This suggests that the mechanism of the reaction involves, as a first step, coördinate bond formation between the oxygen of the alkyl boron oxide and the boron or aluminum halide. Whether the subsequent reaction involves internal displacement (SNi reaction) or some other mechanism cannot be decided with the data so far available.

The applicability of this general reaction to the preparation of alkyldichloroboranes has been demonstrated in some of our preliminary studies. *n*-Butyldichloroborane[3] has been prepared in good yield by the reaction of boron chloride with butylboronic acid or butyl boron oxide. Further work on the preparation of alkyldichloroboranes is in progress.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT STANDARD OIL COMPANY (INDIANA)]

Synthesis of 4-Aryl-1,2-dithiole-3-thiones by Reaction of Cumenes with Sulfur

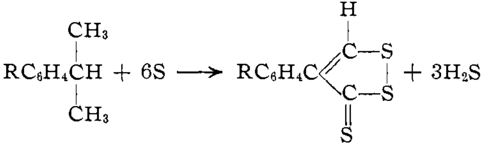
BY ELLIS K. FIELDS

RECEIVED SEPTEMBER 29, 1954

Cumenes react with sulfur at atmospheric pressure in the presence of bases to give good yields of 4-aryl-1,2-dithiole-3-thiones. The scope of the reaction has been studied and four new dithiolethiones have been prepared. Bases of greatly different strength give about the same results. The cumenes probably are converted to α-methylstyrenes, which in turn rapidly react with sulfur to give dithiolethiones. Many aryldithiolethiones can be made easily from readily available saturated hydrocarbons by means of this new reaction.

Aryldithiolethiones can be prepared by the reaction of arylalkenes with sulfur.[1] This method of preparation suffers from four disadvantages: (a) the yields are low, (b) the high reaction temperatures of 190–250° often make pressure equipment necessary, (c) tedious purification is required because of the excess sulfur that must be used, and (d) few arylalkenes are readily available.

In the presence of catalytic amounts of bases, cumenes have been found to react with sulfur and give good yields of aryldithiolethiones according to the equation



The reaction proceeds at atmospheric pressure. Excess hydrocarbon is used rather than excess sulfur; almost pure dithiolethiones crystallize directly from the reaction mixture.

Five cumenes have been converted to dithiolethiones, of which four are new. Properties of the cumenes are listed in Table I. The effect of different *para*-substituting radicals on the rate of reaction with sulfur has been studied.

TABLE I

CUMENES USED FOR PREPARING DITHIOLETHIONES

Cumene	Boiling point °C.	Boiling point Mm.	$n^{20}{}_D$	Yield, %
Cumene	152	745	1.4912	..
Cymene	175	745	1.4889	..
p-Ethylcumene[a]	73	10	1.4935	27
p-*t*-Butylcumene[b]	74–76	2.5	1.4930	67
p-*t*-Amylcumene[b,c]	81.5–83	2.3	1.4934	41

[a] Prepared according to Klages and Keil, *Ber.*, **36**, 1632 (1903). [b] Prepared according to Barbier, *Helv. Chim. Acta*, 19, 1345, 1349 (1936). [c] $d^{20}{}_4$ 0.684. *Anal.* Calcd. for $C_{14}H_{22}$: C, 88.42; H, 11.58; mol. wt., 190. Found: C, 88.55; H, 11.58; mol. wt., 194.

Preparations

The dithiolethiones listed in Table II were prepared by heating a mixture of 1 mole of hydrocarbon, 1.5 gram atoms of sulfur and 0.00165 mole of di-*o*-tolylguanidine at reflux (cumene, *p*-cymene) or at 185–200° until no free sulfur remained.[2] After the mixture was chilled at 0–10° for several hours, the crystals were filtered and recrystallized from benzene alone or diluted with hexane. Analyses of the materials prepared are given in Table III. The methiodide derivatives were made in nearly quantitative yields from the dithiolethiones and excess methyl iodide in *n*-butyl acetate at reflux for 2 hours.

