containing 25% of its dimer V, were allowed to react in a quartz flask in the presence of 90 mg. of *t*-butyl hydroperoxide and ultraviolet light irradiation at ambient temperatures. After 14 hr. the reaction was discontinued and the crude adduct mixture was fractionated to yield 11% of XI, boiling at 73–75° (0.2 mm.). N.m.r. (in CCl_4) gave a multiplet, δ = 1.78 (J = 7 c.p.s.) (S—C—CH_2—C—S); triplet, 2.50 (S—CH_2CCH_2—S); doublet, 3.09 (CH_2 of SCH_2CH═CH_2); multiplet, 5.08 (J = 7 c.p.s.) (═CH_2); and a multiplet, 5.83 p.p.m. (J = 9, 17, and 7 c.p.s.) (—CH═).

Anal. Calcd. for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.05. Found: C, 56.87; H, 8.55; S, 34.14.

Preparation of 2-Chloropropanethiol.—A mixture of 7.6 g. (0.1 mole) of 2-chloropropene, 6.8 g. (0.2 mole) of hydrogen sulfide, and 90 mg. (0.001 mole) of *t*-butyl hydroperoxide was irradiated at −70° for 36 hr. The reaction produced 8.7 g. of a dark mobile liquid. Distillation of 6.2 g. of the latter afforded 2 g. of 2-chloropropanethiol, b.p. 41–42° (18 mm.) (lit.[28] b.p. 125–125.5° at 764 mm.). N.m.r. (neat) gave a doublet, δ = 1.59 (J = 7 c.p.s.) (CH_3); multiplet, 2.83 (CH_2); and a multiplet, 4.13 p.p.m. (CH).

Preparation of 1,2-Bis(allylmercapto)propane.—To a solution of 21.6 g. (0.4 mole) of sodium methoxide in 100 ml. of methanol 21.6 g. (0.2 mole) of 1,2-propenedithiol was added under stirring. Then 48.4 g. (0.4 mole) of allylbromide was added and the mixture was kept at reflux for 2 hr. Stirring was continued without heating overnight. Upon addition of twice its volume of water the reaction mixture separated in two layers. The upper layer was separated, washed with water, and dried over anhydrous sodium sulfate. Distillation afforded 27 g. (72%) of 1,2-bis-(allylmercapto)propane, b.p. 69–73° (0.25 mm.). N.m.r. (neat) gave a doublet, δ = 1.29 (J = 6.5 c.p.s.) (CH_3); doublet, 2.17 (J = 9 c.p.s.) (CH_2 of —CH—CH_2S); multiplet, 2.58 (CH of —CH—CH_2); doublets at 3.12 and 3.18 (J = 6.5 c.p.s.) (CH_2 of S—CH_2—CH═CH_2); multiplets at 4.09 and 5.10 (═CH_2); and multiplets at 5.88 and 5.90 p.p.m. (—CH═).

Anal. Calcd. for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.05. Found: C, 57.41; H, 8.49; S, 34.13.

Acknowledgment.—The authors wish to thank their colleagues Dr. R. B. Long for a donation of pure allene and Dr. W. Naegele for providing the n.m.r. analyses. The skillful assistance of Mr. A. M. Palmer in carrying out experiments and the help of Miss M. J. Doolan and Mrs. M. Brooks in providing g.l.c. analyses is gratefully acknowledged.

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[27] E. Fromm and E. Baumann, *Chem. Ber.*, **22**, 1035 (1889).

[28] B. Sjöberg, *ibid.*, **75**, 29 (1942).

7- and 12-Thienylbenz[*a*]anthracenes[1]

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The title compounds were prepared and their properties as well as mode of formation were studied. Analysis of the spectral patterns have also been made.

Much work has been done in recent years on the synthesis of polynuclear aromatic compounds containing sulfur. A notable example is the paper of Tilak[3] concerning 15 years of work on carcinogenesis by thiophene isosteres of polycyclic hydrocarbons. Because of our long interest in benz[*a*]anthracene chemistry,[4] and because of the obvious importance of the title compounds, we sought to prepare them by a simple extension of a known reaction route.[4] The problem turned out to be far from a simple extension of known reactions and several interesting observations came to light.

