distinct priorities for experimental work. Whether one considers both definitions, or merely selects one arbitrarily and views it as approximately equivalent to the other, is not immaterial; they have different powers of connotation and reflect different conceptions of the interplay between definitions and mechanisms.

Conclusion

The kinetic results and the nmr spectroscopic detection of a triazoline–phenyl isocyanate complex serve to identify the main outlines of the reactions leading to the adducts **3**. Although many details of these cycloadditions remain unelucidated, their prime characteristics are now known and planning for the other types of experimentation required for a more complete understanding of the reactions has become feasible.

Experimental Section

Materials.—Reagent-grade phenyl isocyanate, α-naphthyl isocyanate, *p*-bromphenyl isocyanate, and α-chloronaphthalene were used without further purification. *p*-Nitrophenyl isocyanate was recrystallized from carbon tetrachloride and had mp 56.5–58° (lit.[18] mp 56–57°). The triazoline 1 after recrystallization from methanol had mp 98.4–100.2°.

Kinetic Method.—A battery jar suspended in a marine plywood framework and insulated with glass wool served as the constant-temperature bath. A magnetic stirrer was positioned under the framework about 3 cm below the bottom of the bell jar. The mineral oil in the bath was maintained to ±0.03° with two knife-blade heaters, one controlled by a Variac, the other by a proportional controller using a thermistor as a sensor.[19] Reaction flasks for the kinetic runs were flattened 15–20-ml bulbs connected to a 10-cm stem of 7-mm tubing sealed with a rubber septum, secured to the threaded-glass stem with a suitable screw-cap.

For each run the connection between the reaction bulb and the pressure-sensing apparatus was made by inserting a hypodermic needle sealed to 1-mm polyethylene tubing through the rubber septum, the bulb containing a magnetic stirring bar was inserted into the kinetic bath with all but 1–2 cm of the stem submerged, the triazoline-aryl isocyanate-α-chloronaphthalene solution (approximately 0.01 *M* in triazoline) was injected through the septum, and, after a delay of a few minutes, the valve on the pressure bridge was closed and data collection commenced.

The polyethylene tube coming from the reaction bulb connected with a four-way junction of 1-mm capillary tubing; one route led through a stopcock to the atmosphere, another led to a 10-ml bulb surrounded by circulating water at 25 ± 0.01°, and the other branch led to a U-tube of 3-mm capillary tubing partially filled with mercury. A photocell was mounted on the U-tube and connected to a relay so that, as nitrogen was evolved in the reaction, the mercury level dropped in the U-tube and the photocell activated a servomotor, driving a syringe which withdrew di-*n*-butyl phthalate from the 10-ml bulb until the original pressure was reattained. A system of gears connected the servomotor to a potentiometer which in turn gave a signal proportional to the increase in volume in the system required to maintain a constant pressure; this signal was plotted against time on a strip-chart recorder.

Analog to digital conversion was accomplished by hand and the resulting data were used to calculate with a least-squares program and an IBM 7094 the best pseudo-first-order rate constants for each run. The precision of the experimental method can be gauged from the summaries of data in Table I and II and the Figures 1 and 2.

Registry No.—1, 4928-90-9.

Acknowledgment.—We thank Professors J. F. Bunnett and S. G. Smith for helpful suggestions pertinent to this investigation.

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[18] P. P. T. Sah, *Rec. Trav. Chim.*, **59**, 232 (1940).

[19] R. Anderson, *J. Chem. Educ.*, in press.

The Chemistry of Indenothiophenes. I. 8H-Indeno[2,1-*b*]thiophene

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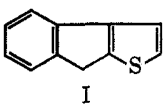
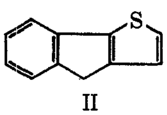
The synthesis of the title compound (I) has been achieved by the following route: conversion of 3-phenyl-2,5-thiophenedicarboxylic acid (VIII) into the diacid chloride (IX) and subsequent cyclization affords 8-oxo-8H-indeno[2,1-*b*]thiophene-2-carboxylic acid (X). Decarboxylation of X affords the corresponding ketone XIII, while Wolff–Kishner reduction of X affords the title compound I. Metalation of I with *n*-butyllithium followed by carbonation yields exclusively 8-H-indeno[2,1-*b*]thiophene-8-carboxylic acid (XV). In contrast to this, 2-benzylthiophene under the same conditions yields only 2-benzylthiophene-5-carboxylic acid.

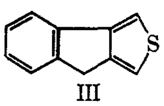
There are three possible indenothiophenes, namely, 8H-indeno[2,1-*b*]thiophene (I), 4H-indeno[1,2-*b*]thiophene (II), and 8H-indeno[1,2-*c*]thiophene (III).



