Hydrogenolysis of the acetate function of $C_{11}H_{10}CH_2OCOCH_3$ occurred as the main reaction.

The aldehyde, $C_{10}H_{11}CHO$, readily lost carbon monoxide.

The cyclic acetal, $C_{10}H_{11}\overline{CHOCH_2CH_2O}$, did not dehydrogenate smoothly. The only dehydrogenated product isolated, 2-methylnaphthalene, resulted from hydrogenolysis of the acetal.

The ketones $C_{10}H_{11}COCH_3$, $C_{10}H_{11}CH_2COCH_3$ and $C_{10}H_{11}CH_2CH_2COCH_3$ gave fair yields of the corresponding aromatic ketones. The ketonic group of the first was reduced to a methylene group to a considerable extent. Small amounts of the last two were pyrolyzed to form hydrocarbons, with a resulting loss of a two-carbon fragment in each case.

COLUMBUS 10, OHIO RECEIVED JANUARY 28, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CATHOLIC UNIVERSITY OF AMERICA]

Pyrolysis of Butadiene[1]

BY MARY THOMAS MURPHY[2a] AND ANN CHARLES DUGGAN[2b]

In the pyrolysis of unsaturated hydrocarbons in this Laboratory, it has been observed that the liquid products are frequently colored yellow. This was noted particularly in the pyrolyses of butadiene, isoprene,[3] and isobutylene,[4] where it appeared in the C_7-C_8 region of products. Similar observations were reported in 1932 by Frey and Hepp[5] in a study of the production of aromatic oils from the pyrolysis of simple paraffins. At 850° and atmospheric pressure, butane gave benzene, toluene, xylenes, and a number of olefins and diolefins, principally butadiene and cyclopentadiene. A few degrees above the boiling point of toluene a bright yellow hydrocarbon was obtained; another yellow hydrocarbon appeared in the xylene fraction. Neither of these was identified because they were present in such small amounts.

The first step in this investigation has been to pyrolyze large quantities of butadiene in order to isolate the yellow fraction in amounts large enough to analyze.

Experimental

The apparatus used for the pyrolysis was a quartz furnace 60 × 3 cm., connected to a series of traps, a manometer, a glycerol-filled vacuum pump and a gas meter. The traps were cooled to −78°. To prevent clogging, the first trap was cooled only to −10°. The furnace was heated by two external resistance heaters, and the temperature at the center was measured with a chromel-alumel thermocouple. The temperature was maintained within 10° during a given run. The pressure did not vary more than 2 mm.

The butadiene obtained from Shell Oil Company was of better than 98% purity; it was used without further purification. The hydrocarbon was introduced to the furnace from a pressure bottle kept in an ice-salt-bath, the input rate, usually a mole an hour, being regulated by a needle valve, and the amount put through determined by the loss in weight of the bottle. The tar, largely naphthalene, collected in the first trap, while the lower aromatic fractions condensed mainly in the second and third traps. Nearly all of the unchanged butadiene condensed in the traps, but 2-5% of the total volume was detected in the effluent gases. The gaseous products (insoluble in glycerol, except acetylene to some extent) passed through the gas meter and escaped into the air. During the course of a run several samples were taken for analysis. At the end of each run the products collected were transferred to weighed bottles and stored at −15° until they were analyzed.

Five runs were made in all. In Table I are given the data for run 3. The analysis of the products was made as follows:

The gases were determined on a modified Hempel apparatus developed in this Laboratory.[6] The reagents for the absorption of the various gases were: acetylene, potassium mercuric iodide; isobutylene, 62.5% sulfuric acid; butenes, 71% sulfuric acid; propylene, 82.5% sulfuric acid; ethylene, fuming sulfuric acid. The different concentrations of acid were those recommended by Hurd and Spence[7] for the detection of the various hydrocarbons. Butadiene was determined by its reaction with maleic anhydride.[8] Since, according to Hurd and Spence, butadiene would be absorbed in both the propylene and isobutylene reagents, the values reported for the C_3 and C_4 hydrocarbons are affected by this amount. The saturated portion of the gas was analyzed for hydrogen by oxidation over copper oxide at 285°. The average value, 25%, checked analyses by combustion data which gave 25.8% for hydrogen and 12% for methane.

The tar in the first trap was collected over several runs and distilled. It was found to contain naphthalene and a small yellow fraction boiling above naphthalene, which we have not yet identified.

