Method A, this urea was obtained in 97% yield, the product having m.p. 57–61°.

Anal. Calcd. for $C_7H_{16}N_2O_2$: N, 15.90. Found: N, 15.48.

1,3-Disubstituted 5,6-diaminouracils were prepared by the procedure of Blicke and Godt[20] except that the nitrosation was carried out at 85°.

1-(2-Methylallyl)-3-methyl-5,6-diaminouracil was obtained in 48.6% yield and had m.p. 149–153°.

Anal. Calcd. for $C_9H_{14}N_4O_2$: C, 51.42; H, 6.71; N, 26.65. Found: C, 51.62; H, 6.64; N, 26.52.

1-Allyl-3-ethyl-5,6-diaminouracil was obtained in 40.2% yield and had m.p. 138.5–141.5°.

Anal. Calcd. for $C_9H_{14}N_4O_2$: N, 26.65. Found: N, 26.52.

General procedure for the preparation of 1,3-disubstituted 5-thioureido-6-aminouracils. To a solution of 0.1 mole of the appropriate 1,3-disubstituted 5,6-diaminouracil in 100 ml. of chloroform is added 0.1 mole of the desired isothiocyanate. When the exothermic reaction has subsided the solution is heated under reflux for 1 hr. The product may precipitate during heating, or cooling in an ice bath may be necessary to effect crystallization. The thioureido derivatives can be recrystallized from 95% ethanol. Compound IX to XV were prepared by this procedure and the physical properties, yields, and analytical data are shown in Table I.

General procedure for the preparation of 1,3-disubstituted 5-ureido-6-aminouracils. A. *By desulfurization of the thiourea.* The appropriate 1,3-disubstituted 5-thioureido-6-aminouracil (0.03 mole) is suspended in 0.06 mole of sodium hydroxide in 100 ml. of water and the mixture is heated to 40°. There is added, dropwise, 0.12 mole of 30% hydrogen peroxide and on completion of addition, which is exothermic, the mixture is heated at 75–80° for several minutes. On cooling, the product is removed by filtration and the urea may be recrystallized from either 95% ethanol or chloroform and benzene. Compounds XVI, XVIII to XXI, XXV, XXVII, and XXVIII were prepared in this manner and the physical properties, yields, and analytical data are shown in Tables II and III.

B. *By reaction of an isocyanate and a diaminouracil.* To a solution of 0.024 mole of the appropriate 1,3-disubstituted 5,6-diaminouracil in 50 ml. of chloroform is added 0.024 mole of the desired isocyanate. On completion of the exothermic reaction the solution is heated under reflux for 30 min. Some benzene is added to induce crystallization and the product is recrystallized from either 95% ethanol or chloroform and benzene. Compounds XVII, XXII to XXIV, XXVI, XXIX, and XXX were prepared in this manner, and the physical properties, yields, and analytical data are shown in Tables II and III.

1-(2-Methylallyl)-3-methyl-5-ureido-6-aminouracil. To a solution of 10 g. (0.0476 mole) of 1-(2-methylallyl)-3-methyl-5,6-diaminouracil in 4.24 ml. (0.0476 mole) of concd. hydrochloric acid diluted with 44 ml. of water was added 7.72 g. (0.0952 mole) of potassium cyanate. A vigorous exothermic reaction ensued accompanied by precipitation of the product. The mixture was stirred for 1 hr. followed by filtration of the product and washing with water. The yield of urea was 10 g. (82.5%). It was impossible to determine the melting point of the product since it ring closes on heating. Recrystallization also proved impossible due to insolubility of the material. The spectral data were consistent with the proposed structure.

Anal. Calcd. for $C_{10}H_{15}N_5O_3$: N, 27.66. Found: N, 27.19.

Acknowledgment. I would like to acknowledge the help of the following persons who contributed materially to this research. Dr. Robert T. Dillon and his associates for analyses and determination of physical properties. Drs. Viktor Papesch and Elmer F. Schroeder for supplying compounds used as intermediates in this study and for very helpful advice on the chemistry of substituted 6-aminouracils. Messrs. Donald Zitzewitz and Frank Madden for the preparation of intermediates used in these syntheses.

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[20] F. F. Blicke and H. C. Godt, Jr., *J. Am. Chem. Soc.*, **76**, 2798 (1954).