Two methods may be considered as practical approaches to the synthesis of the ketones, **9–12**, that are cyclized to the final aromatic products, **13–16**. Method A (see Chart I) offers the advantage that the aryl nitriles used may be easily prepared by a Rosenmund–von Braun reaction on the appropriate aryl chlorides which are easier to obtain than the aryl bromides which

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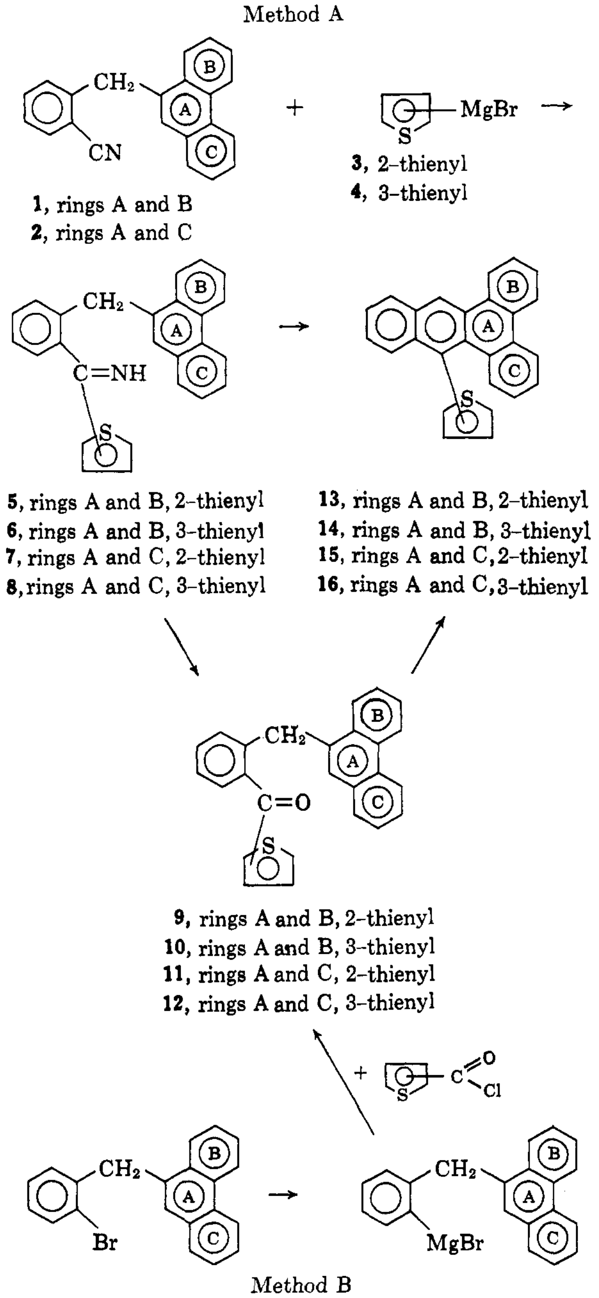
[1] This investigation was supported by a research grant, AP-00088-06, from the Division of Air Pollution, Bureau of State Services, U. S. Public Health Service.

[2] Taken from the Ph.D. Theses of S. G. Quo and P. Polss presented to the Virginia Polytechnic Institute in 1959 and 1962, respectively.

[3] B. D. Tilak, *Tetrahedron*, **9**, 76 (1960).

[4] For a recent example of syntheses in this area, see F. A. Vingiello, E. B. Ellerbe, T. J. Delia, and J. Yanez, *J. Med. Chem.*, **7**, 121 (1964).

CHART I



are used in method B. However, method B yields ketones directly while method A proceeds through a ketimine. These ketimines are difficult to purify for elemental analysis and for this reason the ketones are often prepared[5] without isolation and characterization of the intermediate ketimines. The ketimines are often difficult to hydrolyze.[6] Finally, in the specific case of the preparation of the 3-thienyl ketones, we note that the 3-thienylmagnesium halides, required by method A, are very difficult to prepare.

While ketones **9**, **10**, **11**, and **12** were prepared and characterized by infrared analysis, satisfactory elemental analyses were not obtained. Column chromatography as well as careful fractional distillation gave ketones pure enough for synthetic work but not pure enough to provide satisfactory elemental analysis. All attempts to crystallize these viscous oils failed.

The four title compounds were prepared *via* acid-catalyzed aromatic cyclodehydration of the corresponding ketones. The benz[*a*]anthracenes **13**, **14**, **15**, and **16** fluoresce blue under ultraviolet light and form 1:1 adducts with 2,4,7-trinitrofluorenone. In each case the assigned structure is consistent with elemental analysis and ultraviolet and infrared spectral patterns. The compounds vary in color from white to yellow. Compounds **13** and **15** were also prepared by ring closure of the corresponding ketimines, **5** and **7**.

