

sodium, which separated a small amount of material boiling below 140°. The purified 2-methyl-4-ethylthiophene was obtained in 20% yield (based on ethyllevulinic acid).

2,3-Dimethylthiophene.— β -Methyllevulinic acid was obtained by the excellent method of Pauly, Gilmour and Will,⁶ and boiled from 130–132° (uncorr.) at 10 mm. On heating 30-g. portions of this acid with 35-g. portions of powdered phosphorus pentasulfide, a vigorous reaction took place and the product was distilled out as soon as the reaction slowed down. The crude product was worked up as before. The purified 2,3-dimethylthiophene was obtained in 20% yield.

As a check on the high boiling point observed, a specimen of 5-chloromercuri-2,3-dimethylthiophene was purified by crystallization until it melted with slight decomposition at 218.5–219.5 (corr.). Steinkopf⁷ gives the melting point of this compound as 213–214° (with decomposition). The 2,3-dimethylthiophene was recovered quantitatively from this mercury compound by heating with hydrochloric acid, and the specimen thus obtained boiled entirely in the range 140.2–141.2° (corr.). The constants of both specimens are given in the table.

Summary

The preparation and physical properties of 2,3-dimethylthiophene, 2-methyl-4-ethylthiophene and 2,5-methylethylthiophene are presented.

⁶ Pauly, Gilmour and Will, *Ann.*, **403**, 145 (1914).

⁷ Steinkopf, *ibid.*, **424**, 46 (1923).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. IX. THE PRODUCTS OF DESTRUCTIVE DISTILLATION OF EBONITE

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Introduction

It has been shown that there is a definite relationship¹ between the rubber molecule and its pyrolysis products, and consequently the thermal decomposition of ebonite has been undertaken to throw light on the nature of the rubber sulfur complex.

It was relatively simple to correlate the pyrolysis products of raw rubber with the formula of the parent molecule, as the rubber formula had been previously established by oxidation. However, the formula of ebonite is still unknown, and cannot be arrived at by ordinary methods, because ebonite is amorphous, insoluble, non-volatile, completely saturated, and inert toward chemical agents. A correlation of its pyrolysis products may thus be the only way of establishing its formula.

The pyrolysis products of ebonite, the decomposition products of a mixture of rubber and sulfur, and the interaction of sulfur and the pyrolysis

¹ Midgley and Henne, *THIS JOURNAL*, **51**, 1215 (1931).

products of raw rubber have been investigated to establish a basis from which the formula of ebonite may be derived.

The present paper presents the study of the products obtained when ebonite is destructively distilled.

Procedure.—Thirty-six kilograms of ebonite were destructively distilled in the manner reported previously. The volatile products were progressively condensed by means of warm water ice water and solid carbon dioxide. The non-condensed gases were washed through a copper sulfate solution to eliminate hydrogen sulfide, and finally led through another condenser cooled with carbon dioxide. The condensed products were subjected to fractional distillation, and from the various cuts thus obtained the thiophene homologs were separated by mercuration.

Results.—The amount of hydrogen sulfide liberated during pyrolysis accounted for approximately one-half of the sulfur originally present in the ebonite. As a consequence, the oils obtained were of a highly unsaturated character. An examination of the oils boiling below 170° established the presence of mercaptans, sulfides, thiophene homologs and *m*-xylene. The examination failed to detect disulfides. The oils boiling above 170° were rich in sulfur; they were not further investigated. The limited stability of a portion of the sulfur compounds precluded their separation, and hence the determination of their constitution. The thiophenes and the hydrocarbons were stable enough to be successfully investigated, and it was thus possible to isolate and identify 2-methylthiophene, 2,3-dimethylthiophene, 2,4-dimethylthiophene, 2,5-methylethylthiophene and *m*-xylene. At the same time it was shown that benzene, toluene, thiophene, 2,5-dimethylthiophene, 2,3-methylethylthiophene or trimethylthiophenes were not present in significant quantities. Similarly, the absence of other isomers of the thiophene homologs was established. The yields were: thiophenes, 1%; xylene, 0.1%, of the total quantity of ebonite used.