An approximate analysis from mass spectrometer data[9] for the liquid samples from the other traps showed, in agreement with Staudinger[10] that the liquids are almost exclusively aromatic. The relative abundance of the compounds was as follows: benzene, $> 90\%$; toluene, $\leqq 1\%$; indene, $< 1\%$; dihydroindene, $< 1\%$; tetralin, $< 0.5\%$; styrene, $< 1\%$; ethylbenzene, $\leq 1\%$. Other peaks not accounted for occurred at 83, 85, 117 and 119. It will be noticed that the benzene/toluene ratio of 90/1 found by the mass spectrometer differs widely from the ratios reported in Tables I and II (15.4/1.0 and 10.8/1.0, respectively), but no explanation for this deviation is apparent.

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[1] Taken from the dissertation presented by Sister Ann Charles Duggan for the degree of Doctor of Philosophy at the Catholic University.

[2] (a) Sister Mary Thomas Murphy, S.S.J., College of Chestnut Hill, Philadelphia, Pa.; (b) Sister Ann Charles Duggan, O.P., Barry College, Miami, Florida.

[3] M. T. Murphy, Ph.D. dissertation, The Johns Hopkins University, 1938, pp. 38, 44.

[4] L. Wall, Ph.D. dissertation, Catholic University of America, 1945, p. 10.

[5] Frey and Hepp, *Ind. Eng. Chem.*, **24**, 282 (1932).

[6] Rev. Aquinas Sweeney, C.P., Master's thesis, Catholic University of America, 1945.

[7] Hurd and Spence, THIS JOURNAL, **51**, 3356 (1929).

[8] Tropsch and Mattox, *Ind. Eng. Chem., Anal. Ed.*, **6**, 104 (1934).

[9] We are indebted to Dr. Leo Wall of the National Bureau of Standards for this analysis.

[10] Staudinger, Endle and Herold, *Ber.*, **46**, 2466 (1913).

TABLE I

PYROLYSIS OF BUTADIENE, RUN 3

Temperature, °C.		838
Pressure, mm.		20
Length of run, min.		392
Contact time, sec.		0.5
Butadiene used, g.		323
Butadiene recovered, g.		153.9
Products recovered, g.	Liquid and solid	74.5
	Gaseous	78.6
Difference in weight balance, g.		16.0
% decomposed, based on recovered products		47.5

Gaseous products	Moles	Moles/mole C_4H_6 decomposed
Hydrogen	0.89	0.313
Methane	.42	.148
Acetylene	.42	.148
Ethylene	1.37	.482
Propylene	0.35	.123
Isobutylene	.09	.033
Liquid and solid products		
Cyclopentane	.038	.013
Benzene	.463	.163
Toluene	.030	.011
Ethylbenzene	.038	.013
Isopropylcyclopentene	.005	.002
Isopropylcyclopentane	.009	.003
Xylenes	.007	.002
Naphthalene	.07	.025
Carbon (tar)	.075	.264
Carbon in furnace	.075	.264

The liquid products were analyzed by distillation at both ordinary and reduced pressures. In run 3, the liquid products were hydrogenated, before distillation on an 11-mm. Podbielniak column.

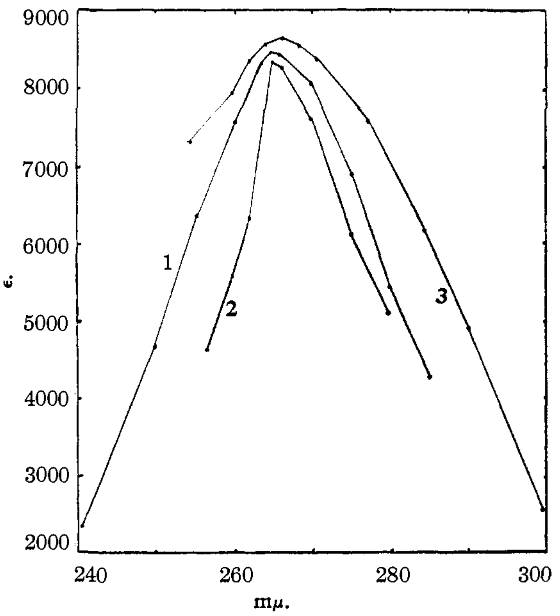

Fig. 1.—Ultraviolet absorption spectra of dimethylfulvene and yellow pyrolysis product: 1, dimethylfulvene in 2,2,4-trimethylpentane; 2, pyrolysis product in *n*-hexane; 3, pyrolysis product in 2,2,4-trimethylpentane.