I



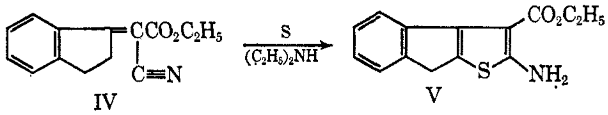
II



III

Compounds I, II, and III have not been reported in the literature and very little work has been recorded pertaining to derivatives of these compounds. The only known derivatives of I are 8H-indeno[2,1-*b*]thiophen-8-one[1,2] (XIII), prepared as a low-yield byproduct from the diazotization of 2-aminophenyl 2′-thienyl ketone, and 8H-indeno[2,1-*b*]thiophen-8-ol[2] (XIV) for which satisfactory analytical data were not reported. Poirier[3] has recently described some substituted keto derivatives of II and III. The present work describes the synthesis of I and its metalation reaction with *n*-butyllithium.

Our first attempt to prepare I was by projected removal of the amine and ester functions of ethyl 2-amino-8H-indeno[2,1-*b*]thiophene-3-carboxylate (V), prepared in 95% yield by treating ethyl (1-indanylidene)-cyanoacetate (IV) with sulfur in the presence of di-



IV V

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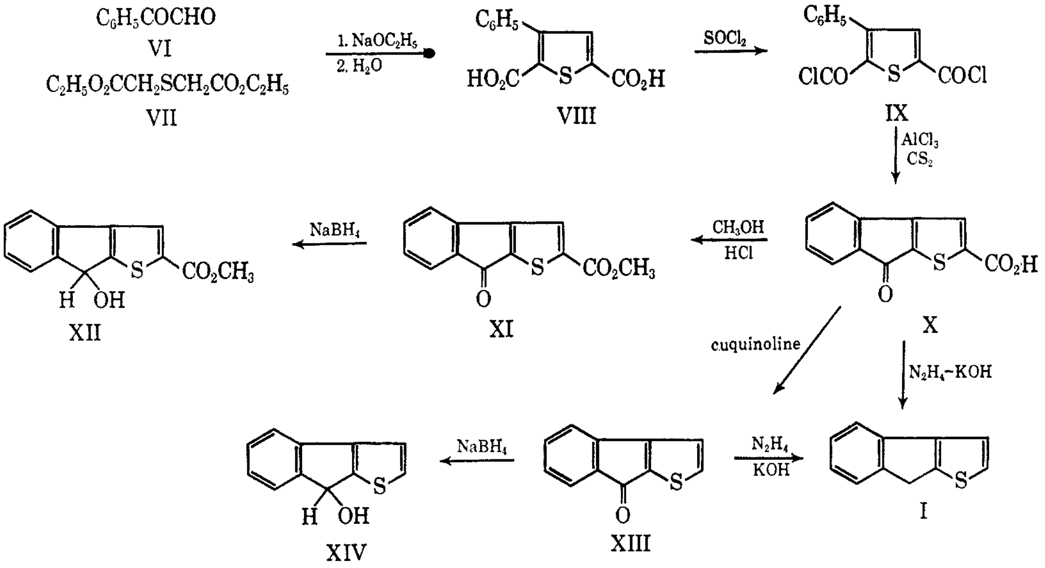
[1] W. Steinkopf and E. Gunter, *Ann. Chem.*, **522**, 28 (1936).

[2] C. L. Arcus and E. C. Barrett, *J. Chem. Soc.*, 2098 (1960).

[3] Y. Poirier and N. Lozac'h, *Bull. Soc. Chim. France*, 1062 (1966).

Scheme I



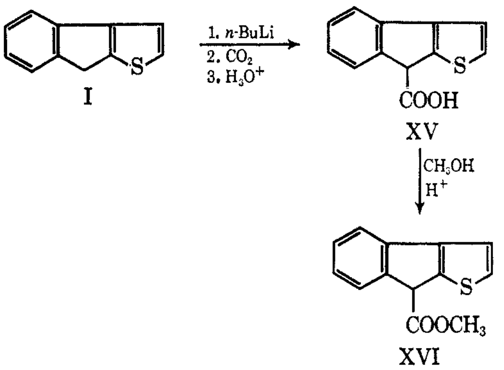
ethylamine. This method has been developed by Gewald, *et al.*,[4] for the preparation of 2-aminothiophene derivatives.

Amino ester V was very insoluble in aqueous acid and formed deep blue unworkable mixtures on treatment with aqueous or alcoholic alkali. All attempts to saponify the ester function were unsuccessful. Also, attempts to diazotize V using nitrous acid, nitrosylsulfuric acid, nitrosyl chloride, or *n*-butyl nitrite failed to give any characterizable material.