Experimental Part

The ebonite used in this investigation was prepared by the Inland Manufacturing Company of Dayton, Ohio, through the kindness of Dr. A. H. Flower, to whom we here wish to express our thanks. The following mix was used: first latex crepe, 100, sulfur, 32, diphenylguanidine, 2, "Kadox," 2, stearic acid, 2. The mix was cured for eight hours at 148°; analysis showed 0.1% free sulfur at the end of this time.²

² The effect of the ingredients other than sulfur and rubber in the ebonite may be discounted, as shown by the following experiments. A small batch of ebonite, prepared from a crepe rubber-sulfur mix containing 32% sulfur and no accelerators, was destructively distilled. In the distillate, 2-methylthiophene, 2,3-dimethylthiophene and *m*-xylene were positively identified. Thiophene, benzene, toluene, 3-methylthiophene and *p*-ethyltoluene were absent, while 2,4-dimethylthiophene and 2-ethyl-5-methylthiophene appeared to be present, although they were not positively identified. An ebonite was also prepared from sodium-rubber containing 32% sulfur and no accelera-

Thirty-six kilograms of this ebonite were cracked as previously described. The vapors were progressively condensed at 100, 0 and -80° . The condensate obtained at -80° was chiefly hydrogen sulfide and quite free of hydrocarbons boiling below 30° . A rough estimate of the amount of hydrogen sulfide liberated was made by passing the cracked gases through copper sulfate solutions. Table I summarizes the results.

TABLE I

	Liquid	H ₂ S	Water	Coke	Uncondensed gases and loss
Yield on ebonite, %.....	59	13	4	6	18

The liquid was topped to 200° . The higher boiling materials contained 14.2% sulfur; they were not further investigated. The distillate below 200° (3600 g. or 10% of the original liquid) was systematically fractionated. After three runs, the material boiling below 120° was repeatedly washed with alkali to remove mercaptans completely, and the fractionation was resumed and carried out to its practical limit. Table II shows the results of the final fractionation together with the physical properties and sulfur content of the fractions. Double bond determinations were made only on the fractions containing little sulfur.

TABLE II

Temp., $^{\circ}$ C.	Volume, cc.	dV/dT	d_{15}^{20}	n_D^{20}	Δ	S, %
30-36	14	2	0.672	1.389	0.9	
36-40	8	2	.675	1.400	.9	
40-51	6	0.5		1.399	.8	1.1
51-57	12	2	.702	1.392	.6	2.1
57-61	22	5	.704	1.393	.7	1.7
61-65	13	3	.714	1.400	.7	1.1
65-69	26	7	.725	1.413	.9	1.3
69-73	22	5	.743	1.425	1.0	1.5
73-77	12	3	.770	1.436	0.9	2.2
77-80	12	4	.761	1.429	.8	1.9
80-88	17	2	.755	1.416	.6	1.7
88-90	15	8	.742	1.410	.7	1.0
90-94	21	5	.739	1.413	.8	0.6
94-96	18	9	.741	1.416		
96-105	22	2	.797	1.441		
105-107	23	12	.847	1.461		
107-109	54	27	.867	1.468		13.0
109-111	125	63	.873	1.471		14.5
111-113	55	28	.856	1.464		13.5
113-119	28	5	.835	1.454		9.1
119-125	30	5	.813	1.446		7.4
125-130	33	7	.843	1.457		11.4
130-134	40	10	.861	1.467		13.9
134-136	26	13	.873	1.472		14.0
136-138	111	56	.894	1.485		14.5
138-140	194	97	.909	1.490		15.4
140-142	39	20	.916	1.491		16.8

tors. The pyrolysis products of this sodium rubber ebonite were also quite similar to those from crepe rubber ebonite. The mercuration treatment allowed the recovery of small amounts of thiophene homologs, similar in their indophenin reactions to those obtained from the crepe rubber ebonite.

