in the above menstruum, especially when the amine hydrochloride is present in excess.[1] Some typical results are given below:

	Quantity of nitrile. Cc.	Quantity of alcohol. Cc.	Amine hydrochloride. Gm.	Ammonium chloride. Gm.	Theoretical amine hydrochloride. Gm.
Methyl cyanide....	5	50	3.8	0.63	7.9
	5	75	7.6	0.0	7.9
	5	100	7.58	0.0	7.9
Ethyl cyanide.....	5	50	4.36	0.5	7.0
	5	75	6.4	0.07	7.0
Propyl cyanide....	5	75	6.1	0.03	6.3
	5	100	6.0	0.06	6.3

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THIOPHENE ANALOGS OF TRIPHENYLETHYL.

[PRELIMINARY NOTE.]

BY M. GOMBERG AND R. L. JICKLING.

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Thus far the discussion of the triphenylmethyl question has been limited to the study of compounds containing phenyl groups or some of its many homologs. We have now endeavored to extend our study of this subject into compounds of the hetereocyclic series and have attempted to prepare analogs of triphenylmethyl containing other than exclusively aromatic groups.

By means of the Grignard synthesis, thienyldiphenyl carbinol (m. p. 128°) has been prepared from α-iodothiophene and benzophenone.[2] Treating the carbinol with hydrogen chloride gives the chloride, melting at 81°. Analysis: calculated Cl, 12.41%; found Cl, 12.40%. The chloride as first obtained is colorless but becomes more or less colored upon exposure, being in this respect much more sensitive than triphenylmethyl chloride. A benzene solution of the chloride assumes at once a deep red color, when treated with molecular silver or other metals. That the hydrocarbon thus formed is unsaturated in character, has been shown by its absorption of oxygen. By shaking the chloride in nitrobenzene with molecular silver, sealed in the presence of air, the absorption was found to be 5.48%, calculated 5.60%. Similar experiments with benzene as solvent gave 5.98% and 6.07% absorption of oxygen. By shaking the chloride in benzene with silver out of presence of air and afterward exposing to air the hydrocarbon thus formed, the rate of absorption of oxygen has been found to be much lower than that of triphenylmethyl, the amount of absorption finally reaching, however, about three-fourths the theoretical. In this respect the thienyl compound resembles diphenylenephenyl methyl.[3]

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[1] Winkler, *Ann.*, 93, 324; Ray and Rakshit, *J. Chem. Soc.*, 99, 1471.

[2] *Bull. de soc. chim.*, 5, 734 (1909).

[3] *Ber.*, 39, 2969 (1906).

The amount of oxygen absorbed indicates the formation of a peroxide, similar to that formed in the case of triphenylmethyl:

$$2C_4H_3S(C_6H_5)_2C + O_2 = C_4H_3S(C_6H_5)_2C.O.O.C(C_6H_5)_2C_4H_3S.$$

But the peroxide as such has not been isolated in a condition sufficiently pure for analysis.

Dithienylphenyl carbinol (m. p. 90°) has also been prepared by the Grignard synthesis from benzoic ester and thienyl iodide, but the conditions for its conversion into the chloride have not as yet been determined. In connection with the thiophene derivatives the corresponding furfurane derivatives will be studied.

ANN ARBOR, MICHIGAN.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

1,4-DITHIENES. I.

BY TREAT B. JOHNSON, ROBERT C. MORAN, AND EDWARD F. KOHMANN.

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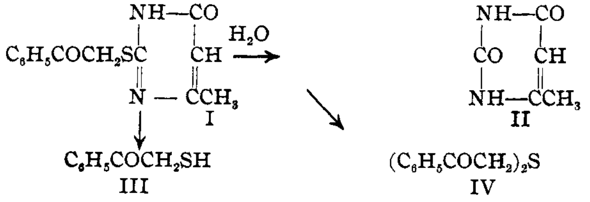
This paper is a contribution to our knowledge of the chemistry of sulfur compounds containing the thioglycollide grouping —S—CH_2—CO—.

In a recent publication from this laboratory,[1] Johnson and Moran described the behavior of 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine I, on hydrolysis. They made the interesting observation that this mercaptopyrimidine undergoes hydrolysis smoothly, by digestion with strong hydrochloric acid, forming 4-methyluracil II, as expected, and a crystallin sulfur compound, which did not possess the properties of a mercaptan III, and also was not identical with the phenacylsulfide (m. 77°) IV, described by Tafel and Mauritz.[2] The high percentage of sulfur obtained by analysis and the characteristic properties of the compound indicated that we were dealing with a representative of a new type of substances. The data, which we have obtained and now discuss in this paper, confirms our original assumption.



We now conclude that this hydrolytic product is a representative of a class of cyclic sulfur compounds to which we shall assign the name—*dithienes*. In other words, the compound is a diphenyl-derivative of the heterocycle VI, and its structure is to be represented by formula V. The

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[1] *Am. Chem. J.*, 48, 307.

[2] *Ber.*, 23, 3474.