A common procedure for cyclizing the ketones involves dissolving them in acetic acid, then adding 48% hydrobromic acid, and heating the solution. While attempting to dissolve these oily ketones in acetic acid, crystals were noticed in the solution. The crystals were identified as the corresponding cyclized compounds. This interesting observation suggests that the cyclized material may be formed during the reaction of the Grignard reagent with the acid chloride. This observation pertains to experiments using method B only.

Although this interesting observation will have to be investigated further before a meaningful mechanism may be postulated, the following experimental observations are noteworthy. An ultraviolet spectrum of the reaction mixture prior to hydrolysis indicates that the same amount of cyclized material is present before as after hydrolysis. Hydrogen chloride gas is evolved during the reaction, which is carried out under anhydrous conditions. The presence of excess Grignard reagent greatly reduces the amount of cyclized product formed. The amount of cyclized product did not increase when the reaction product, ketone and cyclized material, was heated with thenoyl chloride. This indicates that the possibility of the formation of ketone before hydrolysis and its cyclization by thenoyl chloride is not likely. The amount of cyclized material increased from about 15 (2-hr. reaction time) to about 50% (16-hr. reaction time), but additional reaction time did not further increase this yield.

Two ketimines, **5** and **7**, were also used to prepare their corresponding cyclized products. The two 2-thienyl ketones **9** and **11** were difficult to cyclize, perhaps owing to extended conjugation involving resonance with the lone pair of electrons on the sulfur which decreases the effective positive charge on the carbon atom which effects ring closure.[7] In both cases this problem was circumvented by the facile cyclization of the corresponding ketimines, **5** and **7**. This situation of easier cyclization of a ketimine compared with its corresponding ketone gives support to the thought that the ketimines are cyclodeaminated directly rather than being hydrolyzed to the ketone which then suffers ring closure. This thought was expressed by Quo[8] who observed that the ketimine **5** could be cyclized to **13** but could not be hydrolyzed to the corresponding ketone, **9**.

Spectral Interpretations. 1. Infrared Spectra.—It is generally accepted that conjugation results in a shift of the carbonyl band to a lower frequency.[9] We should

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(5) F. A. Vingiello and M. M. Schlechter, *J. Org. Chem.*, **28**, 2448 (1963).

(6) F. A. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, **78**, 1240 (1956).

(7) See F. A. Vingiello and J. G. Van Oot, *ibid.*, **73**, 5070 (1951), for a detailed discussion of a possible mechanism for this reaction.

(8) S. G. Quo, Ph.D. Thesis, Virginia Polytechnic Institute, 1959, p. 56.

(9) R. S. Rasmussen, D. D. Runnicliff, and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

then expect to find that the C=O bond exhibits absorption at lower frequencies in the 2-thiophene substituted ketones than in the 3-isomers.[10] In each case of the three pairs of 2- and 3-thienyl ketones listed in Table I below the same observation was noted.

TABLE I

Isomer pairs	Frequency, cm.$^{-1}$	
	2-Isomer C=O	3-Isomer C=O
Thenoyl diphenylmethanes[a]	1632	1650
2-(1-Naphthylmethyl)phenyl thienyl ketones (**9**, **10**)	1637	1655
2-(2-Naphthylmethyl)phenyl thienyl ketones (**11**, **12**)	1645	1655

[a] These data are included to complete the presentation. For the preparation of these compounds, see F. A. Vingiello, S. G. Quo, P. Polss, and P. Henson, *J. Med. Chem.*, **7**, 832 (1964).

Gronowitz[11] noted an extremely strong band at 13.1 μ in the infrared spectrum of 3-bromothiophene. This band seemed to be typical for 3-substituted thiophenes. He also found that 2-bromothiophene showed a sharp maximum at 10.26 μ which seemed almost absent in 3-bromothiophene. Although Gronowitz suggested that this maximum could be used to determine the composition of mixtures of 2- and 3-bromothiophene he did not mention whether this maximum was typical for 2-substituted thiophenes in general. These two peaks (13.1 and 10.26 μ) were not found in the infrared spectra of the 2- and 3-thienyl compounds dealt with in the present research. Close examination of the infrared spectra of the thienyl substituted isomers of the various cyclized materials, however, revealed that the region from 14 to 16 μ can be used to differentiate between the 2- and 3-thienyl isomers. Table II illustrates the frequencies at which these differentiating peaks occur.