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION]

Oxidation of Alkylbenzenes with Sulfur and Water

WILLIAM G. TOLAND

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It has been found that sulfur and water will oxidize the methylbenzenes to their respective carboxylic acids by heating to 200° to 400° under autogenous pressure. Mixing of all three components at reaction temperature minimizes side reactions. Sulfur dioxide and sulfuric acid will also function, if initiated with small amounts of hydrogen sulfide. The reactions with sulfur and water are reversible. Intermediate sulfur compounds can be isolated in most cases. By control of conditions, o-xylene can be made to yield thiophthalide, an intermediate, as the major product. Some of the theoretical implications are considered.

The use of sulfur, water, and a base, such as caustic or ammonia, as an oxidizing agent for organic compounds has been studied and reported previously.[1] Other forms of sulfur, such as sulfite, thiosulfate, and sulfate triggered by hydrogen sulfide function similarly.[2] Products are carboxylic salts. If ammonia is the base used, amides are also produced. Sulfuric or other mineral acid is required to liberate the free carboxylic acids.

Current studies show that with the methylbenzenes sulfur and water can be used as the oxidant and a base is not required. The free carboxylic acids are obtained directly, according to the reaction:

$$C_6H_5CH_3 + 3\ S + 2\ H_2O \longrightarrow C_6H_5CO_2H + 3\ H_2S \quad (1)$$

Yields of about 85% can be obtained with complete

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[1] W. G. Toland, Jr., D. L. Hagmann, J. B. Wilkes, and F. J. Brutschy, *J. Am. Chem. Soc.*, **80**, 5423 (1958).

[2] W. G. Toland, *J. Am. Chem. Soc.*, **82**, 1911 (1960).

conversion of hydrocarbon. Some intermediate thio compounds are also produced.

Success with this oxidant depends upon avoiding the direct interaction of sulfur with the organic compounds to be oxidized, which gives entirely different products, including stilbenes, bibenzyls, and tetraphenylthiophenes. This is achieved by heating the organic compound with a large molar excess of water prior to any appreciable reaction with the sulfur. Presolution of the compound in water is most effective, but adding it to a preheated mixture of sulfur and water is also satisfactory. Reaction proceeds in from fifteen minutes to two hours between about 200° and 400° under autogenous pressure. At temperatures above the critical, miscibility of water and hydrocarbon is ensured. However, solubility of xylene in water is sufficiently high (about 10% at 320°) that this is not necessary. Examples of the effects of mixing are illustrated in Table I, Runs 1 *vs.* 2 and 5 *vs.* 6.

One of the surprising features of this oxidation is its reversibility. This was discovered when prolonged reaction times not only failed to complete conversions from stoichiometrically equivalent proportions of sulfur and aromatic, but actually gave lower yields. This reversibility was established by treating toluic acid and hydrogen sulfide in water and obtaining xylene and sulfur from the products. The lowered yields with time were the result of this reversibility followed by the nonreversible sulfur-hydrocarbon reactions mentioned earlier. This reducing action of hydrogen sulfide was recognized by Willgerodt[3] in the disappearance of the carbonyl group of acetophenone during its oxidation with polysulfide to form phenylacetic acid, but the direct reduction of the carboxyl group in this way has not been described.

Complete conversions of alkyl aromatics are favored by use of excess oxidant, as is to be expected from Equation 1. An alternate method is removal of one or more of the products. By releasing hydrogen sulfide at reaction temperature, less intermediate thiocompounds remain. Chemical methods may also be used. Base, of course, can function by neutralizing acidic products; but an alternate method was found to be the addition of sulfur dioxide. This reacts with the hydrogen sulfide, drives the reaction to completion, and generates more sulfur. It can, in fact, be used as the sole oxidant in place of sulfur, preferably with a small amount of sulfur or hydrogen sulfide as an initiator. The over-all reaction then becomes:

$$C_6H_5CH_3 + SO_2 \longrightarrow C_6H_5CO_2H + H_2S \qquad (2)$$

This reaction has been studied by Strickland[4] in the vapor phase over vanadia catalysts. He states that large excesses of hydrocarbon over sulfur