TABLE II

PREPARATION OF 4-ARYL-1,2-DITHIOLE-3-THIONES

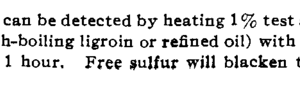
Catalyst: 0.00165 mole of di-*o*-tolylguanidine

Hydrocarbon	Temp., °C.	Time, hours	Yield,[a] %
Cumene	156	174	78
p-Cumene	185	21	76
p-Ethylcumene	199	4.5	40
p-*t*-Butylcumene	193	24	61
p-*t*-Amylcumene	190	15.5	36

[a] Based on sulfur.

In a typical preparation a mixture of 1108 g. (8.25 moles) of *p*-cymene, 400 g. (12.5 gram-atoms) of sulfur and 8.2 g. of ditolylguanidine was refluxed at 185° for 21 hours. Hydrogen sulfide was evolved steadily. The mixture then was kept at 5° for 2 hours to allow the dithiolethione to crystallize. The red crystals were collected on a filter, washed with 400 ml. of 1:3 benzene:hexane, and sucked dry. There was obtained 355 g. (1.58 moles, 77% based on sulfur) of 4-*p*-tolyl-1,2-dithiole-3-thione, m.p. 119–120°. After one recrystallization from benzene, it melted at 122.5–123°.

Vacuum distillation of the filtrate from the dithiolethione crystals gave 575 g. of *p*-cymene (b.p. 34–39° at 10 mm.) and 330 g. (1 mole) of a deep-red viscous residue which may be



$$p\text{-}CH_3C_6H_4\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}SS\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}C_6H_4CH_3\text{-}p$$

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(1) B. Böttcher and A. Lüttringhaus, *Ann.*, **557**, 89 (1947); A. Lüttringhaus, H. B. König and B. Böttcher, *ibid.*, **560**, 201 (1947); J. Schmitt and A. Lespagnol, *Compt. rend.*, **230**, 551 (1940); M. G. Voronkov, A. S. Braun and G. B. Karpenko, *J. Gen. Chem.* (*U.S.S.R.*), **19**, 1927 (1949); N. Lozac'h, *Bull. soc. chim. France*, 840 (1949).

(2) Free sulfur can be detected by heating 1% test sample in an inert hydrocarbon (high-boiling ligroin or refined oil) with a polished copper strip at 100° for 1 hour. Free sulfur will blacken the strip.

TABLE III

EXAMINATION OF 4-ARYL-1,2-DITHIOLE-3-THIONES

Dithiolethiones	M.p., °C.	Mol. wt.		Carbon, %		Hydrogen, %		Sulfur, %		Methiodide analysis				
											Sulfur, %		Iodine, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	M.p., °C.	Calcd.	Found	Calcd.	Found
4-Phenyl	122	210	209	51.42	51.30	2.86	3.00	45.72	45.90	194 d.	27.27	27.10	36.08	35.90
4-*p*-Tolyl[a]	122.5–123	224	229	53.60	54.00	3.57	3.80	42.83	42.60	178.5–179	26.21	26.40	34.70	34.50
4-*p*-Ethylphenyl[a]	108	238	240	55.43	55.40	4.20	4.00	40.37	40.20	163–164	25.25	25.00	32.40	32.60
4-*p*-*t*-Butylphenyl[a]	145–146	266	262	58.61	58.90	5.27	5.20	36.09	35.70	161–161.5	23.52	23.80	31.11	31.40
4-*p*-*t*-Amylphenyl[a]	112	280	270	60.00	60.50	5.72	5.48	34.28	34.40	155–156 d.	22.74	22.50	30.10	29.90

[a] New compound.

Anal. Calcd. for $C_{20}H_{26}S_2$: C, 72.73; H, 7.88; S, 19.39; mol. wt., 330. Found: C, 73.40; H, 6.95; S, 19.70; mol. wt., 322.