The synthesis of I was accomplished by the method shown in Scheme I. The Hinsberg Stobbe type[5] of condensation between phenylglyoxal (VI) and diethyl thiodiglycolate (VII) using sodium ethoxide furnished, after saponification of the reaction mixture, 3-phenyl-2,5-thiophenedicarboxylic acid (VIII) in 57% yield. Conversion of VIII to IX followed by ring closure with aluminum chloride gave 8-oxo-8H-indeno[2,1-*b*]thiophene-2-carboxylic acid (X). The keto acid X was also transformed to the ester XI. Reduction of XI with sodium borohydride to the hydroxy ester (XII) was carried out in the hope that treatment of XII with stannous chloride and hydrogen chloride[6] would lead to replacement of the hydroxyl group by hydrogen. However, a characterizable product was not obtained. Decarboxylation of X led to a 51% yield of XIII. Sodium borohydride reduction of XIII gave XIV in 65% yield whose analytical data and spectral properties were in accordance with the assigned structure.

The preparation of I was accomplished by several methods. Wolff–Kishner reduction of XIII gave a 37% yield of I. Heating XIII with excess hydrazine gave a 10% yield of I. Wolff–Kishner reduction of X caused both decarboxylation and reduction to occur and I was obtained nearly pure from the reaction mixture by azeotropic distillation in 64% yield.

It is known that metalation of diphenylmethane and fluorene occurs in the methylene position exclusively.[7] However, metalation of 2,2′-dithienylmethane and its 5-methyl and 5,5′-dimethyl derivatives occurs in a thiophene ring.[8] During the course of this work, it was reported that metalation of 5-methyl-4H- and 5-methyl-6H-cyclopenta[*b*]thiophene was detected only in the cyclopentadiene ring.[9] Thus a competition between the methylene and thiophene ring positions may exist in metalation of I. We have found that metalation of I with *n*-butyllithium followed by carbonation gave a 70% yield of 8H-indeno[2,1-*b*]thiophene-8-carboxylic acid (XV) which arises from metalation in the methylene position. No evidence was found in the nmr spectrum for the presence of any product resulting from thiophene ring metalation.



The nmr spectra of XV and the corresponding methyl ester derivative (XVI) showed singlets owing to one methine proton at τ 5.05 and 5.21, respectively. For comparison, the nmr spectra of fluorene-9-carboxylic acid and methyl fluorene-9-carboxylate showed methine absorptions at τ 5.09 and 5.21, respectively. To verify that metalation of I in the methylene position is a result of resonance stabilization of the conjugate anion owing to the fluorene-type structure, we carried out a similar metalation reaction on 2-benzylthiophene (XVII), which lacks fluorenic character. The product formed in 77% yield from the metalation and carbonation of XVII was found to consist exclusively of 2-benzyl-

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(4) K. Gewald, E. Schenke, and H. Bottcher, *Chem. Ber.*, **99**, 94 (1966).

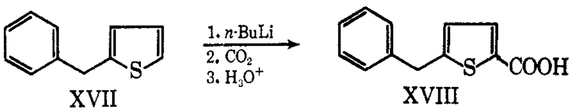
(5) (a) D. E. Wolf and K. Folkers, *Org. Reactions*, **6**, 410 (1951); (b) H. Wynberg and H. J. Kooreman, *J. Am. Chem. Soc.*, **87**, 1739 (1965).

(6) B. Sjoberg, *Arkiv Kemi*, **11**, 447 (1957).

(7) H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 258 (1954).

(8) (a) Ya. L. Goldfarb and M. L. Kirmalova, *J. Gen. Chem. USSR*, **25**, 1321 (1955); (b) Ya. L. Goldfarb and M. L. Kirmalova, *ibid.*, **29**, 881 (1959).

(9) O. Meth-Cohn and S. Gronowitz, *Acta Chem. Scand.*, **20**, 1733 (1966).



XVII XVIII

thiophene-5-carboxylic acid (XVIII) which results from thiophene ring metalation. The nmr spectrum of XVIII showed a coupling constant of 4 cps for the 3,4 hydrogens on the thiophene ring. This is consistent with 2,5-disubstitution on the thiophene ring.[10]

It can be seen that the fluorene-type structure of I is necessary for metalation to occur in the methylene position. The syntheses of II and III are at present underway and the investigation of the acidities of I, II, and III is planned.

Experimental Section[11]

Ethyl 2-Amino-8H-indeno[2,1-*b*]thiophene-3-carboxylate (V).—Into a 500-ml, one-necked flask fitted with a condenser and drying tube was introduced a mixture of ethyl (1-indanylidene)-cyanoacetate[12] (36.0 g, 0.157 mole, mp 104–105°) and sulfur (6.0 g, 0.19 mole) in 250 ml of absolute ethanol. The contents were stirred and heated until the cyano ester had dissolved and 0.8 ml of diethylamine was added to the mixture. An immediate green color appeared which changed to purple as the reaction proceeded. The reaction was allowed to continue for 2 hr with gentle refluxing. The mixture was then transferred to a 500-ml beaker and allowed to cool to room temperature. The deep blue crystals (41 g) which had formed were collected and washed with cold hexane. Sublimation at 130–150° (1.0 mm) gave 39 g (95%) of white solid, mp 130–131°. An analytical sample prepared by resublimation had mp 131–132°.

Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; S, 12.37. Found: C, 64.84; H, 5.07; S, 12.44.

The ultraviolet maxima occurred at 245 mμ (ϵ 31,600) and 305 (7800); nmr absorptions ($CDCl_3$) occurred at τ 1.70–1.95 (1 H multiplet, aromatic), 2.50–3.09 (3 H multiplet, aromatic), 3.90 (2 H broad, NH_2), 5.40, 5.52, 5.64, 5.76 (2 H quartet, methylene of ethyl, J = 7 cps), 6.41 (2 H singlet, methylene), and 8.40, 8.52, 8.64 (3 H triplet, methyl of ethyl, J = 7 cps); the infrared spectrum (KBr) showed absorptions at 3400, 3280 (NH_2), and 1640 cm^{-1} (C=O). Identical spectra were obtained for the unpurified blue crystals obtained from the reaction mixture.

Ethyl 2-Acetylamino-8H-indeno[2,1-*b*]thiophene-3-carboxylate.—Acetic anhydride (15 ml), dry pyridine (15 ml), and V (4 g, 0.015 mole) were mixed in a glass-stoppered flask and allowed to react at room temperature for 6 hr. The mixture was poured onto ice and filtered to give a quantitative yield of the amide, mp 185–186°. Sublimation gave a fine white powder, mp 188.5–189°.

Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.54; H, 5.18; N, 4.63.

The infrared spectrum (KBr) showed medium absorption at 3200 cm^{-1} (NH) and strong absorptions at 1680 (ester C=O) and 1650 (amide C=O); nmr absorptions ($CDCl_3$) occurred at τ −1.11 (1 H broad singlet, NH), 2.00–2.25 (1 H multiplet, aromatic), 2.66–3.22 (3 H multiplet, aromatic), 5.63 (2 H quartet, methylene of ethyl, J = 7 cps), 6.46 (2 H singlet, methylene), 7.13 (3 H singlet, methyl of acetyl), and 8.50 (3 H triplet, methyl of ethyl, J = 7 cps).

3-Phenyl-2,5-thiophenedicarboxylic Acid (VIII).—The reaction was carried out in a 3-l., three-necked flask fitted with a stirrer, condenser, and dropping funnel under an atmosphere of dry nitrogen. A solution of freshly prepared phenylglyoxal[13] (100 g, 0.75 mole) and diethyl thiodiglycolate (160 g, 0.78 mole) was added to a stirred, freshly prepared solution of sodium ethoxide (50 g of sodium, 2.17 g-atom, in 1.5 l. of absolute ethanol) which was maintained at 5° during the reaction. As the reaction proceeded, the contents became thick, with the formation of a yellow suspension. Stirring was continued for 2 hr at 5–10°. The contents were allowed to come to room temperature and remain without stirring for 2 days, during which a tan solid separated. The mixture was poured into 1 l. of cold water and most of the ethanol was removed on a rotary evaporator. The red aqueous solution was washed twice with 300-ml portions of ether which were discarded. Acidification of the cold solution with cold 6 *N* hydrochloric acid gave a yellow precipitate which was filtered by suction and dried *in vacuo* at 60° for 48 hr. The dry yellow solid weighed 106 g (57%) and had mp 294–296° dec. An analytical sample was prepared by recrystallization from ether–hexane, mp 296–297° dec.

Anal. Calcd for $C_{12}H_8O_4S$: C, 58.05; H, 3.25; S, 12.91. Found: C, 57.86; H, 3.36; S, 12.74.

Ultraviolet maxima occurred at 236 mμ (ϵ 14,000) and 276 (9130); the nmr showed peaks (deuterioacetone) at τ 0.10 (2 H broad, acid proton), 2.52 (1 H singlet, thiophene 4-proton), and 2.62–2.94 (5 H multiplet, aromatic); the infrared spectrum showed absorptions (KBr) at 3000 (acid) and 1685 cm^{-1} (C=O).

3-Phenyl-2,5-thiophenedicarboxylic Acid Chloride (IX).—A mixture of VIII (15 g, 0.061 mole) and thionyl chloride (35 ml) was placed in an apparatus protected from moisture and fitted with a hydrogen chloride escape tube. The mixture was heated until the acid dissolved (4 hr) and then was refluxed and stirred for 12 hr. Most of the excess thionyl chloride was removed from the dark solution on a rotary evaporator leaving a crude yellow solid. Crystallization from carbon tetrachloride gave 14 g (81%) of pure acid chloride as long yellow needles, mp 137–138°.

Anal. Calcd for $C_{12}H_6Cl_2O_2S$: C, 50.54; H, 2.12; Cl, 24.87; S, 11.25. Found: C, 50.29; H, 2.08; Cl, 24.66; S, 11.33.

The infrared spectrum (CCl_4) showed absorption at 1750 cm^{-1} (C=O).