TABLE II

Isomer pairs	Frequency, cm.$^{-1}$	
	2-Isomer	3-Isomer
Thienyl anthracenes[a]	700	660
7-Thienylbenz[*a*]anthracenes (**13**, **14**)	700	665
12-Thienylbenz[*a*]anthracene (**15**, **16**)	702	665

[a] See Table I, footnote *a*.

It is apparent then that one can differentiate between a 2- and a 3-thenyl ketone as well as between a 2- and a 3-thienyl substituted aromatic compound by examining the infrared spectra at approximately 1600–1700 and 600–700 cm.$^{-1}$, respectively.

2. **Ultraviolet Spectra.**—It is well known that increasing conjugation stabilizes the excited state more than the ground state causing a bathochromic shift.[12] Gronowitz[13] has made a study of the ultraviolet spectra of 20 monosubstituted 2- and 3-thiophene compounds and found in every case a bathochromic shift in the 2-substituted thiophenes. This serves as evidence for the greater conjugation in this series.

The primary absorption band of thiophenes in the ultraviolet region occurs at approximately 220–240 mμ. This area is, for the most part, obscured by the powerful absorption of the aromatic ring systems into which the thiophene ring has been substituted in this investigation. The cyclized materials do exhibit a small peak in the 330–340-mμ region. As is illustrated in Table III below, the 2-substituted compound of each isomeric pair exhibits a bathochromic shift of this peak.

TABLE III

Isomer pairs	Wave length, mμ	
	2-Isomer	3-Isomer
Thienylanthracenes[a]	332	330
7-Thienylbenz[*a*]anthracenes (**13**, **14**)	337	336
12-Thienylbenz[*a*]anthracenes (**15**, **16**)	336	334

[a] See Table I, footnote *a*.

While these peaks and their bathochromic shifts are small, the consistency with which they appear suggests that they may be significant.

One other spectral observation which merits mention concerns the effect of steric hindrance on the ultraviolet spectra. The ultraviolet spectra of benz[*a*]anthracenes are characterized by a series of peaks in the region between 260 and 295 mμ. If the planarity of the structure is distorted the resonance stabilization is decreased and the ultraviolet spectrum is effected. The 12-thienyl substitued benz[*a*]anthracenes offer greater opportunity for steric interference to resonance than do the 7-thienyl isomers. This expected change in spectra was observed. This hypsochromic shift of the 12-substituted isomers is shown in Table IV.

TABLE IV

Compd.	Wave length, mμ	
	First band	Second band
7-(2-Thienyl)benz[*a*]anthracene (**13**)	294	282
7-(3-Thienyl)benz[*a*]anthracene (**14**)	295	282
12-(2-Thienyl)benz[*a*]anthracene (**15**)	289	279
12-(3-Thienyl)benz[*a*]anthracene (**16**)	289	279

It is interesting to note that in the 12-substituted compounds, which exhibit the hypsochromic shift, the primary absorption bands are of greatly diminished intensity.

Experimental[14,15]

2-(1-Naphthylmethyl)phenyl 2-Thienylketimine (5).—A Grignard reagent was prepared from 6 g. (0.25 g.-atom) of magnesium, 40 g. (0.25 mole) of 2-bromothiophene, and 150 ml. of dry ether. When the reaction was complete the ether was replaced with dry benzene and a solution of 48.6 g. (0.20 mole) of 2-(1-naphthylmethyl)benzonitrile in 100 ml. of dry benzene was added. The mixture was stirred and heated under reflux overnight, cooled, and decomposed with a 20% solution of ammonium chloride and worked up in the usual way. The product crystallized from benzene, 50 g. (77%), m.p. 99–100°.

Anal. Calcd. for $C_{22}H_{17}NS$: C, 80.69; H, 5.23; N, 4.28; S, 9.80. Found: C, 80.46; H, 5.42; N, 4.04; S, 9.95.

2-(2-Naphthylmethyl)phenyl 2-Thienylketimine (7).—This compound was prepared essentially as was compound **5**. The Grignard reagent prepared from 6 g. (0.25 g.-atom) of magnesium and 40 g. (0.25 mole) of 2-bromothiophene was allowed to react with 24 g. (0.10 mole) of 2-(2-naphthylmethyl)benzonitrile giving 20 g. (64%) of white crystals, m.p. 103.5–104.5° (from absolute ethanol).

Anal. Calcd. for $C_{22}H_{17}NS$: C, 80.69; H, 5.23; N, 4.28; S, 9.80. Found: C, 80.66; H, 5.43; N, 3.97; S, 9.86.