TABLE I

OXIDATION OF ALKYL AROMATICS

Run	Compound	Moles	Oxidant[a]	Water[a]	H_2S[a]	Mix[b] Order	Temp.	Time,[c] min.	Termination[d]	Conversion, %	Yield of Acid, % Benzoic	Toluic	Phthalic
1	Toluene	2	1.56 S	50	0	1	315	90	A	44	39.3	—	—
2		2	6 S	50	0	2	335	60	A	100	68.0	—	—
3		2	1.3 SO_2	50	0.25	4(20)	335	20	D	100	82.0	—	—
4		0.5	0.8 H_2SO_4	100	1.5	2	330	60	A	100	49.4	—	—
5	*p*-Xylene	0.5	9.4 S	200	0	1	330	120	A	100	—	13.2	41.8
6		1	6 S	100	0	3(1)	345	153	A	100	4.7	—	65.8
7		4	2 SO_2	25	0.125	4(20)	330	75	C	100	0.8	—	76.2
8		0.5	1.5 H_2SO_4	100	3.0	2	330	60	A	100	—	12.2	36.8
9	*m*-Xylene	1	6 S	100	0	3(2)	345	91	A	100	4.3	—	71.5
10		4	2 SO_2	25	0.125	4(20)	330	73	C	100	—	—	83.0
11		0.5	1.5 H_2SO_4	100	1.8	2	330	60	A	100	—	—	57.6
12	*p*-Toluic acid	0.5	4 S	200	0	2	315	90	A	82	—	—	85.7
13	*m*-Toluic acid	1.0	3.1 S	100	0	2	315	120	A	24.7	—	—	100
14	Cumene	1.0	6 SO_2	100	0.5	4(20)	315	60	D	100	24.4	—	—
15	Acetophenone	0.5	6.2 S	100	0	2	335	60	A	100	41.0	—	

[a] Moles/mole compound to be oxidized. [b] Order of mixing of reactants: 1—All mixed cold, then heated. 2—All added cold, not mixed until at temperature. 3—Sulfur and water mixed cold, organic pumped in at temperature. 4—Organic and water mixed cold, sulfur dioxide pumped in at temperature. Number in parentheses is pumping rate, ml./min. of liquid. [c] Total time at temperature, including any pumping interval. [d] Termination technique: A—cooled before opening autoclave; B—hot release of liquid and vapor phase; C—hot release of vapor phase, cooled for liquid phase; D—hot release of liquid phase, then vapor phase.

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(3) C. Willgerodt and F. H. Merk, *J. prakt. Chem.* (2), **80**, 192 (1909).

(4) T. H. Strickland and A. Bell, U. S. patent 2,821,552 to Eastman Kodak Co., issued January 28, 1958.

TABLE II

OXIDATION OF *Ortho*-SUBSTITUTED AROMATICS

Run	Compound	Moles	Oxidant[a]	Water[a]	H_2S[a]	Mix[b] Order	Temp.	Time,[c] min.	Termination[d]	Conversion, %	Yield, mole %			
											of Acid			of Thiophthalide
											Benzoic	Toluic	Phthalic	
16	*o*-Xylene	1	6.25 S	100	5	3(5)	340	40	C	90.3	8.3	0	45.1	1.0
17		1	6.25 S	100	5	3(5)	340	55	A	82.0	0	0	0	62.2
18		4	2 SO_2	25	0.125	4(20)	335	80	Part B	100			(10	1)[e]
											4.1	2.5	53.5	15 2
19									Part A	100			(2	1)[e]
20		2	2.6 SO_2	50	0.25	4(20)	335	25	D	100	0	14.8	75.4	0
21	*o*-Toluic acid	1	6 S	100	0	2	330	60	A	100	16.4	0	47.1	3.0
22	Thiophthalide	0.9	3.4 S	110	0	2	315	90	A	96.0	17.1	0	74.8	—
23	Durene	1	6 SO_2	100	0.5	4(20)	335	40	D	100	—	—	52.8[f]	—

See Table I for footnotes *a–d*. [e] These are molar ratios, showing effect of termination method on distribution. [f] Pyromellitic acid.

dioxide must be used to obtain good yields of benzoic acid. He reports dibasic acids are difficult to obtain. Our work in the presence of water in liquid phase, on the other hand, shows that high yields of the phthalic acids are obtainable; and no catalyst is necessary. This is due in part at least to the ability to handle the free liquid sulfur formed by reaction of excess sulfur dioxide with product hydrogen sulfide, which creates problems in catalytic vapor phase systems. Results with sulfur dioxide are summarized in Table I, Experiments 3, 7, 10, and 14.