8-Oxo-8H-indeno[2,1-*b*]thiophene-2-carboxylic Acid (X).—Into a dry, 1-l., three-necked flask fitted with a stirrer, condenser and drying tube, and addition funnel were introduced 150 ml of dry carbon disulfide and 11 g (0.087 mole) of anhydrous aluminum chloride. The apparatus was flushed with dry nitrogen for 30 sec. A solution of 10.7 g (0.039 mole) of IX in 150 ml of carbon disulfide was added dropwise at room temperature with stirring. A black complex formed during the addition. After the addition was completed, the stirring was stopped and the contents were refluxed gently for 12 hr. The mixture consisted of a hard black complex and a black carbon disulfide suspension. The suspension was poured onto 200 g of ice and shaken vigorously, causing an orange solid to form. The carbon disulfide was removed from the mixture by distillation and the residual solid was collected by filtration. A mixture of 100 g of ice and 100 ml of water was added to the hard black complex which remained in the reaction flask. This mixture was heated on a steam bath until the complex had been completely hydrolyzed to the orange product. The orange material was filtered and combined with the solid obtained from the carbon disulfide suspension. After drying, the crude product weighed 13 g. The crude acid was treated with 100 ml of warm 10% sodium hydroxide and stirred for 2 hr. A tan solid was filtered from the basic mixture, resubjected to the sodium hydroxide treatment, and then filtered, leaving some insoluble material which was discarded. The aqueous solutions were combined and washed with ether (100 ml). Acidification of the cold aqueous solution with cold 6 *N* hydrochloric acid yielded an orange precipitate which was filtered and dried giving 5.2 g (59%) of product, mp 245–247.5° dec. An analytical sample was prepared by recrystallization from benzene–hexane, mp 245–247° dec.

Anal. Calcd for $C_{12}H_6O_3S$: S, 13.99 N.E. 230. Found: S, 14.14 N.E. 229.

The ultraviolet spectrum had maxima at 249 mμ (ϵ 24,610), 263 sh (19,870), 320 (9010), and 334 (9200); nmr absorptions (DMSO) occurred at τ 2.00 (1 H singlet, thiophene 3-proton) and 2.10–2.89 (5 H multiplet, aromatic and acid protons); the infrared spectrum showed absorptions (KBr) at 3000 (acid) and 1690 cm^{-1} (C=O).

Methyl 8-Oxo-8H-indeno[2,1-*b*]thiophene-2-carboxylate (XI).—The crude acid product from the preparation of X (*ca.* 13 g) was mixed with 200 ml of methanol and 5 ml of concentrated hydrochloric acid and refluxed for 8 hr. The hot mixture contained some insoluble material which was removed by filtration

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[10] S. Gronowitz, *Advan. Heterocyclic Chem.*, **1**, 8 (1963).

[11] All temperature readings are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Nuclear magnetic resonance spectra were recorded on a Varian HA-60 spectrometer using tetramethylsilane as an internal standard (τ 10) and solvents as specified. The ultraviolet spectra were determined in 95% ethanol on a Perkin-Elmer Model 350 spectrophotometer. Infrared spectra were recorded on the Perkin-Elmer Model 21 and Model 137 spectrophotometers.

[12] A. C. Cope and L. Field, *J. Am. Chem. Soc.*, **71**, 1589 (1949).

[13] H. A. Riley and A. R. Gray, "Organic Syntheses," Coll. Vol. II, H. Gilman and A. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p 509.

and sublimed to give XI (1 g) as an orange product. The filtrate on cooling afforded crystals of the ester XI (6 g). The combined solids were recrystallized from methanol yielding 6.7 g (70%, based on 0.039 mole of IX) of bright orange needles, mp 167–170°. Sublimation at 120–150° (0.3 mm) furnished 6.5 g (68%) of analytical material, mp 173–174.5°.

Anal. Calcd for $C_{13}H_8O_3S$: C, 63.92; H, 3.30; S, 13.13. Found: C, 63.65; H, 3.48; S, 13.20.

The ultraviolet maxima occurred at 250 mμ (ε 30,400), 265 (30,200), 274 sh (27,700), 307 sh (4400), 320 (5500), and 334 (5500); nmr absorptions ($CDCl_3$) occurred at τ 2.49 (1 H singlet, thiophene 3-hydrogen), 2.62–3.17 (4 H multiplet, aromatic), and 6.20 (3 H singlet, methyl); the infrared spectrum (KBr) showed carbonyl absorptions at 1720 and 1700 cm^{-1}.

