[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Aliphatic Olefins with Thiophenol[1]

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The alkylation of aromatic hydrocarbons[2] and the C- and O-alkylation of phenols[3] with olefins in the presence of catalysts such as sulfuric or phosphoric acid lead to the formation of compounds having structures which are in accordance with Markownikoff's rule. The mechanism for these reactions has been described[2,3c,4] as involving intermediate ester formation between the acid catalyst and the olefin. Posner,[5] however, reported that the reaction of thiophenol and olefins in the presence of a mixture of sulfuric acid and acetic acid proceeds abnormally, *i. e.*, contrary to Markownikoff's rule.

If Posner's proof of structure, which is open to criticism, is accepted, then one must conclude that either sulfuric acid played no part in the reaction or, what would be less probable, that it formed an intermediate ester of abnormal structure.

Repetition of some of Posner's experiments revealed several errors. The reaction of thiophenol with trimethylethylene in the presence of sulfuric acid yields *t*-amyl- and not *s*-isoamyl phenyl sulfide as reported by him. The compound Posner reported as *t*-amyl phenyl sulfone (m. p. 70°, no analysis) obtained by the metathesis of sodium benzene sulfinate and *t*-amyl bromide was probably benzene sulfinic acid (m. p. after first recrystallization 71°). All attempts to synthesize *t*-alkyl phenyl sulfones by this method led to the isolation only of benzene sulfinic acid and diphenyl disulfide. The disulfide no doubt results from the decomposition of the sulfinic acid by heat in the presence of solvents.[6,7]

Because of the discrepancies in Posner's work further investigation of the reaction of thiophenol with aliphatic olefins was deemed necessary. It was found that in the absence of catalysts thiophenol adds to aliphatic olefins[8] contrary to the mode of addition implied by Markownikoff's rule. Sulfuric acid (diluted with water or acetic acid), however, catalyzes the reaction to yield the normal alkylation product, and not the abnormal product as erroneously reported by Posner. The presence of phosphoric acid scarcely affects the course since the olefins react more readily with thiophenol than with the acid.

The yield of the alkyl phenyl sulfide formed in the absence of any added catalyst depends upon the temperature, contact time and reactivity of the olefin used.

The alkyl phenyl sulfides obtained in these reactions were identified by comparison of their physical properties with those synthesized by the reaction

$$C_6H_5SNa + RBr \longrightarrow C_6H_5\text{—S—R} + NaBr \qquad (A)$$

and by preparation of solid derivatives (Table II). *t*-Butyl- and *t*-amyl phenyl sulfides could not be prepared by (A) but were obtained for the first time by treating thiophenol with the corresponding *t*-alkyl sulfides according to the method of Lee.[9] All the alkyl phenyl sulfides are water-white liquids possessing a pleasant odor.

It is interesting to note that in the presence of both 75% sulfuric acid, and the sulfuric acid–acetic acid catalyst used by Posner, isopropylethylene underwent isomerization at 0–20° during the alkylation of the thiol group—just as it has been found[10] to do in the presence of 96% sulfuric acid at 0° during the alkylation of benzene—to give a high yield of product containing only the *t*-amyl group.

This study is being extended to investigate the mode of addition to olefins of other compounds containing the thiol group, such as hydrogen sulfide, aliphatic mercaptans and thio acids. The application of these reactions to the problem of identification of olefins is also under investigation.

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[1] Presented before the Organic Division of the American Chemical Society at Milwaukee, Wis., Sept. 5–9, 1938.

[2] Ipatieff and Pines—V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., New York, N. Y., 1937, p. 656.

[3] (a) Ipatieff, Pines and Schmerling, THIS JOURNAL, **60**, 1161 (1938); (b) Ipatieff, Pines and Friedman, *ibid.*, **60**, 2495 (1938); (c) Niederl and Natelson, *ibid.*, **53**, 273 ,1928 (1931).

[4] Ipatieff, Pines and Corson, *ibid.*, **60**, 577 (1938).

[5] Posner, *Ber.*, **38**, 649 (1905).