TABLE II (Concluded)

Temp., °C.	Volume, cc.	dV/dT	d_{15}^{20}	n_D^{20}	Δ	S, %
142-145	20	7	.905	1.488		16.2
145-151	15	3	.887	1.482		14.5
151-156	25	5	.884	1.480		14.6
156-159	55	18	.906	1.487		18.3
159-160	129	129	.920	1.494		
160.0-160.5	125	250	.929	1.497		
160.5-161.5	125	125	.935	1.500		19.6
161.5-162.7	100	83	.938	1.502		Composite sample
162.7-165.0	120	52	.936	1.504		
165-169	100	25	.935	1.505		17.1
169-172	100	33	.926	1.501		16.9
172-175	100	33	.919	1.497		17.3
175-180	100	20	.919	1.495		

Each of the three main fractions, b. p. 109-111°, 138-140° and 160-160.5°, was a complex mixture. Distillation from aniline separated these mixtures roughly into hydrocarbon-rich fractions and sulfur-rich fractions, but since this was insufficient, chemical methods were preferred.

Mercaptans and Disulfides.—A mercaptan concentrate was isolated by steam distilling the alkali washings of the ebonite fraction boiling below 120°. It weighed only 8 g. and boiled chiefly from 66-80°. It had the characteristic mercaptan odor and gave typical mercaptan reactions with iodine, alcoholic lead acetate, sodium plumbite and mercuric oxide. The ebonite fractions boiling from 100-180° contained mere traces of mercaptans.

Disulfides were absent from the ebonite fractions boiling below 170°; this was shown by the failure to form mercaptans on reduction with zinc and glacial acetic acid.³

Thiophenes and Aromatic Hydrocarbons.—Thiophene and its lower homologs are very readily mercurated.⁴ Thiophene is quantitatively extracted from benzene⁵ by a boiling solution of mercuric acetate in dilute acetic acid; it forms a di-mercuri compound, and is readily regenerated from this compound by boiling hydrochloric acid. The various ebonite fractions were refluxed for thirty minutes or more with Dimroth's reagent (40 g. mercuric oxide), 40 cc. glacial acetic acid and 200 cc. water) and subjected to steam distillation. This operation removed unreacted aromatic and saturated hydrocarbons and left behind a complex mixture, from which the thiophenes were regenerated in a fair state of purity by boiling hydrobromic acid. The mercuric acetate treatment always caused the loss of the olefins and of up to 70% of the sulfur compounds. In order to show that this loss of sulfur derivatives was not due to the preferential destruction of some definite thiophene homolog, the mercuration and regeneration of thiophene, 2-methylthiophene, and of 3-methylthiophene were checked. None was appreciably oxidized; all were completely regenerated from their mercury compounds by hydrobromic acid. This check was regarded as important because Volhard reports that 2,5-dichloromercuri-3-methylthiophene is very difficult to split with acids.

Other Sulfur Compounds.—Many unsuccessful attempts were made to isolate by

³ Faragher, Morrell and Monroe, *Ind. Eng. Chem.*, **19**, 1281 (1927).

⁴ Volhard, *Ann.*, **267**, 172 (1892); Steinkopf and Bauermeister, *ibid.*, **403**, 50-72 (1914); (a) Steinkopf, *ibid.*, **413**, 310-333 (1917); (b) **424**, 23-61 (1921); (c) **428**, 138 (1922).

⁵ Dimroth, *Ber.*, **32**, 759 (1899).

other methods the sulfur compounds lost in the mercuration procedure. Significant are the following observations.

Fractions containing these sulfur compounds react with mercurous nitrate monohydrate, a reagent used by Faragher, Morrell and Monroe⁵ for the quantitative removal of sulfides from thiophene and hydrocarbons.

Diethyl sulfide may be recovered from its mixture with a hydrocarbon and thiophene by shaking with a solution of mercuric acetate and steam distilling the mercuric acetate solution but no sulfur compound is recoverable from the 109–113° cuts in this way.

The ebonite distillates did not react appreciably with dimethyl sulfate, a reagent which reacts with dimethyl sulfide on gentle warming.

The early experiments with aniline fractionation showed that in the case of the large fractions boiling at 107–113°, 136–142° and 159–165°, the sulfur compounds lost had physical properties not widely different from the thiophenes with which they were associated.

A proposed explanation is that the lost sulfur compounds represent members of an homologous series of dihydrothiophenes.

Tests for Individual Compounds.—The mercuration procedure was systematically applied to all the ebonite distillates boiling in the range 60–165°. Unless otherwise stated, all mercury derivatives were prepared and purified exactly according to the directions of Steinkopf.^{4b}

Thiophene and Benzene.—One drop of oil was recovered from the mercury compounds obtained from the ebonite fractions boiling from 66–88°. This drop did not give the indophenin reaction; thiophene was therefore absent. The steam distillate from the mercury compounds was treated with bromine water and steam distilled; 1 cc. of an oil was obtained. Nitration to dinitrobenzene was attempted but none could be isolated.