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(10) S. Gronowitz [*Arkiv Kemi*, **13**, 295 (1959)] has made this observation regarding 2- and 3-thiophene substituted compounds containing a C=O group.

(11) S. Gronowitz, *ibid.*, **7**, 267 (1954).

(12) S. Gronowitz, *ibid.*, **13**, 295 (1959).

(13) S. Gronowitz, *ibid.*, **13**, 239 (1959).

(14) All melting points were taken on a Thomas–Hoover capillary melting point apparatus and are corrected.

(15) All analyses were carried out by Geller Laboratories, Bardonia, N. Y.

7-(2-Thienyl)benz[*a*]anthracene (13).—A solution of 12 g. (0.037 mole) of 2-(1-naphthylmethyl)phenyl 2-thienylketimine, 480 ml. of glacial acetic acid, and 240 ml. of 48% hydrobromic acid was heated under reflux for 40 hr. The solution was then cooled and diluted with water, and the crystals were filtered; the yield was essentially quantitative. The crude product was recrystallized from absolute ethanol yielding 8.0 g. (70%) of pale yellow flakes which fluoresced blue under ultraviolet light, m.p. 162–162.5°.

Anal. Calcd. for $C_{22}H_{14}S$: C, 85.12; H, 4.55; S, 10.33. Found: C, 85.04; H, 4.44; S, 10.19.

The 2,4,7-trinitrofluorenone adduct was prepared[16] by mixing solutions (10% benzene and 90% ethanol) of the compound and TNF. The adduct was recrystallized from a solution of 2% benzene and 98% ethanol giving brown, matted needles, m.p. 212–213°.

Anal. Calcd. for $C_{35}H_{19}N_3O_7S$: C, 67.19; H, 3.06; N, 6.72; S, 5.12. Found: C, 67.36; H, 3.18; N, 6.46; S, 5.35.

12-(2-Thienyl)benz[*a*]anthracene (15). A.—A solution of 4.0 g. (0.012 mole) of 2-(2-naphthylmethyl)phenyl 2-thienylketimine, 160 ml. of glacial acetic acid, and 80 ml. of 48% hydrobromic acid was heated under reflux for 24 hr. The solution was cooled, diluted with water, and extracted with benzene. The benzene extract was washed with water, dried over magnesium sulfate, filtered, concentrated, and poured onto 40 g. of neutral alumina. The alumina product mixture was extracted with petroleum ether (b.p. 60–90°) for about 12 hr. in a Soxhlet extractor. The resulting solution was concentrated and the residual oil was crystallized from absolute alcohol yielding pale yellow needles which fluoresced blue under ultraviolet light, yielding 2.7 g. (71%), m.p. 142–142.5°.

Anal. Calcd. for $C_{22}H_{14}S$: C, 85.12; H, 4.55; S, 10.33. Found: C, 85.54; H, 4.64; S, 10.01.

The 2,4,7-trinitrofluorenone adduct was prepared as has been described above for **13** and was obtained as deep red, matted needles, m.p. 182–183°.

Anal. Calcd. for $C_{35}H_{19}N_3O_7S$: C, 67.19; H, 3.06; N, 6.72; S, 5.12. Found: C, 67.48; H, 3.24; N, 6.38; S, 5.23.

B.—A Grignard reagent was prepared from 44 g. (0.15 mole) of 2-(2-naphthylmethyl)bromobenzene and 3.9 g. (0.16 g.-atom) of magnesium in dry ether. The Grignard reagent was titrated and found to have formed in 87% yield. The Grignard reagent was added to a boiling solution of 22 g. (0.15 mole) of 2-thenoyl chloride in dry benzene. Solvent was removed until the boiling temperature was 65° and the mixture was heated for 5 hr. The mixture was then cooled, decomposed, and worked up in the usual way giving 16 g. (32%) of a viscous, yellow oil, b.p. 225–235° (0.5 mm.). The oil was refractionated using a spinning-band column and boiled at 61–62° (0.25 mm.). This material is presumably 2-(2-naphthylmethyl)phenyl 2-thienyl ketone. The infrared data are consistent with this structure but the samples prepared for elemental analysis were always outside the acceptable limits.

A solution of 8.0 g. (0.02 mole) of the oil, 275 ml. of glacial acetic acid, and 138 ml. of 48% hydrobromic acid was heated under reflux for 24 hr. The solution was cooled, neutralized with a 25% sodium hydroxide solution, and extracted with benzene. The benzene layer was washed with water, dried over magnesium sulfate, filtered, and concentrated. The residual oil was crystallized from absolute ethanol giving 1.5 g. (20%) of crude **15**, m.p. 135–140°.