[6] Otto and Rössing, *Ber.*, **19**, 1235 (1886).

[7] Smiles and Gibson, *J. Chem. Soc.*, **125**, 176 (1924).

[8] No attempt was made to free the reactants from peroxides or disulfides or to run the reaction in the absence of air. In a private communication Prof. M. S. Kharasch stated that he is investigating the effect of antioxidants on the addition of thiol compounds to olefins. *Cf.* Ashworth and Burkhardt, *J. Chem. Soc.*, 1791 (1928); also *Trans. Faraday Soc.*, **30**, 18 (1934).

[9] Lee, U. S. Patent 2,020,421; *C. A.*, **30**, 489 (1936).

[10] Ipatieff, Pines and Schmerling, THIS JOURNAL, **60**, 353 (1938).

TABLE I

ALKYL PHENYL SULFIDES

PREPARATION AND PROPERTIES

Alkyl	B. p., °C.	Press., mm.	$n^{20}\text{D}$	d^{20}_4	Yield[b]	Condition of reaction temp.		Method[a]	Analyses, %					
						°C.	Hours		Calcd.			Found		
									C	S	H	C	S	H
n-Propyl	218.5–219.5	750	1.5571	0.9995				A		21.05			20.85	
					72	120	10	B						
					20	60	6	C						
					60	120	8	C						
					15	60	6	B						
Isopropyl	206.5–207.5	750	1.5468	.9855				A	71.05		7.89	71.17		8.00
					16	120	6	D						
n-Butyl[c]	94.5–97	4	1.5463	.9852				A						
					73	100	8	C						
s-Butyl[d]	90–91	4	1.5425	.9789				A						
Isobutyl[c]	107–108	13	1.5430	.9803				A						
	85–87	4			90	33	20	C						
					50	120	5	B						
t-Butyl	73	5	1.5335	.9895	70			E	72.28		8.43	72.34		8.50
n-Amyl	117–118	8	1.5396	.9714				A				73.40		8.72
	93–94	4.5			25	50	12	C						
Isoamyl	100–100.5	6	1.5380	.9681				A	73.33		8.88	73.36		8.96
	87–88	3.5	1.5378		80	55	16	C						
					58	120	8	C						
2-*s*-Amyl	91–92.5	4.5	1.5357	.9642				A				73.43		8.92
3-*s*-Amyl	107–107.5	9	1.5385	.9738				A				73.40		8.82
Active amyl	99–101	4.5	1.5408	.9783				A				73.27		8.94
s-Isoamyl	83.5–86	3.5	1.5393	.9794				A				73.27		8.87
	99–100	5	1.5395		60	Room	168	C[e]						
t-Amyl	91–91.5	6	1.5351	.9679	69			E[f]				73.29		8.81
	88–88.5	3.5	1.5351		15			E[g]						
					88			F[e,g]						

[a] Method
- A, C_6H_5SK + RBr.
- B, C_6H_5SH + Olefin + 90% phosphoric acid.
- C, C_6H_5SH + Olefin.
- D, C_6H_5SH + Alkyl phosphate.
- E, C_6H_5SH + Olefin + 75% H_2SO_4.
- F, C_6H_5SH + Olefin + sulfuric and acetic acids according to directions given by Posner.[5]

[b] Based on mercaptan charged. Method A gave yields ranging from 60 to 85% of the theoretical. [c] Mann and Purdie, *J. Chem. Soc.*, 1549 (1935) report 137–139 (12 mm.) for *n*-butyl phenyl sulfide and 126–127 (12 mm.) for isobutyl phenyl sulfide. [d] Taylor, THIS JOURNAL, **58**, 2649 (1936), reported 104–105 (25 mm.). [e] Trimethylethylene. [f] *t*-Amyl alcohol. [g] Isopropylethylene.

