lar reactions (with the possible exception of nitrogen pentoxide) agree with theories based on the assumption that reaction occurs whenever a definite amount of energy becomes localized in one or, at most, several degrees of freedom.

The thermal decomposition of hydrazoic acid was found to be catalyzed by the pyrex walls of the reaction vessel.

The thermal decomposition of methyl azide was found to be homogeneous and first order during a given experiment but the rate constant becomes lower at lower initial pressures.

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[Contribution from the Chemistry Laboratory of the University of Michigan]

SOME THIOPHENE ANALOGS OF DI-, TRI- AND TETRAPHENYLMETHANE COMPOUNDS[1]

By Wesley Minnis

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In the course of an attempt to extend the results of a previous investigation[2] of free radicals containing the thiophene ring, studies were made of various analogs of di-, tri- and tetraphenylmethane compounds in which one phenyl group was replaced by the thienyl group.

In general, methods of synthesis used in the benzene series were successfully applied. Usually the thiophene analogs were isolated with more difficulty, probably because of the greater reactivity of the thiophene nucleus, which tends toward the formation of by-products. After isolation, decomposition often occurred under conditions which do not similarly affect the phenyl compounds. For example, phenylthienyl ketone dichloride could not be distilled under reduced pressure without decomposition, whereas benzophenone dichloride is readily purified in such manner. The diphenylcarbinol halides have been made and are moderately stable, but attempts to prepare phenylthienylcarbinol halides resulted in deep-seated decomposition. The reduction of diphenylthienylcarbinol gave only a 50% yield of methane as contrasted with the practically quantitative yield of triphenylmethane from its carbinol. Diphenylthienylcarbinol halides were much less stable than the triphenylcarbinol halides, and the same was true of the corresponding free radicals.

The instability of the free radical, diphenylthienylmethyl, was reminiscent of the behavior of phenylthioxanthyl,[3] and it is tentatively suggested

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[1] This article is an abstract of Part II of the dissertation submitted to the faculty of the University of Michigan, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. 1922.

[2] Gomberg and Jickling, This Journal, **35**, 446 (1913).

[3] Gomberg and Minnis, *ibid.*, **43**, 1940 (1921).

that the presence of a bivalent-ring sulfur atom in its structure confers instability upon a free radical.

Of novel interest may be noted the preparation of a di-triphenylmethyldithienyl by a peculiar side reaction during a Grignard reaction; and of α-naphthylphenylthienylcarbinol, one of the few asymmetric triarylcarbinols so far described.

Phenylthienyl Ketone Dichloride, $C_6H_5CCl_2C_4H_3S$.—Phenylthienyl ketone was prepared by the method described in the literature[4] but with higher yield than heretofore claimed, namely, 87%. A mixture of 19 g. of ketone and 22 g. (5% excess) of phosphorus pentachloride was heated at 60 to 80° for one hour. The phosphorus oxychloride formed in the reaction was distilled under reduced pressure and the partial vacuum maintained for one hour in order to remove excess pentachloride. The residual liquid could not be distilled under 20 mm. pressure without decomposition.

Anal. Calcd. for $C_{11}H_8Cl_2S$: Cl, 29.18. Found: Cl, 29.39.

Phenylthienylcarbinol, $C_6H_5CHOHC_4H_3S$.—The procedure of Montagne[5] for reducing a ketone to the corresponding carbinol by means of zinc dust and sodium alcoholate gave a product with sulfur content 3% under the theoretical. The method of Cohen[6] gave good results. To 5 g. of ketone dissolved in 40 cc. of alcohol and 10 cc. of concd. ammonium hydroxide solution was added 10 g. of aluminum amalgam and the mixture was refluxed for six hours. After cooling and filtration, the filtrate was poured into water, whereupon crystals separated after long standing. Recrystallized from ether, the crystals melted at 57 to 58°. Non-identity with the ketone was proved by a mixed melting point.

