distilled off under reduced pressure after the preparation of the reagent, in order to remove benzene formed by moisture or other side reactions. The mixture of anisole and pyridine dissolves not only water in the quantity used but also the basic magnesium compounds.

The hydrocarbons obtained in the decompositions were burned over cupric oxide, and the radioactivity of the water obtained as well as that of the initial water used in the reaction was determined by means of a Geiger-Müller counter [2].

Some experiments with methylmagnesium iodide were carried out in order to check the influence on the isotope effect of the concentration of the Grignard reagent, the rate of addition, the diameter of the syringe summit, and the conditions of drying the methane. Provided the addition rate was low enough and the summit sufficiently thin, reproducible results were obtained, and the concentration of the Grignard reagent was found to be of little importance.

With methylmagnesium iodide the syringe addition method was used, and decompositions were carried out at different temperatures, 20°, 25°, 30° and 40° C, for the measurement of the temperature coefficient of k_T/k_H and in order to give an estimation of the difference between the apparent activation energies of the tritium and protium reactions. The results are given in Fig. 1, where k_T/k_H is plotted on a logarithmic scale as a function of the (inverted) absolute temperature. The slope of the line corresponds to a difference in the apparent energy of activation of about 1 kcal/mole.

At 20° C, where k_T/k_H for the methane formation is 0.67 ± 0.01 that for the benzene formation was found to be 0.61 ± 0.03. In the latter experiments the addition was carried out drop by drop. This is probably one reason why the experimental irregularities are larger, and it is not certain, indeed, whether there is a real difference between the two figures given.

It should further be noted that the results given in this preliminary paper have not been corrected for the slight change in the specific activity of the water during the reaction, causing a systematic error of about 0.01 in k_T/k_H.

Experiments on the same reactions, carried out in other, more indifferent solvents are made, the intention being also to extend the investigations to the formation of other hydrocarbons than methane and benzene.

Added in proof: A review[3] of the scarce experimental facts concerning this type of reaction has been published after the accomplishment of this paper.

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Calculation of the Directive Influence of a Nitro Group in Position 2 in Thiophene

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In many respects thiophene is very similar to benzene, the sulphur atom being a substitute for a $-CH=CH-$ fragment of the latter. According to Longuet-Higgins [1] the π-electron structure of thiophene might be treated in substantially the same way as that of benzene, the sulphur atom providing two orbitals of pd^2 type instead of the two missing carbon p-orbitals. The only difference from benzene in the MO LCAO treatment, then, is that the resonance and overlap integrals between adjacent orbitals belonging to atoms of different kinds are assumed to be smaller than those between orbitals of atoms of the same kind, the latter integrals being assumed to have the same values as in benzene. The magnitudes of the former integrals, supposed to be proportional to one another, were found to be 80 % of the latter from the requirement that the resonance energies of thiophene and benzene, experimentally 30 and 40 kcal mole^{-1}, respectively, should be in the experimental ratio. The value 20 kcal mole^{-1} for thiophene, recently proposed by Sunner [2], will reduce the figure to about 60 %.

The picture of the π-electron system of thiophene referred to makes it an intermediate between those of benzene and butadiene plus ethylene, and consequently an entering substituent will prefer the position close to sulphur, irrespective of whether the attack is electrophilic, radical,

Table 1. (For explanations, see the text.)

Compound	Position	Kind of attack	Polarization energy		
			$x = 1$ [5]	$x = 0.8$	$x = 0.6$
Thiophene [4]	2	el., rad., nucl.	1.849	1.678	1.523
		electrophilic	1.861	1.694	1.544
2-Nitrothiophene	5	radical	1.809	1.636	1.480
		nucleophilic	1.757	1.578	1.416
Thiophene [4]	3	el., rad., nucl.	1.849	1.851	1.837
2-Nitrothiophene	4	el., rad., nucl.	1.852	1.856	1.845

or nucleophilic [3,4]. When there is already a *meta*-directing substituent, such as a nitro group, in the 2-position, however, the question arises as to the point of the next attack. The sulphur atom tends to direct it towards the 5-position, but by analogy with benzene the nitro group would be expected to tend to direct it towards the 4-position.

In connexion with some experimental work in progress, it was found of interest to apply the method of Wheland [5] to the thiophene model of Longuet-Higgins and calculate the ''polarization energies'', *i. e.* the π-electron energy of the two hypothetical substitution intermediates
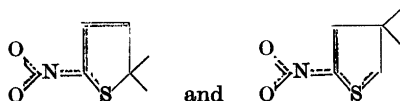
relative to the initial molecule
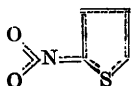
(In these figures the extension of the π-electron system is indicated by dotted lines.) As other magnitudes involved could be assumed to be mainly independent of the position, the intermediate of lowest energy could be expected to correspond also to the lowest activation energy and hence to the most rapid reaction. It should be emphasized, however, that the intermediate is not identical with the activated complex of the reaction, the latter being passed before the former is reached, at least in ordinary nitrations [6], but their energy heights will generally be correlated.

The calculations were carried out in exactly the same way as those of Wheland [5], and with the same values of the

quantum mechanical parameters of the nitro group. The results are given in Table 1, where x denotes the assumed ratio between the two kinds of exchange and overlap integrals mentioned above. The column for $x = 1$ will consequently correspond to a perfect benzene ring, and these values are found in Wheland's paper. For comparison, the values previously computed for unsubstituted thiophene [4] have also been included. The energy unit is Wheland's $-\beta_0$, a positive quantity equivalent to about 38 kcal mole $^{-1}$.

In a very recent paper [7], which appeared after the present calculations were completed, Matlow and Wheland give a somewhat modified set of parameters for the nitro group. These minor changes are not believed to influence the general conclusions which could be drawn from Table 1.

The results are just what could be expected from a superposition of the two directing influences, the much stronger directing power of the sulphur atom even at x as high as 0.8 being predominant. The agreement with existing experimental facts [8], which cannot be expected to be better than qualitative, seems to be satisfactory.

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