The corresponding residue from the preparation of phenyl, dithiolethione from cumene was cumene disulfide. *Anal.* Calcd. for $C_{18}H_{22}S_2$: C, 71.57; H, 7.26; S, 21.17; mol. wt., 302. Found: C, 71.60; H, 7.40; S, 21.40; mol. wt., 293.

To prove the structure of cumene disulfide, a solution of 30 g. of cumene disulfide in 150 ml. of tetrahydrofuran was added dropwise over 1 hour to 10 g. of lithium aluminum hydride in 300 ml. of tetrahydrofuran. The mixture was refluxed 3 hours, decomposed with ice-water and 15% sulfuric acid, and extracted with 200 ml. of isopropyl ether. The ether solution was washed with water, dried, and distilled to give 15 g. of cumene mercaptan,[3] b.p. 63–64° at 2.3 mm., $n^{20}D$ 1.5500. *Anal.* Calcd. for $C_9H_{12}S$: C, 71.03; H, 7.90; S, 21.06; mol. wt., 152. Found: C, 71.35; H, 7.79; S, 20.9; mol. wt., 150.

In an attempted reaction of sulfur and *p*-cymene without catalyst, 67 g. (0.5 mole) of *p*-cymene and 24 g. (0.75 gram-atom) of sulfur were refluxed for 72 hours. The mixture evolved but little hydrogen sulfide and, on cooling, precipitated 92% of the original sulfur. After refluxing the same mixture under ultraviolet radiation for 48 hours, 88% of the original sulfur was recovered. No dithiolethione could be isolated in either case.

Three hydrocarbons failed to react with sulfur in the presence of di-*o*-tolylguanidine. *n*-Propylbenzene at 163° gave 63% unreacted sulfur after 219 hours; *t*-butylbenzene at 175° gave 80% unreacted sulfur after 100 hours; 1-methyl-3-*t*-butyl-4-isopropylbenzene at 195° gave 82% unreacted sulfur after 48 hours.

Reaction Rates

Comparative rates of reaction with sulfur were determined for (a) α-methylstyrene and cumene, (b) cymene in the presence of different bases and (c) different cumenes.

To compare the rate of reaction of α-methylstyrene with that of cumene, a mixture of 236 g. (2 moles) of α-methylstyrene, 96 g. (3 gram-atoms) of sulfur and 1.97 g. of di-*o*-tolylguanidine was heated at 156°. After 18 hours, it contained no free sulfur. Cumene, treated the same way, took 174 hours to react with all the sulfur. The yield of dithiolethione from α-methylstyrene was only 25% (based on sulfur). A much better yield of dithiolethione resulted when 47.2 g. (0.4 mole) of α-methylstyrene was added dropwise over 8.5 hours to a solution of 19.2 g. (0.6 gram-atom) of sulfur and 0.394 g. of di-*o*-tolylguanidine in 95 ml. of *t*-butylbenzene at 156°. The red solution was kept at 156° for 16 hours, then cooled to 5°. There crystallized 17.9 g. (70% based on sulfur) of 4-phenyl-1,2-dithiole-3-thione, melting at 120–121°.