Anal. Calcd. for $C_{11}H_{10}OS$: C, 69.43; H, 5.30; S, 16.86. Found: C, 69.29; H, 5.23; S, 17.09. *Mol. wt.* Calcd.: 190. Found (cryoscopic in benzene): 195, 187.

Attempts to prepare the carbinol halides by passing dry hydrogen chloride or hydrogen bromide into solutions of the carbinol produced dark-colored oils which evolved gases while drying in a vacuum desiccator, leaving black lava-like solid residues.

Diphenylthienylcarbinol $(C_6H_5)_2C(OH)C_4H_3S$.—This has been described by Thomas[7] and Gomberg and Jickling[2] as prepared from benzophenone and the Grignard reagent from iodothiophene. A slightly higher yield was obtained by synthesis from phenylmagnesium bromide and phenylthienyl ketone, and the product melted at 131°, higher than either of the temperatures previously reported. Condensation of benzophenone dichloride with thiophene in carbon disulfide solution by means of aluminum chloride gave a much lower yield.

When boiled with formic acid[8] the carbinol was reduced to the methane.[9] About half of the carbinol, however, reacted to form a new compound, m. p. 174°, which gave analytical values corresponding to the methane but had a molecular weight of about double that of the methane.

Diphenylthienylcarbinol Bromide $(C_6H_5)_2CBrC_4H_3S$.—A solution of the carbinol in benzene or a suspension in low-boiling petroleum ether was saturated with dry hy-

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[4] Comey, *Ber.*, **17**, 790 (1884).

[5] Montagne, *Rec. trav. chim.*, **25**, 402 (1906).

[6] Cohen, *ibid.*, **38**, 86 (1919).

[7] Thomas, *Bull. soc. chim.*, **5**, 730 (1909); Thomas and Couderc, *ibid.*, **23**, 326 (1918).

[8] Kauffmann and Pannwitz, *Ber.*, **45**, 766 (1912).

[9] Levi, *ibid.*, **19**, 1623 (1886).

drogen bromide. A few lumps of calcium bromide were added to take up the water formed in the reaction. After filtration and evaporation under reduced pressure, crystals of melting point 110 to 111° were obtained. Originally only slightly colored, they quickly turned deep purple, even in a sealed tube in the dark.

Anal. Calcd. for $C_{17}H_{13}BrS$: Br, 24.31. Found: Br, 24.30, 24.09.

Diphenylthienylcarbinol Chloride.[2]—Best results were obtained by suspending the carbinol in petroleum ether with a few lumps of calcium chloride and slowly passing in dry hydrogen chloride to saturation. The solution was evaporated under reduced pressure and the crystals were washed with very small amounts of ice-cold petroleum ether and dried in a current of dry air at room temperature. They melted at 80 to 81° and the yield was 90%. The anilide, $(C_6H_5)_2C_4H_5SCNHC_6H_5$, melts at 118–119°.

After standing for a short time the crystals of the carbinol chloride became colored but no change in the chlorine content could be detected by analysis. No hydrogen chloride was given off when the crystals were held at 65° for twelve hours, or when a benzene solution was held at 65° for twenty-four hours.

Diphenylthienylmethyl.—The free radical was prepared by shaking benzene, bromobenzene or xylene solutions of the chloride or bromide with molecular silver at room temperature. The solutions were immediately colored red. Measurements of the amount of free radical formed by the usual oxygen absorption test[10] gave very erratic results. Depending upon the length of time the sample was left in the apparatus, absorptions ranged from 25 to 200% of the quantity theoretically required for the formation of a peroxide. Determination of the amount of silver chloride formed proved that the metal reacted completely with the halogen.