Methyl 8-Hydroxy-8H-indeno [2,1-*b*]thiophene-2-carboxylate (XII).—Sodium borohydride (2.5 5g) was added in 0.5-g portions to a stirred suspension of XI in s0 ml of ethanol at room temperature. The contents became lightly warm and a white solid separated on the sides of the flask. Stirring was continued for 1 hr. The contents were poured into a separatory funnel containing 100 ml of ether. Water (50 ml) was added and the mixture was shaken vigorously. The ether layer was separated and the aqueous layer was saturated with sodium chloride and extracted thoroughly with ether (100 ml). The combined ether extracts were dried ($MgSO_4$) and concentrated on a rotary evaporator. A dark oil remained which solidified on cooling to give 4 g of crude tan product. One recrystallization from hexane gave 2.9 g (72%) of yellow crystals, mp 143–146°. Sublimation of 0.5 g of the yellow product at 130–140° (1 mm) gave slightly less than 0.5 g of analytical product as bright yellow needles, mp 147–148°.

Anal. Calcd for $C_{13}H_{10}O_3S$: C, 63.40; H, 4.09; S, 13.02. Found: C, 63.22; H, 3.87; S, 13.20.

Ultraviolet maxima occurred at 247 mμ (ε 60,000), 252 (61,600), and 321 (2540); nmr peaks ($CDCl_3$) occurred at τ 0.65 (1 H broad, OH), 2.31–2.98 (5 H multiplet, aromatic), 4.41 (1 H singlet, CH), and 6.36 (3 H singlet, CH_3); the infrared spectrum showed absorptions (KBr) at 3450 (OH) and 1675 cm^{-1} (C=O).

8H-Indeno[2,1-*b*]thiophen-8-one (XIII).—A mixture of X (2.7 g, 11.7 mmoles) and 30 ml of freshly distilled quinoline was heated to 200° in an apparatus protected from moisture. Copper powder (0.3 g) was added in 0.1-g portions during 15-min intervals. The mixture was stirred and heated at 220° for 2 hr. The cooled dark contents were poured onto 50 g of ice and acidified with 6 *N* hydrochloric acid. After separation of the copper powder by filtration and washing the residue with ether, the filtrate was thoroughly extracted with ether. The ether extracts were dried ($MgSO_4$) and concentrated, giving a dark liquid which solidified on standing, 2 g (92%). One crystallization from hexane (Norit) gave 1.1 g (51%) of long golden needles, mp 106–107°. An analytical sample was prepared by sublimation at 90–100° (0.5 mm) as a bright yellow solid melting at 109–110° (lit.[1] mp 109–110°).

Anal. Calcd for $C_{11}H_6OS$: C, 70.94; H, 3.25; S, 17.22. Found: C, 70.99; H, 3.27; S, 17.29.

The ultraviolet spectrum showed maxima at 242 mμ (ε 36,800), 247.5 (40,970), 300 (4320), and 330 (4080); nmr peaks ($CDCl_3$) occurred at τ 2.28, 2.35 (1 H doublet, thiophene 2-proton, J = 5 cps), 2.21–3.05 (5 H multiplet, aromatic) which contained a doublet at 2.99, 3.06 (thiophene 3-proton, J = 5 cps); the infrared spectrum showed absorption (KBr) at 1690 cm^{-1} (C=O).

8H-Indeno[2,1-*b*]thiophene (I). Method A.—Into a 50-ml flask fitted with a distilling head and condenser was introduced keto acid X (2.0 g, 8.7 mmoles), potassium hydroxide (1.3 g, 23.2 mmoles), 95% hydrazine (3 ml), and diethylene glycol (15 ml). The mixture was heated to 200° and the distillate was collected. The residue was cooled and 20 ml of water was added to the flask and the contents were distilled. White solid material collected on the sides of the condenser and was removed with a metal spatula. This procedure was repeated until no more solid collected in the condenser. The solid was taken up in ether, dried ($MgSO_4$), and the ether was evaporated yielding 0.95 g (64%) of white product, mp 65–67°. Sublimation at 60° (1 mm) gave 0.91 g (62%) of analytical material, mp 66–67°.

Method B.—A mixture of ketone XIII (0.3 g, 1.68 mmoles) and 95% hydrazine (1 ml) was heated at 200° for 3.5 hr. The contents were mixed with water and heated causing azeotropic distillation of the white product. The solid was taken up in ether, dried, and the ether was removed yielding 0.03 g (10%) of I, mp 57–60°.

Method C.—Into a 25-ml flask fitted with a distilling head and condenser were introduced XIII (0.5 g, 2.68 mmoles), potassium hydroxide (0.5 g, 8.92 mmoles), 95% hydrazine (1 ml), and diethylene glycol (5 ml). The contents were heated slowly to 200° with vigorous evolution of gas occurring at 150°. After excess hydrazine and water had distilled, the distilling head was replaced with a vertical condenser and the reaction was continued for 2 hr at 200°. The dark reaction mixture was cooled and poured onto 50 g of ice and acidified with 3 *N* hydrochloric acid. The aqueous solution was extracted thoroughly with ether (200 ml). The ether extract was dried ($MgSO_4$) and concentrated yielding a dark oil which was dissolved in hexane and passed through acid-washed alumina giving 0.17 g (37%) of I as a white powder, mp 57–60°. Sublimation gave 0.165 g of pure material, mp 66–67°.