7-(3-Thienyl)benz[*a*]anthracene (14).—This compound was prepared essentially as was the isomer **15** using the second method (B). A Grignard reagent prepared from 44 g. (0.15 mole) of 2-(1-naphthylmethyl)bromobenzene and 3.9 g. (0.16 g.-atom) of magnesium was allowed to react with 22 g. (0.15 mole) of 3-thenoyl chloride. The mixture was worked up in the usual way and gave 15 g. (31%) of a viscous yellow oil, b.p. 215–250° (0.25 mm.). An analytical sample was prepared by redistilling the oil and collecting a fraction which boiled at 200–203° (0.08 mm.). This material is presumably **10**. The infrared spectrum showed a strong carbonyl peak but a satisfactory elemental analysis for pure ketone could not be obtained. As usual the carbon content was high suggesting the presence of some ring-closed material; the sulfur was low suggesting desulfurization had occurred.

Anal. Calcd. for $C_{22}H_{16}OS$: C, 80.45; H, 4.91; S, 9.77. Found: C, 87.85; H, 5.09; S, 9.62.

A solution of 5.0 g. (0.015 mole) of the oil and 50 ml. of glacial acetic acid was allowed to stand overnight and the solid was filtered giving 0.85 g. (18%) of **14**. The filtrate was diluted with 150 ml. of glacial acetic acid, 100 ml. of 48% hydrobromic acid was added, and the solution was heated under reflux for 2 hr. The solution was cooled and worked up in the usual way. The extraction procedure given for **15** method A was used. The product crystallized from absolute ethanol as pale yellow flakes which fluoresced blue under ultraviolet light, total yield 2.5 g. (54%), m.p. 184–184.5°.

Anal. Calcd. for $C_{22}H_{14}S$: C, 85.12; H, 4.55; S, 10.33. Found: C, 84.88; H, 4.92; S, 10.53.

The 2,4,7-trinitrofluorenone adduct was prepared as has been described previously for **13** and was obtained as reddish brown, matted needles, m.p. 198.5–199.5°.

Anal. Calcd. for $C_{35}H_{19}N_3O_7S$: C, 67.19; H, 3.06; N, 6.72; S, 5.12. Found: C, 67.31; H, 3.23; N, 6.61; S, 5.07.

12-(3-Thienyl)benz[*a*]anthracene (16).—This compound was prepared essentially as was the isomer **14**. A Grignard reagent prepared from 44 g. (0.15 mole) of 2-(2-naphthylmethyl)bromobenzene and 3.9 g. (0.16 g.-atom) of magnesium was allowed to react with 22 g. (0.15 mole) of 3-thenoyl chloride. The mixture was worked up in the usual way and gave 14 g. (28%) of a viscous yellow oil, b.p. 200–240° (0.20 mm.). An analytical sample was prepared by redistilling the oil in a spinning-band column and collecting a fraction of 80–81° (0.10 mm.). This material was presumably **12**. The infrared spectrum showed a strong carbonyl peak but a satisfactory elemental analysis for pure ketone could not be obtained. As usual the carbon content was high, the sulfur low.

Anal. Calcd. for $C_{22}H_{16}OS$: C, 80.45; H, 4.91; S, 9.77. Found: C, 82.91; H, 4.86; S, 9.54.

A solution of 10 g. of the oil and 200 ml. of glacial acetic acid was allowed to stand overnight and the solid was filtered giving 1.3 g. (13%) of **16**. To the filtrate was added 100 ml. of 48% hydrobromic acid, and the solution was heated under reflux for 2 hr. The solution was cooled and worked up in the usual way. The product crystallized from absolute ethanol as white needles which fluoresced blue under ultraviolet light, total yield 5.2 g. (52%), m.p. 139–139.5°.

Anal. Calcd. for $C_{22}H_{14}S$: C, 85.12; H, 4.55; S, 10.33. Found: C, 85.14; H, 4.52; S, 9.99.

The 2,4,7-trinitrofluorenone adduct was prepared as has been described previously for **13** and was obtained as dark brown, matted needles, m.p. 190.5–191.5°.

Anal. Calcd. for $C_{35}H_{19}N_3O_7S$: C, 67.19; H, 3.06; N, 6.72; S, 5.12. Found: C, 67.24; H, 3.03; N, 6.46; S, 5.39.

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[16] All adducts were prepared by Mr. Paul Henson in our laboratories.