A natural extension of this oxidation system is the use of free sulfuric acid as the oxidant. The literature describes the use of concentrated or fuming acid. In these cases, the acid is reduced to sulfur dioxide. In dilute aqueous solutions when oxidation is initiated by some lower valence of sulfur, such as hydrogen sulfide or free sulfur, sulfuric acid is completely reduced to hydrogen sulfide. The over-all reaction is:

$$4\ C_6H_5CH_3 + 3\ H_2SO_4 \longrightarrow 4\ C_6H_5CO_2H + 3\ H_2S + 4\ H_2O \quad (3)$$

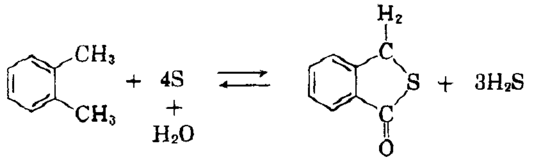
Water is now a product, not a reagent. Examples are given in Table I, Experiments 4, 8, and 11.

o-Xylene. The oxidation of *o*-alkyl-substituted benzenes, such as *o*-xylene and durene with sulfur and aqueous ammonia, gives relatively poor yields of the corresponding carboxylic acids. Such yields, lower than with other isomers, are due to decarboxylation of one of any pair of adjacent carboxyl groups. This is favored when at least one of the carboxyls is present in ionized form, such as the ammonium salt.

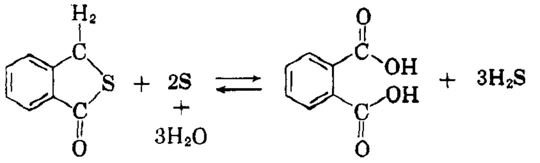
By the use of sulfur or sulfur dioxide and water in the absence of any salts or bases, relatively little ionization occurs; and, hence, there exists much less tendency toward decarboxylation. As a consequence, over 80% yields of *o*-phthalic acid can be obtained. The reaction is complete in ten to fifteen minutes at 330°, much more rapidly than for the other xylenes. Pyromellitic acid was obtained in over 50% yield from durene, with no attempt made to optimize conditions. Results are summarized in Table II.

One major difference was found between *o*-xylene and its isomers. Because of the opportunity-for cyclization between *ortho* carbon atoms, and the relative stability of such cyclic structures, it is possible to arrest the oxidation before completion. The presence of intermediates in appreciable quantities is, in fact, the normal situation in this reaction unless conditions are tailored deliberately to avoid them. On the other hand, the most stable intermediate, thiophthalide, can be made the principal product if desired. The reactions are as follows:

Both reactions are reversible and can be carried out independently if desired. Thiophthalide is favored if reaction products are cooled under hydrogen sulfide pressure. To favor phthalic acid,



(4)



(5)

hydrogen sulfide is released from the reaction products before cooling or sulfur dioxide is used to form sulfur from hydrogen sulfide. The net effect is to drive Reaction 5 to completion.

Whether *o*-toluic acid is an intermediate in the same reaction sequences which yields thiophthalide or whether it is formed by another reaction path has not been established. However, it was shown to oxidize to phthalic acid under reaction conditions. Thiophthalide was also converted to phthalic acid.

DISCUSSION

The ability to use sulfur and water as an oxidant in the absence of base is unexpected, although in retrospect the formation of some aldehydes and carboxylic acids from heating the tolyl carbinols with sulfur[5] might be considered as prophetic. In the past, the function of the base has been considered to aid the dissociation of the S_8 and S_6 molecule to smaller species[6]; to form intermediates[7,8]; to solubilize one or both reagents in the reaction medium; and, as nucleophilic agents, to hydrolyze intermediate thiocompounds to the oxygen analogs.[1] Formation of simple polyatomic sulfur aggregates need not require base. They have been reported from the reaction of hydrogen sulfide with sulfur dioxide, for example.[9,10]

The form of the oxidant which attacks the organic compound in absence of base is difficult to determine. Among the possibilities are the lower sulfur aggregates and radicals from monatomic sulfur and S_3, H_2S_2,[11,12] and even S_2O, a species never isolated but one which might well form along with S_3 during sulfur dioxide reduction with hydrogen sulfide if the same mechanism holds as has been suggested for sulfate reduction by sulfide.[2] Neither is base a necessary component of intermediates, although ammonia and amines can participate in this way. This is evident from results with alkali metal hydroxides and carbonates[1] and the present work.