2-Methylthiophene.—The product isolated boiled at 111.5–112.5° (741 mm.), and had d_4^{20} 1.017, n_D^{20} 1.5132, molecular refraction observed 29.0, theoretical 30.1. It gave the green indophenin reaction characteristic of 2-methylthiophene. The following derivatives were prepared: 5-chloromercuri-2-methylthiophene, m. p. 204°, alone and in a mixture with authentic material; 2-methylthiophene-5-mercurithiocyanate, m. p. 200–201° (decomp.); tribromo-2-methylthiophene, m. p. 83°. Steinkopf gives the melting points of the first two derivatives as 204° and 202–204° (decomp.), respectively. Gattermann, Kaiser and Meyer⁶ give a melting point of 86° for tribromo-2-methylthiophene and state that a mixture of the 2- and the 3-isomers is inseparable by crystallization and melts at 74°. Comparison of the relative amounts of alcohol-insoluble material formed on mercurating the thiophene from ebonite and synthetic 3-methylthiophene indicated⁷ that less than 10% of 3-methylthiophene could have been present in the ebonite product.

Toluene.—The steam distillate containing the toluene was brominated at 0° with bromine water and steam distilled to separate the unreacted constituents from olefin bromides. After washing with sulfuric acid the product boiled at 109.5–111.5° and had n_D^{20} 1.4812. A saturated compound was present with the toluene since the material was not completely soluble in 10% oleum. Nitration gave dinitrotoluene of m. p. 69–70° alone and in a mixture with authentic material. A check experiment showed that no significant amount of toluene could have been mercurated and thus lost in the procedure of separation.

⁶ Gattermann, Kaiser and Meyer, *Ber.*, **18**, 3009 (1885).

⁷ Later experiments have shown that 3-methylthiophene is readily formed by the interaction of isoprene and boiling sulfur.

Dimethylthiophenes.—The thioxene mixture as isolated boiled at 139.5–141.5° (745 mm.) corr. and had n_D^{20} 1.5137 and d_4^{20} 0.984. Mercuration with mercuric chloride according to Steinkopf's procedure yielded a product completely soluble in benzene or alcohol. This shows the absence of 3,4-dimethyl- or 3-ethylthiophene; Steinkopf states that these isomers form di-mercuri compounds insoluble in these or other low-boiling solvents. The boiling point of the mixture is too high to be compatible with the presence of any significant quantity of 2-ethylthiophene (b. p. 132–134° corr.).⁸

Fractional crystallization of the mercury chloride compounds of the ebonite thioxenes from benzene permitted the isolation of 50% of the mercury compounds as 5-chloromercuri-2,3-dimethylthiophene, m. p. 217.5–218.5° (decomp.) alone and in a mixture with authentic material. This substance was converted to 2,3-dimethylthiophene-5-mercurithiocyanate, which shrunk and blackened at about 198° and did not melt up to 240°. Steinkopf states that this compound darkens at 200–202° and does not melt below 240°. Further confirmation of the presence of 2,3-dimethylthiophene was obtained by permanganate oxidation of the original thioxene mixture. A mixture of mono- and dicarboxylic acids resulted and the mono acid was steam distilled out from a very concentrated solution. Recrystallized twice from water it melted at 140–141° and its melting point was raised by mixture with the acid of m. p. 143° obtained similarly from the oxidation of synthetic 2,3-dimethylthiophene. The dicarboxylic acids gave the fluorescein reaction strongly.

Anal. of monocarboxylic acid: (a) from synthetic 2,3-dimethylthiophene; C, 50.8, 50.9; H, 4.1, 4.2. Calcd. for $C_8H_8O_2S$: C, 50.7; H, 4.3. (b) From ebonite thioxene: molecular weight by alkali titration, 141.5; calcd. for $C_8H_8O_2S$, 142.