Experimental Part

Preparation of the Alkyl Phenyl Sulfides

Method A.—Two-tenths of a mole each of thiophenol and potassium hydroxide was dissolved in 50 cc. of hot 95% ethanol. To this mixture kept at 60–70°, 0.2 mole of the alkyl bromide was added dropwise (ten minutes); potassium bromide began to separate at once. The reaction mixture was refluxed for fifteen to twenty minutes longer, cooled, diluted with water, and extracted with ether. The ether layer was washed with alkali, then with water, and dried over anhydrous sodium carbonate. After removal of the solvent the product was distilled. The yields ranged from 60 to 85% of the theoretical.

The attempts to prepare *t*-alkyl phenyl sulfides by this method failed. If the reactants were kept at room temperature, potassium bromide was formed, but the thiophenol was recovered unreacted.

Method B.—The method consisted of placing approximately 0.2 mole of thiophenol, 0.15 to 0.2 mole of olefin, and 0.2 mole of 90% phosphoric acid in a glass liner, provided with a capillary closing, and placed in an Ipatieff type rotating bomb. The latter was charged with 30 atm. (at 25°) of nitrogen to keep the reactants inside the liner during the reaction. After being heated at 120° for five to ten hours, the bomb was opened. The product consisted of two layers: the lower of catalyst, and the upper of alkyl phenyl sulfide. The upper layer was washed with water, alkali, and water, then dried over anhydrous sodium carbonate, and distilled.

Method C.—Propene or the butenes and thiophenol were placed in the glass liner of an Ipatieff bomb and left at room temperature or heated overnight in an atmosphere of nitrogen, the initial pressure of which was 20–30 atm. The pentenes in slight excess and thiophenol were placed in sealed glass tubes which were left at room temperature or heated for a number of hours. The products were washed with alkali, water, dried and distilled.

Method D.—An excess of propene was heated with 90% phosphoric acid in the glass liner of an Ipatieff bomb for six hours at 100°. To 40 g. of the isopropyl phosphate so formed was added 23 g. of thiophenol and the mixture heated at 120° for six hours in the bomb charged with nitrogen (initial pressure being 20 atm.). The acid layer of the product weighed 28.5 g. From the upper layer 6 g. of unreacted thiophenol was separated by washing with alkali, leaving 26 g. of alkali insoluble product which was distilled. Much of it appeared to be products of nuclear

Table I.

Derivatives of Alkyl Phenyl Sulfides

Alkyl	Method[a] of prepn.	Deriv.[b]	M. p., uncorr.	Form[c]	Solvent[d]	Formula	Analyses, %							
							Calculated				Found			
							C	H	N	Pd	C	H	N	Pd[h]
n-Propyl	A, B, C	NS	78.5–79[e]	Prisms										
Isopropyl	A, D	NS	112–113[e]	Rhombic plates										
n-Butyl	A, C	Pd	106–106.5[f]	Orange needles		$C_{20}H_{28}S_2PdCl_2$				20.93				21.39
Isobutyl	A, B, C	Pd	92.5–93.5[f]	Orange prisms										
t-Butyl	E	S	98–99	Bundles of needle-like prisms		$C_{10}H_{14}O_2S$	60.60	7.07			60.64	7.05		
		Pd	84 (>250)[g]	Brick red powder										
n-Amyl	A, C	Pd	75–76	Orange prisms		$C_{22}H_{32}S_2PdCl_2$				19.87				20.19
Isoamyl	A, C	Pd	96–97	Yellow needles		$C_{22}H_{32}S_2PdCl_2$				19.87				20.05
s-Isoamyl	A, C	AS	93–94	Slender prisms	Ether–heptane	$C_{11}H_{17}NO_2S$			6.16				6.21	
t-Amyl	E, F	S	29–30, 72–73 (>250)[g]	Needles	Hexane	$C_{11}H_{16}O_2S$	62.26	7.54			62.22	7.61		