In Table II are given data for the distillation of the liquid products of run 2. In this case the distillation was carried out on a 35-cm. vacuum-jacketed Vigreux column. The first part of the distillation was run rapidly to prevent polymerization of the dimethylfulvene; 25 cc. of hexadecane was added before the distillation to serve as column hold-up. This distillation showed the presence of cyclopentadiene as well as the aromatic products previously reported in butadiene pyrolysis[10] and indicated that the main yellow product was a C_8 compound. It was subsequently identified as dimethylfulvene by its absorption spectra, hydrogenated products and oxygen derivative.

The sample used for the absorption spectra measurements was obtained by fractional crystallization of the liquid products. After most of the dissolved butadiene had been removed by distillation at room temperature, the remaining liquid was cooled to −80° and filtered through a suction funnel likewise cooled. The process of cooling and filtering was repeated until no more solid could be separated from the yellow liquid. Further separation of the residue was accomplished in a bulb to bulb distillation at 1–2 mm., the receiver being cooled in liquid air. In this way 2.5 cc. of bright yellow liquid was obtained for the absorption spectra measurements.

The absorption in the visible and ultraviolet were measured with a Beckmann Model DU quartz spectrophotometer. Since the work on the spectrum of dimethylfulvene[11] had been done before conventions were established for the reporting of spectral data, it seemed advantageous to repeat the work in this Laboratory in order to facilitate the comparison of the dimethylfulvene spectrum with that of our yellow compound. Accordingly, dimethylfulvene was synthesized by the method of Thiele.[12] Solutions were made from a sample which boiled at 46–48° under 11 mm. pressure and had a freezing point of 0.9°. The 2,2,4-trimethylpentane used as a solvent was distilled over sodium hydroxide and filtered through silica gel. The graphs for the spectra of dimethylfulvene and our yellow compound are shown in comparison in Fig. 1. The absorption maxima, 270 and 365 mμ, are the same as those reported by Stark and his co-workers.

Hydrogenation was carried out under the conditions recommended by Pines and Ipatieff.[13] Three hundred twenty grams of pyrolysis product, including unchanged butadiene, was hydrogenated over Raney nickel at 30 atm. and 25–125°. Distillation was then carried out on a Podbielniak fractionating column. Small amounts of the expected hydrogenation products of dimethylfulvene were obtained: 1.5 cc. isopropylcyclopentene, b. p. 120–122°; 1.8 cc. isopropylcyclopentane, b. p. 126–127.5°, m. p. −113°.

The presence of the fulvene was further substantiated by the formation of its oxide. A dilute solution was allowed to stand in air for a month. At the end of this time a flocculent white precipitate had formed. The solution was centrifuged and the precipitate washed with ether and dried. At 80–90° it reacted in the same way as the oxide of dimethylfulvene[14] which had formed in the same manner. Both oxides exploded when heated to 125°.

The yellow substance also gave a positive color reaction with sulfuric and acetic acids. This test described by Thiele[15] is given by all the simple fulvenes.

The mass spectrometer data indicated the presence of indene, dihydroindene and tetralin, but the small amounts which may have been present were not isolated.

Summary

Butadiene has been pyrolyzed at low pressures in order to study the formation of yellow hydrocarbons produced in the pyrolysis. In addition to

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(11) Stark, *et al.*, *Jahrb. Radioakt. Elektronik*, **10**, 139 (1913).

(12) Thiele, *Ber.*, **33**, 666 (1900).

(13) Pines and Ipatieff, THIS JOURNAL, **61**, 1076 (1939).

(14) Engler and Frankenstein, *Ber.*, **34**, 2933 (1901).

(15) Thiele and Balhorn, *Ann.*, **348**, 1 (1906).