The course of oxidation can be studied more readily in the sulfur-water system than when base is present. Being reversible, it permits the detection and isolation of several sulfur-containing intermediates. In the presence of base, none have been found in methylbenzene oxidations.[1,13] The most accessible by the current technique is thiophthalide from *o*-xylene oxidation. In the products from toluene oxidation, a somewhat more complex series was suggested by extraction of neutral products, including trithiobenzoic anhydride. It might be concluded that hydrolysis of the above species is relatively slow in water solution and that the function of bases and their salts with weak acids as nucleophilic agents to aid such hydrolyses is substantiated.

Aside from the mechanical effect of proper mixing, it is believed that success in the absence of base is the result of two factors. One is the fact that water itself can be considered as a nucleophilic agent, capable of donating electrons to aid hydrolysis of sulfur-containing intermediates. The other is the allylic character of methyl groups on the aromatic ring which activates these sites. Paraffins, olefins, and alicyclic hydrocarbons gave much lower yields of carboxylic acids. Organic sulfides, disulfides, and trithiones are favored products, apparently being much less easily hydrolyzed under these conditions.

EXPERIMENTAL

All runs were made in 4.5-l. batch autoclaves of 316 steel, fitted with rockers and heaters, bursting disks, thermowells, inlet and outlet ports. When premixed cold, all reagents were added initially and heated with shaking. Pressures were those generated autogenously. Products were either removed after cooling or the gas phase, containing largely hydrogen sulfide, was vented at temperature or the liquid phase was vented at temperature into ice. To mix reagents at reaction temperature, xylene was pumped into a shaking mixture of sulfur and water or sulfur dioxide was pumped into a preheated shaking mixture of aromatic and water.

Oxidation of toluene. A typical example is Run 2 of Table I. Baker's C.P. toluene was placed in an oversized Pyrex test tube wired to the thermowell in the head of the autoclave. The autoclave was charged with the water and sulfur. After sealing, the autoclave was heated to temperature and shaken. During this time, the pressure rose to 178 atm. After cooling to room temperature, the autoclave was vented through a caustic scrubber which absorbed 150 g. of hydrogen sulfide.

The mixture of yellow and brown solids and water remaining in the autoclave was extracted with ether and filtered. When dry, the cake weighed 223.7 g. and showed by analysis 95.0% free of sulfur. The ether-water filtrate was separated, the water discarded, and the ether evaporated to

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(13) W. A. Pryor, *J. Am. Chem. Soc.*, **80**, 6481 (1958).

dryness. This left 192.7 g. of crude, light yellow benzoic acid, neutral equivalent 131.0 (theory = 122.1), which was taken up in benzene and extracted with dilute aqueous sodium bicarbonate. Acidification of the extract with dilute hydrochloric acid precipitated benzoic acid which, after washing and drying, amounted to 166.3 g. neutral equivalent 122.3.

The benzene, upon evaporation to dryness under vacuum to avoid heat and contact with air, left 13.4 g. of a yellow-brown semisolid. Recrystallization from cyclohexane to reject any free sulfur gave 4.1 g. of yellow solids from a 10-g. aliquot. Digestion with aqueous sodium hydroxide and acidification gave benzoic acid and hydrogen sulfide. While the evidence is not complete, it is suspected of being trithiobenzoic anhydride.

Anal. Calcd. for $C_{14}H_{10}S_3$: C, 61.27; H, 3.68; S, 35.0. Found: C, 62.53, 63.54; H, 3.75, 3.81; S, 30.7, 31.0.

Because this hydrolyzable portion existed here and in other products, a direct caustic extraction of ether fractions was substituted for bicarbonate in other toluene oxidation product isolations. Further characterization of such fractions is under investigation in anticipation of shedding further light on reaction intermediates.