[a] See Footnote (*a*), Table I. [b] Pd = palladous chloride coördination compound; S = sulfone; NS = *m*-nitrophenyl alkyl sulfone; AS = *m*-aminophenyl alkyl sulfone. [c] Colorless unless otherwise stated. [d] See experimental part for directions for recrystallizing palladous chloride complexes; dilute alcohol for all others unless otherwise specified. [e] Baldwin and Robinson, *J. Chem. Soc.*, 1445 (1932), reported 80° for *n*-propyl and 113° for isopropyl. [f] Mann and Purdie, *ibid.*, 1549 (1935) reported 96° for *i*-butyl and 118° for *n*-butyl. Repeated recrystallizations of the latter from various solvents always gave yellow needles melting not higher than 106–106.5°. [g] The low-melting derivatives of the probable formula $(C_6H_5—S—R)_2 \cdot PdCl_2$ were not analyzed. On recrystallization these were always converted to brick red powders which did not melt below 250°. [h] Weighed as metal.

alkylation of the isopropyl phenyl sulfide, but a few grams of material boiling in the propyl phenyl sulfide range was isolated and shown to consist of the isopropyl thioether.

Method E.—Lee's[9] method for preparing *t*-alkyl sulfides was used with slight modifications for the preparation of (1) *t*-butyl- and (2) *t*-amyl-phenyl sulfides.

One hundred grams of 75% sulfuric acid was placed in a 3-necked, 500-cc. flask which was equipped with a mercury-sealed stirrer, a dropping funnel and an inlet tube at the bottom of the flask. The flask was surrounded by an ice-water bath. To prepare (1), isobutene was bubbled through the rapidly stirred acid until 0.2 mole was absorbed. To prepare (2), isopropylethylene or *t*-amyl alcohol (0.2 mole) was added dropwise from the dropping funnel with stirring. Then 0.1 mole of thiophenol was added dropwise with stirring. When the addition was complete, the ice-water bath was removed to allow the flask to come to room temperature. Stirring was continued for another fifteen minutes. Crushed ice was added to the reaction mixture, after which it was extracted with ether. The ether extract was washed with water, alkali, and water, then dried over anhydrous potassium carbonate, and distilled.

Method F.—Posner's directions were followed in mixing the reactants. However, it is not at all necessary to wait two weeks for the reaction to become complete: the yield at the end of one hour was 80%; at the end of two weeks it was 88%.

Preparation of the Derivatives

Derivative Pd: Palladous Chloride Complexes of Alkyl Phenyl Sulfides.—To an aqueous solution containing a slight excess of palladous chloride was added 0.1 cc. of the alkyl phenyl sulfide, and the mixture shaken for a few minutes. The brown precipitate was separated by filtration and recrystallized by use of *cold* solvents. Usually it was dissolved in acetone; the acetone solution was then filtered and diluted with water until a turbidity just appeared. The yellow or orange needles or prisms which appeared on standing were usually sufficiently pure for a melting point determination. Instead of water, heptane or ligroin may be used with the acetone; alcohol may replace the acetone.

On recrystallization of the *t*-butyl- and *t*-amyl-phenyl sulfides, insoluble brick red powders not melting below 250° were obtained. In the presence of an excess of *t*-butyl- or *t*-amyl-phenyl sulfides, palladous chloride gave soluble yellowish precipitates which after a thorough pressing on a porous plate had fairly satisfactory melting points.

Derivative S: Alkyl Phenyl Sulfones.—Two cc. each of 30% hydrogen peroxide and glacial acetic acid was added to 1 cc. of alkyl phenyl sulfide, and the mixture was heated in a 50-cc. beaker on a water-bath in a hood until the acetic acid and water were evaporated. The beaker was then cooled in dry ice–acetone mixture and scratched with a stirring rod to induce crystallization of the sulfone, which was then recrystallized from hexane or dilute alcohol. Or the crude sulfone was taken directly for nitration to form *m*-nitrophenyl alkyl sulfones.

Derivative NS: *m*-Nitrophenyl Alkyl Sulfones.—To the sulfone (from 1 cc. of sulfide) was added 2 cc. of nitrating mixture (3 parts concentrated sulfuric acid; 1 part concentrated nitric) and the mixture heated on a water-bath for five minutes, after which it was poured on crushed ice and extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate, and evaporated on a water-bath. The crude nitro compound was recrystallized from dilute alcohol, or used without purification for preparation of the corresponding amine.