TABLE II

LIQUID PRODUCTS FROM BUTADIENE PYROLYSIS, RUN 2

Amount, g.	Description	B. p. °C.	Mm.	F. p., °C.	n^{20}D	Probable composition
2.5	Colorless liq.	39–42.5		−90	1.4388	Cyclopentadiene
1.7	Colorless liq.	*ca.* 70		−15	1.4807	
2.6	Colorless liq.	78		0.1	1.4967	Mostly benzene
27.6	Colorless liq.	79.5		3.5	1.5000	Benzene
2.8	Colorless liq.	41–42	60	−96	1.4951	Toluene
1.5	Sl. yellow	50–65	60	−70	1.5037	Ethylbenzene, xylenes and dimethylfulvene
1.0	Yellow	66.6	57	−60	1.5251	Dimethylfulvene
2.7	Sl. yellow	59–62	39	−45	1.5383	Styrene
0.7	Yellow	64–65	40	Glass −82	1.5240	
0.8	Colorless liq.	46.5	10	Glass −80	1.5268	
9.0	White solid			75		Naphthalene

the previously reported products, cyclopentadiene, styrene and dimethylfulvene, a yellow hydrocarbon, have been identified. The presence of two higher boiling yellow fractions is indicated, but they have not been identified.

WASHINGTON, D. C. RECEIVED AUGUST 11, 1948

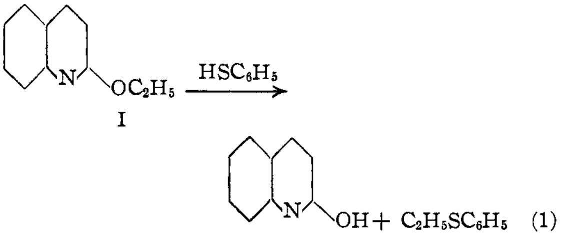
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reactions of Thiols with Some Alkyl and Aryl Heterocyclic Ethers

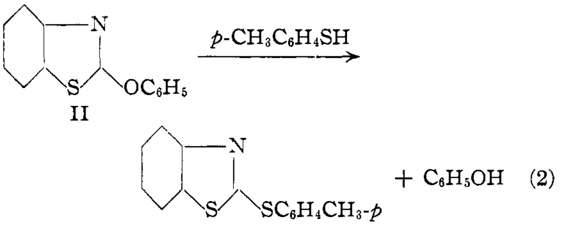
BY GABRIELLO ILLUMINATI AND HENRY GILMAN

Recent work[1] on the action of organolithium compounds on some 2-substituted quinolines has emphasized the special character of the 2-position in quinoline. The present study describes the reactions of aryl thiols on some alkyl and aryl 2- and 4-quinolyl ethers and on corresponding derivatives of 2-benzothiazolyl and 2-benzoxazolyl ethers.

The 2-ethoxy compounds of quinoline (I), benzothiazole and benzoxazole are known to be cleaved by hydrogen chloride[2] to form ethyl chloride and the corresponding 2-hydroxy derivatives. We have now found that a similar cleavage occurs by the action of aryl thiols on these ethoxy compounds at 150–170°, in accordance with the following typical reaction.



This alkylating reaction appears to be general, for 2-benzyloxyquinoline behaves in an analogous manner. However, with aryloxy compounds, the following representative cleavage reaction takes place.



From the results given in Table I it appears that the ease of cleavage of the heterocyclic types varies as follows:

2-Quinolyl > 2-Benzothiazolyl > 2-Benzoxazolyl.—An alkylating reaction appears not to occur with 4-alkoxyquinolines, for 4-ethoxy-7-chloroquinoline (III) reacts in essential accordance with reaction (2).

These reactions generally take place in good yield (see Table I) when aryl thiols like thiophenol, *m*- and *p*-thiocresol and β-thionaphthol are used. An exception in the experiments carried out was *o*-thiocresol, which did not react appreciably with (I), possibly because of steric hindrance. Some reagents containing an acidic hydrogen, other than aryl thiols, have given corresponding exchange reactions with 2-alkoxyquinolines.[3] The fact that benzyl mercaptan cleaved (I) to a small extent (see Table I, Expt. 6) may be accounted for by the lower acidic character of the benzyl mercaptan as compared with that of the aryl thiols.

Aryl thiols can also effect a related reaction with the chlorine atom in the activated positions of quinoline and benzothiazole. For example,

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(1) Gilman and Beel, unpublished results.

(2) Friedlaender and Ostermaier, *Ber.*, **15**, 335 (1882); Jacobson, *ibid.*, **19**, 1077 (1886); Sandmeyer, *ibid.*, **19**, 2655 (1886); MacCoy, *Am. Chem. J.*, **21**, 122 (1899).

(3) Unpublished studies; see, also, ref. 2.