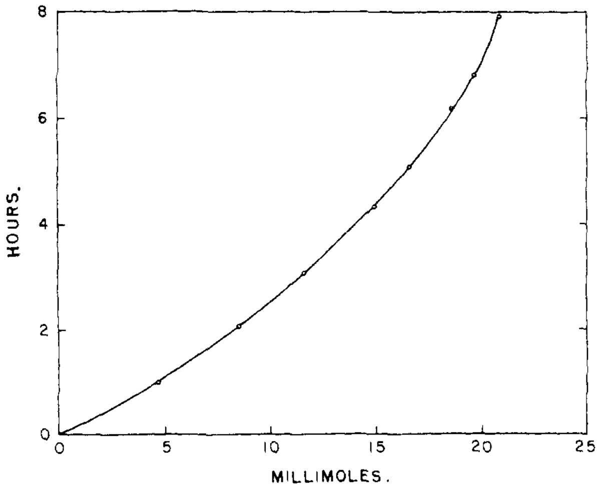


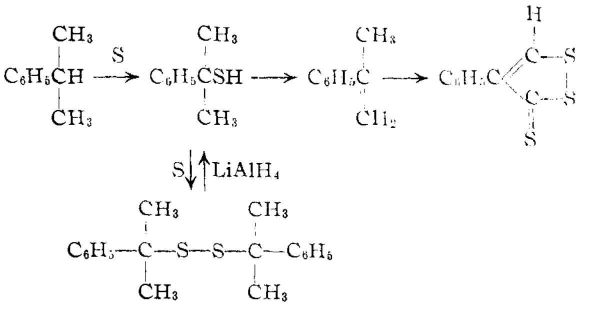
Fig. 1.—Rate of hydrogen sulfide evolution with cymene, sulfur and di-*o*-tolylguanidine at 178°.

To determine the effect of different bases on the rate of reaction, 0.0005 mole of base and 0.05 gram-atom of sulfur in 73.3 ml. of *p*-cymene was kept at 178° and the hydrogen sulfide was determined. Despite widely differing basicities, potassium hydroxide, di-*o*-tolylguanidine, *m*-amylamine, di-*n*-amylamine and quinoline showed no significant differences in a period of 8 hours. Di-*o*-tolylguanidine was preferred in most of this work because it gave lighter-colored dithiolethiones and slightly better yields than the other catalysts.

To determine relative reaction rates for cumenes, a solution of 16 g. (0.05 gram-atom) of sulfur and 0.1195 g. (0.0005 mole) of di-*o*-tolylguanidine in 73.3 ml. of each cumene was kept at constant temperature within 0.2°. A slow stream of dry nitrogen carried the hydrogen sulfide into a gas wash-bottle containing standard cadmium sulfate solution. The wash-bottle was changed at regular intervals and the liberated sulfuric acid was titrated with standard sodium hydroxide. A typical determination with *p*-cymene gave the rate of H_2S evolution shown in Fig. 1.

Discussion

Because *n*-propylbenzene and *t*-butylbenzene fail to react, the cumene structure is necessary for the formation of dithiolethiones from saturated aromatic hydrocarbons and sulfur. Sulfur reactions can be ionic or free radical.[4] Inasmuch as dithiolethione formation from cumene is catalyzed by bases but not by ultraviolet light, the ionic mechanism is strongly indicated, at least in the first steps where cumene mercaptan, α-methylstyrene and cumene disulfide are formed



The bases probably function by forming reactive intermediates with sulfur rather than by loosening the tertiary hydrogen bond; bases of such widely

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[3] New compound; the infrared spectrum shows an –S–H absorption peak at 3.9 μ; all other peaks are similar to those of cumene.

[4] E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, 1519 (1947); A. W. Horton, *J. Org. Chem.*, **14**, 761 (1949); D. Craig, *et al.*, *J. Polymer Sci.*, **8**, 321 (1952).

differing strength as potassium hydroxide and quinoline give about the same reaction rates with cymene and sulfur. The nature of the intermediates has not been determined. Levi[5] has found that amines form definite compounds with sulfur. These compounds are too unstable to exist at the temperatures used in this study. The reaction of α-methylstyrene with sulfur to give the dithiolethione may be by a free radical mechanism.[6]

The relative reaction rates in Table IV, relative to cumene (taken as 1.00), show the order: methyl 4.8, ethyl 1.8 and *t*-butyl 0.5. This sequence lines up with that obtained by Baker and Nathan[7] in the hydrolysis of *p*-substituted benzyl halides, and by Hughes, Ingold and Taher[8] in the hydrolysis of *p*-substituted benzhydryl halides and ascribed by them to hyperconjugation. Good agreement in the rates obtained at constant time and constant percentage conversion indicates the same mechanism is operating in all cases.