Derivative AS: *m*-Aminophenyl *s*-Isoamyl Sulfone.—The reduction of nitrophenyl *s*-isoamyl sulfone was made according to a modified method of Waldron and Reid.[11] The crude nitrophenyl sulfone obtained from 1 cc. of the sulfide was mixed with ten times its weight of iron powder (reduced by hydrogen), 10 cc. of water, and one drop of dilute sulfuric acid. With frequent stirring and adding of water to replace that lost by evaporation and the addition of a drop or two more of the acid, the mixture was heated on a water-bath for one-half to one hour. Sodium bicarbonate was added to the reaction mixture, and the aminosulfone was taken up in ether. The ether extract was treated with dilute hydrochloric acid. The free amine was then isolated by rendering the acid solution basic and extracting with ether. The ether solution was dried over anhydrous potassium carbonate and evaporated on a water-bath. The residue was recrystallized from a mixture of ether and heptane.

Summary

The addition of thiophenol to aliphatic olefins proceeds contrary to Markownikoff's rule. Propene, butene-1, isobutene, pentene-1, isopropylethylene, and trimethylethylene react with thiophenol in the absence of acid catalysts to yield *n*-propyl-, *n*-butyl-, *i*-butyl-, *n*-amyl-, *i*-amyl and *s*-isoamyl phenyl sulfides, respectively. The presence of 90% phosphoric acid scarcely affects the course of the reaction since the olefins react more readily with thiophenol than with the acid.

In the presence of sulfuric acid (diluted with water or acetic acid) the reaction proceeds in accordance with Markownikoff's rule: isobutene and trimethylethylene yield *t*-butyl- and *t*-amyl phenyl sulfides, respectively.

Isomerization occurs during the reaction of isopropylethylene with thiophenol in the presence of sulfuric acid. The product is *t*-amyl phenyl sulfide and not the expected *s*-isoamyl phenyl sulfide.

The physical properties of a number of alkyl phenyl sulfides are described. Several of these were characterized by preparation of solid derivatives.

t-Amyl phenyl sulfone cannot be prepared by the metathesis of *t*-amyl halide and sodium benzene sulfinate, as reported by Posner.

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[11] Waldron and Reid, THIS JOURNAL, **45**, 2399 (1923).

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY]

Studies on the Chemistry of the Fatty Acids. IV. The Purification of Linolenic Acid by Fractional Crystallization of the Fatty Acids of Linseed and Perilla Oils, with Observations on the Properties of this Acid Prepared by Crystallization and by Debromination*

BY G. Y. SHINOWARA AND J. B. BROWN

Linolenic acid is the principal unsaturated fatty acid of the vegetable drying oils; it occurs in small amounts in some of the semi-drying oils. Although it is rarely, if ever, found in animal lipids, unless the animal has eaten vegetable oils containing it, linolenic acid has been shown to replace linoleic as an essential fatty acid.[1] No new methods for the isolation of linolenic acid have been offered for over twenty-five years. The zinc salt purification proposed by Erdmann and Bedford[2] apparently has not been successful in other hands. The hexabromide reduction method[3] has been the one universally employed. This method has the advantage of starting with a pure solid derivative of the acid and gives a water-white product with an iodine number and molecular weight which are close to the theoretical. As in the case of linoleic acid, the method involves bromination–debromination procedures, which greatly reduce the yield, and the product may or may not be the same as the linolenic acid present in the original oil.

In the present work we have attempted to apply the crystallization procedures described by Brown and Stoner, and Brown and Frankel,

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(1) Burr, Burr and Miller, *J. Biol. Chem.*, **97**, 1 (1932).

(2) Erdmann and Bedford, *Ber.*, **42**, 3128 (1909).

(3) Hazura, *J. Soc. Chem. Ind.*, 506 (1888); Hehner and Mitchell, *Analyst*, 313 (1898); Rollett, *Z. physiol. Chem.*, **62**, 410 (1909); **70**, 404 (1910).