Anal. Calcd for $C_{11}H_8S$: C, 76.70; H, 4.68; S, 18.62. Found: C, 76.73; H, 4.86; S, 18.67.

Ultraviolet maxima occurred at 227 mμ (ε 17,900), 233 (17,190), 263 (9060), and 272 sh (7800); nmr absorptions ($CDCl_3$) occurred at τ 2.33–3.05 (6 H multiplet, aromatic) and 6.20 (2 H singlet, CH_2); the infrared spectrum showed (KBr) strongest absorption at 725 cm^{-1}; an nmr spectrum of fluorene showed methylene absorption at τ 6.19 ($CDCl_3$).

8H-Indeno[2,1-*b*]thiophene-8-carboxylic Acid (XV).—Into a 100-ml, three-necked flask fitted with a condenser, magnetic stirring apparatus, and addition funnel under an atmosphere of dry nitrogen were introduced I (0.70 g, 4.7 mmoles, 100% pure by vpc) and dry ether (40 ml). Ethereal *n*-butyllithium[8] (3.3 ml, 1.6 *N*, 5.3 mequiv) was added dropwise to the stirred solution at room temperature causing the appearance of a bright yellow color which gradually changed to orange. After the addition was completed (5 min), the contents were refluxed gently for 0.5 hr during which a white precipitate appeared. Freshly crushed Dry Ice (5–10 g) was added directly to the warm contents causing a vigorous reaction and a white precipitate to form. Enough water was added to dissolve the precipitate and the mixture was transferred to a separatory funnel. The aqueous layer was separated and extracted once with 15 ml of ether. The combined ether extracts were dried ($MgSO_4$) and evaporated to give 0.1 g of starting material. The aqueous solution was cooled and acidified with 6 *N* hydrochloric acid giving a yellow precipitate. The product was taken up in ether and dried ($MgSO_4$); the ether was evaporated yielding 0.61 g (70% based on 4.7 mmoles of starting material) of XV, mp 198–200° dec. An analytical sample was obtained by recrystallization from benzene and had mp 205–206° dec.

Anal. Calcd for $C_{12}H_8O_2S$: C, 66.65; H, 3.72; S, 14.83. Found: C, 66.45; H, 3.65; S, 14.62.

The infrared spectrum (KBr) showed absorptions at 2900 (acid) and 1680 cm^{-1} (C=O); nmr peaks (deuterioacetone) occurred at τ 2.18–2.99 (aromatic multiplet), 5.05 (CH), and 5.40 (broad acid OH). For comparison, the nmr spectrum (deuterioacetone) of fluorene-9-carboxylic acid showed absorptions at τ 2.00–2.82 (aromatic multiplet), 5.09 (CH), and 5.25 (broad acid OH).

Methyl 8H-Indeno[2,1-*b*]thiophene-8-carboxylate (XVI).—A solution of 440 mg (2.02 mmoles) of XV in 6 ml of methanol containing 6 drops of concentrated hydrochloric acid was refluxed for 5 hr. The cooled solution was poured into water and extracted with ether. The ether extract was dried ($MgSO_4$) and evaporated yielding a brown solid which was sublimed at 80° (0.1 mm) to give 0.3 g (64%) of yellow XVI, mp 67–70°. After two recrystallizations from hexane, an analytical sample was obtained as small yellow prisms melting at 79–80.5°.

Anal. Calcd for $C_{13}H_{10}O_2S$: C, 67.80; H, 4.38; S, 13.92. Found: C, 67.58; H, 4.56; S, 13.98.

The infrared spectrum (KBr) showed absorption at 1725 cm^{-1} (C=O); nmr peaks ($CDCl_3$) occurred at τ 2.24–3.00 (6 H multiplet, aromatic), 5.21 (1 H singlet, CH), and 6.29 (3 H singlet, CH_3). For comparison, the nmr peaks ($CDCl_3$) for methyl fluorene-9-carboxylate occurred at τ 2.20–2.91 (8 H multiplet, aromatic), 5.21 (1 H singlet, CH), and 6.36 (3 H singlet, CH_3).

2-Benzylthiophene (XVII).—A mixture of 2-benzoylthiophene (7.0 g, 0.037 mole, mp 56–57°), potassium hydroxide (6 g, 0.11 mole), 95% hydrazine (3 ml), and diethylene glycol (30 ml) was treated according to method A for the preparation of I. The distillate was taken up in ether, dried ($MgSO_4$), concentrated, and distilled giving 3.8 g (59%) of XVII, bp 81–84° (0.2 mm) [lit.[14] bp 75° (0.15 mm)] as a clear, colorless liquid. The infrared absorption (neat) occurred at 690 cm^{-1}; nmr peaks ($CDCl_3$) occurred at τ 2.80 (5 H singlet, phenyl), 2.83–3.32 (3 H multiplet, thiophene), and 5.92 (2 H singlet, CH_2).