The above experiment was duplicated in the presence of 2.0 g. of nickel nitrate to determine if the nickel sulfide formed would catalyze the reaction. The pressure leveled out after 15–20 min., suggesting a rate three to four times that of the uncatalyzed run.

In a duplicate of the original run, 10 ml. of 28% aqueous ammonia was added to catalyze dissociation of sulfur species and to serve as a catalytic quantity of nucleophilic agent. Constant pressure was attained in about 40 min. An 81.9% yield of benzoic acid was obtained.

When 6.5 g. of sodium hydroxide was substituted for the ammonia, the reaction was apparently complete in about 40 min.; and an 83.6% yield of benzoic acid was found. Both bases thus appear to increase yields, probably by acting as stronger nucleophilic agents in the form of carboxylic acid salts than water alone.

A typical experiment with sulfur dioxide as the oxidant (Run 3, Table I) was effected as follows. The autoclave was charged with 1800 ml. of water, 184 g. of toluene, and 17 g. of hydrogen sulfide. After sealing and heating to 335°, shaking was begun and 167 g. of liquid sulfur dioxide was pumped in at a rate of 20 ml./min. over a period of 6 min. Shaking was continued for another 14 min. From an initial pressure of 159 atm. before sulfur dioxide addition, the pressure fell to 145 atm. The head of the bomb was then tilted downward, and the entire liquid phase discharged into 2000 g. of ice. The gas phase was absorbed in aqueous caustic. Work-up of product fractions in the usual way gave an 82.0% yield of benzoic acid.

Runs with sulfuric acid as the oxidant (Run 4, Table I) were handled by premixing reagents in a glass liner which fitted a 4.5-l. autoclave. The liner was charged with 900 ml. of water, 41 g. of 96% of sulfuric acid, 25 g. of hydrogen sulfide, and 46 g. of toluene and heated to 330° for 1 hr. of shaking. There was obtained 30.1 g. of benzoic acid, neutral equivalent 122.0, a 49.4% yield. In the absence of added hydrogen sulfide, there was no apparent reaction, and no hydrogen sulfide was formed.

Oxidation of p-xylene. The autoclave was charged with 1800 ml. of water and 192 g. of sulfur, sealed, and heated to 345° with shaking. The *p*-xylene (Oronite 95% *para*) was then pumped in at a rate of 1 ml./min. for the next 123 min. for a total of 106 g. or 1 mole. Shaking was continued for another 30 min. A maximum pressure of 198 atm. was reached. After cooling to room temperature, 156 g. of hydrogen sulfide was vented from the autoclave and absorbed in aqueous caustic. The autoclave contained dark, yellow solids and a cloudy water phase, and no unreacted xylene. Filtration yielded 148.4 g. of dry cake, and a filtrate from which 5.7 g. of benzoic acid was recovered. A one-fourth aliquot of the cake was extracted with 20 g. of aqueous sodium hydroxide, filtered from 1.1 g. of crude sulfur, and acidified with dilute hydrochloric acid to precipitate the terephthalic acid. After washing and drying, there was obtained 27.4 g. of the acid, neutral equivalent 83.6, representing a 65.8% yield of theory.

The oxidation with sulfur dioxide and with sulfuric acid was effected in the same manner as with toluene. Products were isolated as above.

Oxidation of m-xylene. The same equipment and procedure were used as for *p*-xylene oxidation, except that Oronite 95% *m*-xylene was used.

Oxidation of toluic acids. The equipment was that used for toluene oxidation with sulfur. Products were determined as from *m*-xylene runs.

Oxidation of cumene. This oxidation was effected in the same manner as with toluene, using Baker's C.P. cumene.

Oxidation of acetophenone. Eastman-White Label reagent was used. No phenylacetic acid was noted in the products.