Attempts to isolate the solid free radical by usual methods gave pink crystals of melting point 157 to 162°, which gave oxygen absorptions of only 20% of the calculated value. The general behavior of this free radical was very much like that of phenylthioxanthyl.[3]

5,5′-Di-triphenylmethyl-2,2′-dithienyl, $(C_6H_5)_3CC_4H_2SC_4H_2SC(C_6H_5)_3$.—Triphenylthienylmethane was made by Weisse[11] from triphenylcarbinol and thiophene with phosphorus pentoxide as condensing agent. An attempt was made to prepare this compound from triphenylchloromethane and the Grignard reagent of iodothiophene, by analogy to the method for making tetraphenylmethane.[12] Besides quantities of triphenylmethyl peroxide and triphenylmethane, a new product was obtained, in 5 to 40% yields, which was not the methane of Weisse. The latter melts at 237°, whereas the new substance melted at 277°, after recrystallizing from ethylene dibromide.

The structure of this new product was established by its synthesis from triphenyliodothienylmethane through the Ullmann condensation, using copper-bronze.

$$2(C_6H_5)_3CC_4H_2SI + Cu \longrightarrow (C_6H_5)_3CC_4H_2SC_4H_2SC(C_6H_5)_3 + CuI_2$$

The 5,5′-positions of the triphenylmethyl groups in the thiophene rings have not been proved, but rest on the assumptions of Weisse for the constitution of the products of his phosphorus pentoxide condensations.

Two grams of triphenyliodothienylmethane was mixed with an equal volume of white sand, placed in a small flask and heated in a sulfuric acid bath to 200°. As the temperature rose further, 2 g. of copper-bronze was gradually added with stirring. When the temperature reached 250°, the flask was removed, cooled and the contents extracted with hot benzene. Concentration of the benzene extract gave a 90% yield of crystals of melting point 277°. Comparison of physical properties, solubilities and

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[10] Gomberg and Schoepfle, THIS JOURNAL, **39**, 1661 (1917).

[11] (a) Weisse, *Ber.*, **28**, 1537 (1895); (b) *ibid.*, **29**, 1402 (1896).

[12] Gomberg and Cone, *Ber.*, **39**, 1461 (1906).

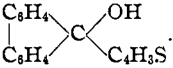
mixed melting point proved the identity of this compound with that from the Grignard condensation. Inasmuch as the latter reaction was carried out in an atmosphere of hydrogen, the formation of the dithienyl required an oxidation at the expense of part of the reacting compounds.

The dithienyl gave no color with concd. sulfuric acid, was markedly insoluble in most solvents in the cold and was moderately soluble in hot carbon tetrachloride, ethyl acetate, naphthalene, nitrobenzene, bromoform, chloroform and benzene.

Anal. Calcd. for $C_{46}H_{34}S_2$: C, 84.88; H, 5.27; S, 9.86. Found: C, 84.85, 84.48; H, 5.62, 5.43; S, 9.81, 9.79. *Mol. wt.* Calcd.: 650. Found:[13] 670 (benzene); 668 (chloroform).

Upon bromination in boiling carbon tetrachloride solution, a dibromo compound, of melting point 287°, was obtained.

Biphenylenethienylcarbinol,



$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\C_4H_3S\end{matrix}$

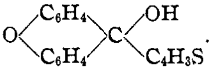
.—To the Grignard reagent from iodothiophene and magnesium in ether was added a benzene–ether solution of fluorenone. The light green precipitate which formed was filtered, washed and treated with ice and acetic acid. The crude carbinol was extracted with ether, washed with sodium carbonate solution and water and dried. After evaporation of the solvent, the oil was recrystallized from petroleum ether. Colorless crystals of melting point 81 to 82° were obtained. After long standing they turned green.

Anal. Calcd. for $C_{17}H_{12}OS$: C, 77.24; H, 4.58; S, 12.13. Found: C, 76.89; H, 4.62; S, 12.20.

α-Naphthylphenylthienylcarbinol $(C_{10}H_7)(C_6H_5)(C_4H_3S)COH$.—α-Naphthylphenyl ketone in ethereal solution was treated with thienylmagnesium iodide. The precipitate was washed, iced and steam distilled. The residue from the distillation was recrystallized from a mixture of ether and petroleum ether, giving colorless crystals with a melting point of 131°.