2-Benzylthiophene-5-carboxylic Acid (XVIII).—Ethereal *n*-butyllithium (4.5 ml, 1.6 *N*, 7.4 mequiv) was added dropwise to a solution of XVII (1.0 g, 5.8 mmoles) in 50 ml of dry ether. The reaction and work-up was carried out according to the procedure described for the preparation of XV. The crude yellow crystalline product weighed 1 g (77%) and had mp 125–127°. An analytical sample was prepared as white plates from benzene and had mp 129–131°.

Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.04; H, 4.62; S, 14.69. Found: C, 66.27; H, 4.80; S, 14.80.

Nmr spectra of the crude material and analytical sample were identical. The nmr peaks ($CDCl_3$) occurred at τ −2.00 (1 H singlet, acid), 2.29, 2.35 (1 H doublet, thiophene, J = 4 cps), 2.75 (5 H singlet, phenyl), 3.20, 3.27 (1 H doublet, thiophene, J = 4 cps), and 5.88 (2 H singlet, methylene); the infrared spectrum showed absorptions (KBr) at 2900 (acid) and 1650 cm^{-1} (C═O).

Registry No.—I, 246-98-0; V, 13132-06-4; VIII, 13132-07-5; IX, 13732-08-6; X, 13132-09-7; XI, 13132-10-0; XII, 13132-11-1; XIII, 13132-12-2; XV, 13132-13-3; XVI, 13132-14-4; XVII, 13132-15-5; XVIII, 13132-16-6; ethyl 2-acetylamino-8H-indeno-[2,1-*b*]thiophene-3-carboxylate, 13127-20-3.

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Preparation and Some Chemistry of Tricyclopropylphosphine[1]

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Tricyclopropylphosphine has been prepared in yields as high as 80% by reaction of cyclopropyllithium with triphenyl phosphite. The pK_a of tricyclopropylphosphine is very nearly the same as that of tri-*n*-propylphosphine. The ylide, tricyclopropylphosphinebenzoylmethylene, has been prepared. Its pK_a has been determined and its rate of reaction with benzaldehyde has been compared with that of triphenylphosphinebenzoylmethylene. Several other derivatives of tricyclopropylphosphine have been prepared and characterized. The pK_a measurements and rate data show quite conclusively that tricyclopropylphosphine has properties like those of other trialkylphosphines.

The interaction of a cyclopropane ring with a bonded unsaturated carbon atom has been the subject of a vast amount of study. It is now well recognized that the cyclopropane ring can function as an electron donor and thus one finds extraordinary stabilization of a cyclopropylcarbinyl carbonium ion for example.[3]

It does not appear that any systematic study has been made of the possible modes of interaction of a cyclopropane ring with third-row elements such as silicon, phosphorus, and sulfur. Such studies will certainly be of interest and this report describes a beginning of a broad study in this area. In particular the synthesis and some properties of tricyclopropylphosphine and some of its derivatives are reported.

Results and Discussion

The general method for preparing trisubstituted phosphines involves the reaction of a Grignard or organolithium reagent with phosphorus trichloride.[4] Attempts to prepare tricyclopropylphosphine by treatment of phosphorus trichloride with cyclopropylmagnesium bromide or cyclopropyllithium were not successful, and thus an alternate route for its preparation was sought. Gilman and Vernon[5] and Willans[6] have prepared trisubstituted phosphines by allowing Grignard and organolithium reagents to react with triphenyl phosphite.

This has been shown to be the method of choice for the preparation of tricyclopropylphosphine and it has been prepared in yields as high as 80% by reaction of excess cyclopropyllithium with triphenyl phosphite. Tricyclopropylphosphine is a liquid, bp 38–42° (0.6 mm); it has the usual disgusting odor associated with the lower trialkylphosphines. It does not spontaneously ignite in air as do trimethyl- and triethylphosphine. The infrared spectrum shows typical absorptions at 9.85 μ. The nmr spectrum consists of a multiplet centered at 0.4 ppm which is of course in agreement with the assigned structure.

Streuli[7] has determined basicities of a wide variety of trisubstituted phosphines in nonaqueous media by a potentiometric method. The results of these determinations were then correlated with the behavior of the more basic phosphines in mixed aqueous–organic solvents, and finally with analogous basicity studies of amines in water and the same mixed solvent systems. In this manner, it was possible to calculate values for the relative pK_a's of the phosphines in aqueous media.

The pK_a of tricyclopropylphosphine is found to be 7.60 by this method. Freshly distilled tri-*n*-butylphosphine was included in the titration series as a control. The observed pK_a was 8.43 (lit.[6] 8.43). Streuli reports the following pK_a values: tri-*n*-propylphosphine, 8.64; triisobutylphosphine, 7.97; tricyclohexylphosphine, 9.70; and triphenylphosphine, 2.73. In general, triarylphosphines are considerably less basic than trialkylphosphines. This is undoubtedly

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