TABLE IV

RELATIVE RATES OF REACTION OF CUMENES WITH SULFUR

Catalyst: 0.00165 mole of di-*o*-tolylguanidine

	Cumene	Cymene	*p*-Ethylcumene	*p*-*t*-Butylcumene
Temperature 151°				
Reacn. in 24 hr., %	5.7	28	10	...
Rel. reacn. rate	1	4.9	1.8	...
Time for 40% reacn., hr.	144	30	82	...
Rel. reacn. rate	1	4.8	1.8	...
Temperature 178°				
Reacn. in 8 hr., %	...	82.3	29.2	8.56
Rel. reacn. rate	...	9.6	3.4	1
Time for 80% reacn., hr.	...	7.5	20.25	71
Rel. reacn. rate	...	9.5	3.5	1

Aryldithiolethiones can now be made easily from readily available saturated hydrocarbons.

WHITING, INDIANA

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(6) A. Lüttringhaus and W. Cleve, *Ann.*, **575**, 122 (1951).

(7) J. N. Baker and N. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

(8) E. D. Hughes, C. K. Ingold and N. A. Taher, *ibid.*, 949 (1940).

[CONTRIBUTION FROM THE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Fractionation of Phosphates from Scenedesmus by Anion Exchange[1]

BY M. GOODMAN,[2] A. A. BENSON AND M. CALVIN

RECEIVED MARCH 14, 1955

The phosphorylated compounds involved in algal metabolism have been extracted and fractionated on Dowex 1 and 2 columns. The separation of hexose monophosphates, phosphoglycerate, hexose diphosphate and ribulose diphosphate is described. The elution characteristics of trace amounts of radioactive phosphate esters were found identical to those of macro amounts. Using P^{32}-labeled algal extracts, relatively large amounts of material have been fractionated. The ion exchange elution data of ribulose diphosphate are described.

Introduction

The fractionations of phosphorylated compounds from algae have been reported by Umbreit, *et al.*,[3] Kamen and Spiegelman,[4] Emerson, *et al.*,[5] Gest and Kamen[6] and Simonis and Grube.[7] The techniques described involved gross fractionation methods. The object of this investigation is to present a preliminary scheme for extending the gross fractionations to permit chemical characterization of compounds in the alcohol–water extracts of algae.

Paper chromatography[8–12] has been used extensively to characterize compounds occurring in algae. Ion exchange chromatography, however, offers the possibility of larger scale isolation for chemical analysis. The purpose of this work is to develop separations of photosynthesis intermediates, particularly ribulose diphosphate.

The separation of phosphorylated compounds by anion exchange has been demonstrated by Khym and Cohn,[13] who used borate complexing to achieve separation. Benson, *et al.*,[8] separated fructose-6-phosphate from fructose-1,6-diphosphate. Horecker and Smyrniotis[14] separated ribose-5-phosphate from ribulose-5-phosphate. The methods developed using pure compounds have been applied to the rather complex mixture in plant extracts.

Experimental

Preparation of Algal Extracts.—Two methods were used to obtain the algae: 1. *Scenedesmus* was grown as a continuous sterile culture under controlled conditions[15] with the addition of ferric Versenate.[16] The algae were harvested, centrifuged from the growth medium, resuspended in water and killed in 80% boiling ethanol while photosynthesizing with 4% carbon dioxide bubbling through the suspension. After an accumulated total of 75 ml. (packed volume) of

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[1] The work described in this paper was sponsored by the U.S. Atomic Energy Commmission.

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[4] M. D. Kamen and S. Spiegelman, *Cold Springs Harbor Symposia Quant. Biol.*, **13**, 151 (1948).

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[7] W. Simonis and K. H. Grube, *Z. Naturforsch.*, **7b**, 194 (1952).

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[11] M. Calvin, "The Harvey Lectures," Charles C Thomas, Springfield, Ill., 1950–1951.

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