The other mercury compounds occurring with 5-chloromercuri-2,3-dimethylthiophene were much more soluble in all solvents, melted mostly at 135–150°, and could not be purified satisfactorily by crystallization. Steinkopf has noted a considerable difference in the rates at which the substituted thiophenes mercurate, and a separation of 2,4-dimethylthiophene derivatives was accomplished by the application of this principle. The above-mentioned mixture of mercury compounds was converted to the thioxenes with hydrogen bromide and the thioxenes were remercured. After five minutes the mercury compound formed was separated from the mercuration mixture and reconverted to the thioxenes. The mercuration was then repeated, and after two minutes the formed mercury compound was again removed. The final amount of this mercury compound corresponded to 10% of the original mixture of mercury compounds obtained from the ebonite thioxenes. Crystallized from benzene, it melted at 168–169° in a bath preheated to 165°; on slower heating it sintered together somewhat above 170° but did not melt. The mercuric chloride addition product of oxidihydrumercuri-2,3-dimethylthiophene is stated by Steinkopf to melt at 167–168° on rapid heating; slow heating causes only a gradual sintering together. From this compound were prepared 5-chloromercuri-2,4-dimethylthiophene, m. p. 137.5–138.5°; 2,4-dimethylthiophene-mercurithiocyanate, m. p. 175–177° (sinters at 173°); and 5,5'-mercuri-bis-2,4-dimethylthiophene, m. p. 160–161° (with sintering). Steinkopf gives the melting points of these substances as 138–139°, 173–175° (sinters at 171°) and 160–161° (with sintering), respectively. The presence of 2,4-dimethylthiophene in the ebonite distillates is thus proved.

An attempt was made to isolate 2,5-dimethylthiophene by a similar method based on the principle that the compound mercurates much more slowly than the 2,3- and 2,4-isomers. None was found.

m-Xylene.—The xylene fraction was separated from olefins in the same way as the toluene. The product had b. p. 138–139° (746 mm.) (corr.), d_4^{20} 0.852 and n_D^{20} 1.4895. Sulfonation with oleum left about 10% of saturated hydrocarbon. According to

⁸ Meyer and Kreis, *Ber.*, 17, 1560 (1884).

Timmermans⁹ *m*-xylene has b. p. 139.3° (760 mm.) and d_4^{20} 0.8641. Ten drops of the xylene fraction was added to 10 cc. of concentrated sulfuric acid and 5 cc. of fuming nitric acid; the mixture was boiled for two minutes, then poured on ice and diluted with water. The precipitate was filtered off, washed with water and then with 15 cc. of cold 50% alcohol. The dried product showed m. p. 177–179°; after one crystallization from 50% alcohol it melted at 181–182° alone and in a mixture with authentic material. This proves the presence of *m*-xylene, substantially free of isomers.

2-Methyl-5-ethylthiophene.—The product first recovered from the mercuration procedure still contained unsaturated compounds and had d_4^{20} 0.957. To eliminate the unsaturated material the procedure of mercuration and regeneration was repeated. The product thus obtained boiled at 159.8–161.3° (chiefly 160.1–160.6°), had a freezing point –74.2°, d_4^{20} 0.958, n_D^{20} 1.5048 and a mol. wt., as determined by the freezing point depression in benzene, of 124.2, 126.5.

Anal. Calcd. for C₇H₁₀S: S, 25.42. Found: S, 24.05, 24.10, 23.90.

A specimen was prepared from the mercury acetate compound crystallized from glacial acetic acid; this preparation boiled at 159.5–160.6°, had a freezing point of –69.4°, d_4^{20} 0.9644, n_D^{20} 1.5063, and contained 25.28, 25.31% S. Presumably the earlier preparation still contained a small amount of hydrocarbon.

Synthetic 2-methyl-5-ethylthiophene boils at 159.8–160.4° and has¹⁰ the freezing point –68.4°, d_4^{20} 0.9663 and n_D^{20} 1.5073. The freezing point of the product from ebonite (f. p. –74.2°) was raised by admixture with the synthetic material. It is noteworthy that this 2,5-disubstituted thiophene mercurates more slowly than the other compounds heretofore described, a behavior which parallels that reported by Steinkopf for 2,5-dimethylthiophene. Both synthetic 2-methyl-5-ethylthiophene and the product from ebonite (f. p. –74.2°) gave an intense red-brown color when added to a solution of isatin in commercial sulfuric acid. Dr. W. R. Brode has very kindly compared the absorption spectra of both these colorations with a spectrophotometer, and has found no difference whatever in the spectra.