Oxidation of propane. The autoclave was charged with 1800 ml. of water and 150 g. of lump sulfur, which settled on the bottom. After sealing, 44 g. of propane (Phillip's 95%) was admitted to the space above the water. At 330° shaking was initiated to mix reagents and continued for 2 hr. The pressure was still increasing after this period, having reached 183 atm. when shaking was terminated, and the bomb cooled. Gases were bled through an aqueous caustic scrubber to absorb hydrogen sulfide and through a Dry Ice cooled trap which condensed 19.3 g. of propane. The mixture of liquid and solid products was adjusted to *p*H 7 with 13.0 g. of sodium hydroxide, indicating the presence of 0.325 mole of acid, and steam distilled to recover any organic sulfides. None were found. Filtration of the still residue gave 24.3 g. of sulfur and neutral by-product. The filtrate was evaporated to dryness, acidified with dilute sulfuric acid to *p*H 1, and extracted with chloroform, which was then fractionally distilled to give 11.6 g. of an acetic-propionic acid mixture, boiling point 112–122°, neutral equivalent 65.9.

Oxidation of trimethylpentenes. Paralleling the oxidation technique with propane, the autoclave was charged with 1800 ml. of water, 150 g. of lump sulfur on the bottom, and 112 g. of a mixture of 2,4,4-trimethylpentene-1 and -2 (commercial diisobutylene) on the top of the water. At 290°, a 2-hr. period of shaking was effected, a constant pressure of 120 atm. being attained after the first hour. Neutralization of products after hydrogen sulfide removal showed the presence of 0.213 mole of acid. Steam distillation yielded 9.3 g. of volatile oily organic sulfide not further identified and 27.0 g. of nonvolatile carbonaceous solids. Distillation of the chloroform extract gave 10.0 g. of isobutyric acid, boiling point 151–161°, neutral equivalent 87. This suggests the trimethylpentenes depolymerized under reaction conditions to isobutene, which was then oxidized to the isobutyric acid.

Oxidation of o-xylene, Run 16, Table II. The system was similar to that with *p*-xylene. To the autoclave was charged 1800 ml. of water, 200 g. of sulfur, and 170 g. of hydrogen sulfide. At 340°, 106 g. of 95% *o*-xylene (Oronite) was pumped in at 5 ml./min., with shaking, which was continued for another 15 min. before cooling the autoclave to 260° and releasing gaseous hydrogen sulfide to an iced caustic absorber until the pressure dropped to 47 atm., essentially steam pressure. The autoclave was then cooled to room temperature, and products steam distilled to recover 1.5 ml. of *o*-xylene, extracted with chloroform, and filtered. A brown solid residue remained of 56.8 g., containing 81.1% total sulfur by analysis. The chloroform solution was extracted with 5% aqueous sodium bicarbonate from which 9.1 g. of benzoic acid, neutral equivalent 123.2, was precipitated with dilute mineral acid. Distillation of the chloroform gave 1.2 g. of thiophthalide, boiling point 144°/7 mm. The water phase was evaporated to dryness, leaving 67.6 of tan *o*-phthalic acid, neutral equivalent 86.9. Recrystallization from water reduced the neutral equivalent to 83.1. A small sample was sublimed as the anhydride, neutral equivalent 74.2. Steam distillation of the caustic absorber yielded 8.8 g. of *o*-xylene. There was thus a 90.3% conversion of xylene, an 8.3% yield of benzoic acid, a 1.0% yield of thiophthalide, and a 45.1% yield of phthalic acid.

Run 18, Table II. The procedure followed that with the other xylenes and sulfur dioxide, except that a 1096-g. aliquot of the liquid phase of the reaction mixture was withdrawn at reaction temperature into ice (Aliquot B) and the remainder removed after cooling the autoclave to room temperature and releasing the hydrogen sulfide (Aliquot A). Using the same isolation procedure as that for *o*-xylene-sulfur reaction products, there was obtained from B, 15.5 g. of sulfur; 6.1 g. of a solid, red neutral by-product; 11.9 g. of benzoic acid; 18.1 g. of thiophthalide; and 200.0 g. of *o*-phthalic acid. From A was obtained 59.4 g. of sulfur, 63.6 g. of black neutral solids, 8.4 g. of benzoic acid, 13.2 g. of toluic acid, 72.7 g. of thiophthalide, and 156.1 g. of phthalic acid. The xylene conversion was 100%, with over-all yields of 4.1% benzoic and 2.5% toluic acids, 15.2% thiophthalide, and 53.5% phthalic acid. The molar ratio of phthalic acid to thiophthalide in B versus A is 10:1 versus 2:1 showing the effect of hydrogen sulfide on the equilibrium.