Anal. Calcd. for $C_{21}H_{16}OS$: C, 79.71; H, 5.10; S, 10.14. Found: C, 79.65; H, 4.92; S, 10.20.

Thienylxanthenol,



$O\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\C_4H_3S\end{matrix}$

.—Xanthone was added in small quantities to the ether solution of thienylmagnesium iodide. The reaction was sluggish and required warming. The yellow precipitate was filtered, iced and extracted with ether. Concentration of the extract and recrystallization from ethyl acetate gave a product with melting point of 168 to 169°.

Anal. Calcd. for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.32; S, 11.44. Found: C, 72.78; H, 4.28; S, 11.42.

Thienylxanthenol chloride was made by passing dry hydrogen chloride into a solution of the carbinol in ethyl acetate. Without isolating the chloride, solutions of metal halides in ethyl acetate were added and the following double salts were obtained: $C_{17}H_{11}OSCl{\cdot}FeCl_3$, bronze plates, m. p. 198°; $C_{17}H_{11}OSCl{\cdot}HgCl_2$, small red crystals, melting with decomposition at 182 to 198°, varying with the rate of heating; $C_{17}H_{11}OSCl{\cdot}ZnCl_2$, red crystals, m. p. 225 to 227°.

The author wishes to express his gratitude to Professor M. Gomberg, who suggested and supervised this investigation, and to the National Aniline and Chemical Company for the aid of its Fellowship.

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[13] By ebullioscopic method of Menzies and Wright, THIS JOURNAL, **43,** 2314 (1921).

Summary

Various compounds, formally derived from di-, tri- and tetraphenylmethane compounds by replacement of one phenyl group with a thienyl group, have been prepared by synthetic methods analogous to those used in preparing the corresponding phenyl compounds. The thienyl compounds were in general less stable than their phenyl analogs. The free radical, diphenylthienylmethyl, was found to possess the same instability as phenylthioxanthyl.

BUFFALO, NEW YORK

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

MONONITRO- AND DINITROTHIOPHENES. II. A STUDY OF VAPOR PRESSURES

BY V. S. BABASINIAN AND J. G. JACKSON

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Introductory

It is a noteworthy fact that, while the physical properties of thiophene have been made the subject of extensive study, its derivatives have received scanty attention only. Aside from sparse references to crystallographic, microscopic, optical, spectrochemical or physico-chemical studies, the literature makes no mention of the critical constants of the numerous derivatives of thiophene. This scarcity of information is probably explained by the fact that difficulty has often been experienced in the synthesis of thiophene compounds. Throughout the literature one is impressed by the glaring omission of references to percentage yields. In their extensive researches on the thiophene series, Steinkopf and co-workers[1] have recently described improved methods of preparation, but if percentage yield be taken as a measure of efficiency, the results of these workers will in numerous instances be found to leave a great deal to be desired.

During the past three years methods have been developed in this Laboratory for the quantity production of mononitro- and dinitrothiophene. The notable absence in the literature of critical data for the thiophene series has suggested a study of the vapor pressures of these nitro compounds.

Preparation and Purification of Materials.—The compounds employed in this study were synthesized by the methods outlined by one of the authors.[2] Mononitrothiophene was readily purified by steam distillation and by subsequent crystallization

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[1] (a) Steinkopf and co-workers, *Ann.*, **403**, 1–72 (1914); (b) **407**, 94–108 (1915); (c) **413**, 310–349 (1917); (d) **424**, 1–71 (1921); (e) **428**, 123–163 (1922); (f) **430**, 41–161 (1923); (g) **437**, 14–36 (1924); (h) **448**, 205–222 (1926).

[2] Babasinian, THIS JOURNAL, **50**, 2749, 2751 (1928).