It is evident that the material from ebonite is 2-methyl-5-ethylthiophene, reasonably free from isomers.

A trimethylthiophene, especially the 2,3,5-isomer, might be expected to mercurate with extreme difficulty, and these compounds were sought in the steam distillate from the mercuration. Youtz and Perkins¹¹ state that 2,3,5-trimethylthiophene dissolves in sulfuric acid and is reprecipitated apparently unchanged on dilution. Schulze¹² has recovered thiophene and its homologs by diluting with water and steam distilling the sulfuric acid washings of various aromatic hydrocarbons obtained from coal tar. Accordingly, the steam distillate from the mercuration of the ebonite fractions boiling in the neighborhood of 160° was carefully washed, cold, with 2 volumes of concd. sulfuric acid. The sulfuric acid extract was drawn off and ice and water were added to it, which caused the separation of an oil. The oil was removed, steam distilled, and then distilled over sodium. There was thus recovered 2 g. of a product of b. p. 158–168° which had n_D^{30} 1.484. A measurement of the depressions of the freezing point of 2-methyl-2-ethylthiophene caused by the addition of this material and of *n*-nonane was made. This measurement showed that at least 50% of the material recovered by sulfuric acid treatment was 2-methyl-5-ethylthiophene, which fact, in view of the low refractive index of the material, shows the practical absence of trimethylthiophenes.

⁹ Timmermans, *J. chim. phys.*, **27**, 2 (1930).

¹⁰ The preparation and physical properties of the synthetic specimen are described in a separate paper now submitted for publication in THIS JOURNAL.

¹¹ Youtz and Perkins, THIS JOURNAL, **51**, 3511–3516 (1929).

¹² Schulze, *Ber.*, **18**, 497 (1885).

Aromatic hydrocarbons were present only in insignificant amount in the ebonite fractions boiling from 156–165°, since less than 1 g. of hydrocarbon (b. p. 160–163°, n_D^{30} 1.472) was recovered from the sulfuric acid washing of the steam distillates.

TABLE III

AMOUNTS OF PRODUCTS RECOVERED BY PYROLYSIS OF 36,000 G. OF EBONITE			
Compound	Recovered, g.	Compound	Recovered, g.
Benzene	<0.5	2,4-Dimethylthiophene	10
2-Methylthiophene	10	<i>m</i> -Xylene	50
Toluene	1	Aromatic hydrocarbon, b. p.	
2,3-Dimethylthiophene	50	<i>ca.</i> 160°	< 1
		2-Methyl-5-ethylthiophene	240

Summary

The following compounds have been identified in the products obtained from ebonite by destructive distillation: 2-methylthiophene, 2,3-dimethylthiophene, 2,4-dimethylthiophene, 2,5-methylethylthiophene and *m*-xylene. These results will be used to derive the structural formula of ebonite.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE PREPARATION OF BENZOYLACETIC ESTER AND SOME OF ITS HOMOLOGS

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Although benzoylactic ester was first prepared by Baeyer¹ by the hydration of phenylpropionic ester, this method has certain disadvantages that reduce its preparative value.² The most satisfactory methods that may be found in the literature are two developed by Claisen. One of these involves the direct condensation of ethyl benzoate with ethyl acetate in the presence of sodium ethoxide,³ and although a 33% yield of product is claimed, the actual weight of benzoylactic ester reported as having been obtained shows the yield to be only 26% of the theoretical. In the other method benzoylactic ester is obtained by the partial hydrolysis of benzoyl-acetoacetic ester.⁴ Recently, failures to duplicate the yield claimed in Claisen's first method and modifications of the second method have been reported by Shriner and Schmidt.⁵

A number of the homologs of benzoylactic ester have been prepared

¹ Baeyer, *Ber.*, **15**, 2705 (1882).

² Hope and Perkin, *J. Chem. Soc.*, **95**, 2047 (1909).

³ Claisen and Lowman, *Ber.*, **20**, 653 (1887).

⁴ Claisen, *Ann.*, **291**, 67 (1896).

⁵ Shriner and Schmidt, *THIS JOURNAL*, **51**, 3636 (1929).