The extent to which phthalic acid can be favored using sulfur dioxide as the oxidant is illustrated by Experiment 20, Table II.

Oxidation of durene. The technique followed that with the xylene and sulfur dioxide. All liquid products were released while still hot into 8000 g. of ice. This mixture was filtered hot (80°) to give 103 g. of brown solids containing 77.7% free sulfur. The filtrate was neutralized to *p*H 7 with 109.5 g. of sodium hydroxide and evaporated to dryness, leaving 263 g. of yellow solids. These were taken up in hot water (400 cc.), carbon treated, acidified with hydrochloric acid to *p*H 1, chilled, and filtered. The washed and dried crystallized pyromellitic acid weighed 134 g., neutral equivalent 64.2 (theory = 63.5). Sublimation of a small sample gave pyromellitic anhydride, which after crystallization from acetone had a neutral equivalent of 54.5.

Reduction of m-toluic acid. The autoclave was charged with 1800 ml. of water, 340 g. of 95% *m*-toluic acid containing 0.55% benzoic acid, and 442 g. of hydrogen sulfide and heated with shaking to 340° for 1 hr. The pressure reached 293 atm. After cooling to room temperature, hydrogen sulfide was released and products were steam distilled to give 5.8 g. of an organic phase which, after washing with dilute caustic and drying, was analyzed by mass spectrography. It contained 76.7% xylene and 21.1% toluene as the major constituents. Filtration of the steam distillation residue gave 295.2 g. of dry solids containing 2.0 g. of elemental sulfur by analysis, 277.0 g. of *m*-toluic acid by isolation, and 0.41 g. of benzoic acid by analysis.

Identification of thiophthalide. In addition to the boiling point, this compound was identified from numerous experiments by first purifying by steam distillation followed by recrystallization from water to give a product with melting point 58.6–58.8°, saponification equivalent 146.4 (theory 150.19).

Anal. Calcd. for C_8H_6OS: C, 63.97; H, 4.03; S, 21.35. Found: C, 63.75, 63.85; H, 4.05, 4.23; S, 21.0; 21.4.

RICHMOND, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vinyl Derivatives of the Metals. IX. Cleavage Reactions of Perfluorovinyltin Compounds[1,2]

DIETMAR SEYFERTH, GUNTER RAAB, AND KARL A. BRÄNDLE

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The preparation of seven new perfluorovinyltin compounds by a Barbier-type reaction of bromotrifluoroethylene, the respective organotin chloride and magnesium in tetrahydrofuran solution is described. Cleavage of the perfluorovinyl group in these compounds could be effected by their reaction with ethanol, acetic acid, hydrogen bromide, iodine, triphenyltin hydride, and alcoholic sodium ethoxide. The following new organotin compounds were prepared during the course of these cleavage studies: diethyl- and di-*n*-butyldiethoxytin, tri-*n*-butylethoxytin, di-*n*-butyltin diiodide, diethyl- and di-*n*-butyltin basic fluorides.

The recent development of the perfluorovinyl Grignard reagents, $CF_2{=}CFMgI$[3] and $CF_2{=}CFMgBr$,[4] has made possible studies in the field of perfluorovinyl-metal compounds. Such studies would be of particular interest, since the chemistry of organometallic compounds containing the vinyl group has been developed extensively in the last four years, thus permitting a comparison between the $M{-}CH{=}CH_2$ and the $M{-}CF{=}CF_2$ systems.

We report here a brief study of perfluorovinyl derivatives of tin. Our early work showed that perfluorovinyltin compounds can be prepared by the reaction of preformed $CF_2{=}CFMgBr$ in tetrahydrofuran (THF) with organotin chlorides. However, special precautions with regard to temperature and reagent concentration are required in the preparation of perfluorovinylmagnesium bromide in this solvent, and yields of $CF_2{=}CFMgBr$ at best were only 50–60%. Yields of products obtained in subsequent coupling reactions also were *ca.* 50–60%, and thus a low over-all yield, based on the expensive bromotrifluoroethylene, made this procedure fairly unattractive. However, it was found that such perfluorovinylations could be carried out readily using a Barbier-type procedure, in which a mixture of bromotrifluoroethylene in slight excess and the organotin chloride to be perfluorovinylated in tetrahydrofuran solution is added to a rapidly

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