was obtained through the courtesy of the Atomic Energy Commission.

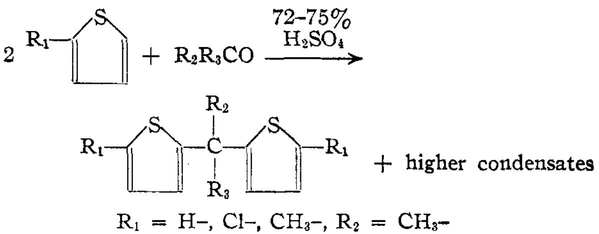
DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
TECHNOLOGY CENTER
CHICAGO, ILL.
RECEIVED OCTOBER 5, 1950

Condensation of Thiophene and Homologs with Ketones

BY JOHN W. SCHICK AND DUNCAN J. CROWLEY

The reaction of thiophene with aldehydes,[1] particularly formaldehyde,[2] in an acidic medium is known to produce 1,1-(2′,2″-dithienyl)-alkanes which on further reaction result in resins and subresinous oils. However, no description of the reaction of thiophene and/or substituted thiophenes with ketones has been found in the literature.

The condensation is illustrated in the equation



R_1 = H–, Cl–, CH_3–, R_2 = CH_3–
R_3 = CH_3–, C_4H_3S–, C_6H_5–, C_2H_5–
$R_2R_3C<$ may be cyclic, *e.g.*, in cyclohexanone

This condensation has been carried out with thiophene, 2-methylthiophene and 2-chlorothiophene with ketones, such as acetone, methyl ethyl ketone, cyclohexanone, acetophenone and 2-acetylthiophene. For this particular reaction, the conditions are somewhat similar to those described for the phenol–ketone condensations.[3,4,5,6,7]

Although 72–75% sulfuric acid was the principal condensing agent employed, it was noted that 37% hydrochloric acid resulted in product yields comparable to sulfuric acid, while 85% phosphoric acid resulted in poorer yields. Table I summarizes the experimental data using 72% sulfuric acid as the condensing agent.

General Experimental Conditions

Thiophene or substituted thiophene (0.8–2.0 moles) and the ketone (1.0 mole) were allowed to react in the presence of 72–75% sulfuric acid (acid–thiophene ratio 1.5:1) at 50–90° for 3–8 hours. The reaction product was separated from the acid layer and washed with water, dilute carbonate, water again, then dried over anhydrous sodium sulfate. The unreacted thiophene or substituted thiophene was removed and the residue distilled at reduced pressure.

TABLE I

THIOPHENE–KETONE CONDENSATIONS[a]

Thiophene	Ketone	Mole ratio, thiophene: ketone	Product structure[b]	Formula	Yield,[c] %	B.p., °C.	Mm.	$n^{20}D$	Sulfur, % Calcd.	Found
Thiophene	Acetone	1.6	T–K–T	$C_{11}H_{12}S_2$	47	86	0.3	1.5855	30.8	30.9
			T–K–T–K–T	$C_{18}H_{20}S_3$	19	188	.3	1.6029	28.9	28.9
Thiophene	Methyl ethyl	2	T–K–T	$C_{12}H_{14}S_2$	66	97.5	.1	1.5806	28.8	29.0
			T–K–T–K–T[d]	$C_{20}H_{24}S_3$	8				26.6	25.9
			T–K–T_4–K–T[e]	$C_{44}H_{54}S_6$	11	. . .	[f]		24.8	24.3
Thiophene	Cyclohexanone	1.6	T–K–T[g]	$C_{14}H_{16}S_2$	39	158	.3		25.8	25.7
			T–K–T_2–K–T	$C_{34}H_{40}S_4$	45	. . .	[f]		22.3	22.4
Thiophene	Acetophenone	1.6	T–K–T	$C_{16}H_{14}S_2$	49	153	.5	1.6319	23.7	23.6
			T–K–T_2–K–T[h]	$C_{40}H_{34}S_4$	30	. . .	[f]		19.9	20.2
Thiophene	Acetylthiophene	1.6	T–K–T	$C_{14}H_{12}S_3$	54	164	.1	1.6399	34.8	34.6
2-Chlorothiophene	Acetone	0.8	T–K–T	$C_{11}H_{10}S_2Cl_2$	61	143	.5		23.1	22.7
2-Methylthiophene	Acetone	1.6	T–K–T	$C_{13}H_{16}S_2$	79	110	.5	1.5691	27.1	26.5

[a] Condensation carried out in 72–75% H_2SO_4 with an acid: thiophene mole ratio of 1.5:1. [b] T = thiophene, K = ketone. [c] Yield based on thiophene consumed. [d] Mol. wt., calcd. 360, found 376. [e] Mol. wt., calcd. 774, found 772. [f] Resinous composition. [g] M.p. 61–62.5°. [h] Mol. wt., calcd. 642, found 639.

SOCONY–VACUUM LABORATORIES
PAULSBORO, NEW JERSEY
RECEIVED SEPTEMBER 18, 1950

---

[1] Steinkopf, "Die Chemie des Thiophens," Edwards Brothers, Ann Arbor, Michigan, 1944, p. 138.

[2] Caesar and Sachanen, *Ind. Eng. Chem.*, **40**, 922 (1948).

[3] Greenalgh, U. S. Patent 1,977,627.

[4] Jordan, U. S. Patent 1,854,940.

[5] Baker and Besly, *J. Chem. Soc.*, 1103 (1940).

[6] McGreal, Niederl and Niederl, THIS JOURNAL, **61**, 345 (1939).

[7] DeBell, Goggin and Gloor, "German Plastic Practices," DeBell and Richardson, Springfield, Mass., 1946, p. 260.

The Separation of Mixtures of Mono- and Disubstituted Alkyl Phosphoric Acids[1]

BY D. C. STEWART AND H. W. CRANDALL

A number of alkyl phosphoric acids are available commercially, but only as mixtures of the mono- (H_2RPO_4) and di- (HR_2PO_4) substituted forms. It seems probable that for many purposes it would be desirable to use one or the other of these in a separated state, as, for example, in studying the mechanisms involved in the extraction of amino acids by their use.[2] It has been found that this separation may be readily accomplished by taking advantage of the differences in the distribution of the two forms between two immiscible phases, generally water and some organic solvent. In this latter case, the disubstituted acid favors the organic phase, whereas the monosubstituted compound shows more affinity for the aqueous layer. By choosing the appropriate solvent, it is then possible to water wash all of the H_2RPO_4 out of the organic layer by a series of batch extractions, leaving only the HR_2PO_4;

---

[1] A portion of this work was performed under the auspices of the Atomic Energy Commission.

[2] E. V. McCollum, A. A. Rider and H. Suss, *Proc. Soc. Exp. Biol. Med.*, **72**, 709 (1949).