Oxidation of Organic Compounds with Aqueous Base and Sulfur

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A variety of organic compounds was allowed to react with sulfur, water and various basic materials to form acids and their derivatives. Nearly theoretical yields of phthalic acids and p-sulfobenzoic acid were obtained from toluic acids and p-toluenesulfonic acid, respectively. Xylenes also gave excellent yields of phthalic acids. Succinic acid was obtained from (four carbon) heterocyclic compounds. The results demonstrate that in contrast to the Willgerodt and Kindler reagents, ammonia and amines are not essential for good yields. This leads to speculation concerning the role of various nucleophilic reagents in these reactions with sulfur.

Introduction

The literature contains many examples of the use of sulfur as an agent for the abstraction of hydrogen from organic molecules. The resulting intermediates produce hydrogen sulfide and one or more of several organic species. Such diverse reactions may occur as dehydrogenation of cyclic compounds to aromatic compounds, formation of thiophenes, dimerization, and formation of mercaptans, sulfides, polysulfides and other sulfur compounds. The course of reaction depends on conditions, the nature of the organic compounds used, and other reagents present.

We reported earlier our results with one of the simpler systems, m- and p-toluic acids and sulfur, in which dimerization of the intermediates leads to the corresponding stilbenedicarboxylic acids.[1] Reaction of p-toluic acid and sulfur in the presence of several atmospheres pressure of hydrogen sulfide led also to the formation of 4,4'-bibenzyldicarboxylic acid.[2] This work has been extended to determine the effects of introducing additional components into the system. The objective was to forestall dimerization and induce the initially formed intermediates to react with the new components to change the course of the reaction, and thus form new products. The present investigation was originally designed to induce participation of water in the sulfur–toluic acid system. The desired over-all reaction was

$$CH_3C_6H_4CO_2H + 3S + 2H_2O \longrightarrow$$
$$HO_2CC_6H_4CO_2H + 3H_2S$$
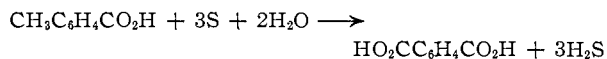
In order to provide homogeneity under reaction conditions, a base, sodium hydroxide, was added. When present in equimolar amounts with toluic acid the latter was dissolved as the sodium salt. In larger quantities the base reacted with sulfur as well to produce a mixture of water-soluble sulfur species. It was found that in the temperature range of about 200–350° under autogenous pressures excellent yields of iso- and terephthalic acids could be obtained with no evidence of the dimerization reaction.

The scope of the reaction was then expanded to demonstrate that sulfur, mixed with any one of a number of alkaline aqueous media to increase the solubility of one or both reactants in water, can be an extremely potent and selective oxidizing agent for the preparation of carboxylic acids from a

(1) W. G. Toland, J. B. Wilkes and F. J. Brutschy, THIS JOURNAL, **75**, 2263 (1953).

(2) W. G. Toland, J. B. Wilkes and F. J. Brutschy, *ibid.*, **76**, 307 (1954).

variety of organic compounds. Further extensions of this type of oxidation are to be reported in future papers.

Results

Although many more runs were made, typical results are shown in Table I.

TABLE I

COMPOUNDS OXIDIZED WITH SULFUR AND AQUEOUS BASE

Compound	Base[a]	Product, acid	Yield,[b] mole %
m-, p-Toluic acid	1.0 NaOH	Iso-, terephthalic	100.0
m-, p-Toluic acid	8.5 NaOH	Iso-, terephthalic	97.8
p-Toluenesulfonic acid	2.0 NaOH	p-Sulfobenzoic	94.8
p-Toluenesulfonic acid	1.0 NaOH	p-Sulfobenzoic	38.5
		Benzoic	29.0
m-Xylenesulfonic acid	1.0 NaOH	Isophthalic	63.6
p-Xylenesulfonic acid	1.0 NaOH	Terephthalic	46.2
Toluene	2.0 CaCO₃	Benzoic	61.0
m-Xylene	2.0 NaOH	Isophthalic	61.0
m-Xylene	1.3 Na₂CO₃	Isophthalic	70.8
		Benzoic	10.4
m-Xylene	2.0 CaCO₃	Isophthalic	11.1
		m-Toluic	12.0
m-Xylene	1.2 Na₂IP[c]	Isophthalic	33.5
m-Xylene	10 NH₄OH	Isophthalic	87.2
m-Xylene	... None	Isophthalic	29.0
p-Xylene	2.0 NaOH	Terephthalic	77.0
p-Xylene	1.1 Na₂S	Terephthalic	79.0
p-Xylene	2.4 Na₂CO₃	Terephthalic	86.0
p-Xylene	8.0 Na₂B₄O₇	Terephthalic	76.0
p-Xylene	10 NH₄OH	Terephthalic	96.2
Acetophenone	1.0 NaOH	Benzoic	28.0
1-Butanol	4.0 NaOH	Propionic and acetic	48.0
Furan	2.0 NH₄OH	Succinic	30.0
Thiophane	4.0 NH₄OH	Succinic	19.5
Propylene	1.1 KSH	Propionic	12.5
		Acetic	7.2
Acetone	1.3 NaOH	Acetic	4.5

[a] Moles per mole of compound. [b] Yields are based on the moles of stated product obtained and actual moles of starting material not recovered which could yield this product. [c] Disodium isophthalate.

The cleanest reactions are those of the substituted and unsubstituted lower alkylbenzenes, particularly the methylbenzenes. In such compounds, the reaction is simplified by the presence of methyl groups as the only points for attack. The presence of a salt-forming polar substitutent which increases the water solubility of the organic molecule can be an advantage. This solubility effect is demonstrated by toluic and p-toluenesulfonic acids, which are oxidized essentially quantitatively to the corresponding dicarboxylic and sulfobenzoic acids. On the other hand, the solubility of the xylenes in water can be increased by the use of ammonia as the base. Oxidation of m- and p-xylene is capable of giving excellent yields of iso- and terephthalic

amides and ammonium salts under proper conditions. Such structures are particularly stable to oxidation at positions other than the methyl groups, permitting considerable latitude of oxidation temperatures. For the same reason, an excess of oxidizing agent can be employed to favor complete conversion of starting material without product degradation. Carbon chains of two or more, whether substituted on an aromatic nucleus, an aliphatic molecule or part of a heterocyclic ring, may be degraded to simpler molecules. Normal butanol, acetophenone and furan, for instance, yielded products some of which contain fewer carbon atoms.

On oxidizing 1-butanol at different temperatures, conversions increase with temperature; but yields based on converted material pass through a maximum. Considered with the relatively large proportion of acetic acid formed at higher conversions, this can be interpreted as due to over-oxidation and degradation of the initial oxidation products at higher temperatures, with ultimate destruction even of acetic acid. The most copious evolution of carbon dioxide upon acidification of reaction products was noted in runs at the highest temperature. Apparently little, if any, butyric acid is formed; or it is further oxidized under the conditions studied.

The pH of the reaction medium is important in the case of aromatic sulfonic acids. If insufficient base is added, hydrolysis may remove this group completely from the products. Thus p-toluenesulfonic acid may be oxidized to favor either benzoic or p-sulfobenzoic acid. The xylene sulfonates hydrolyze even more readily to give the corresponding phthalic acids. With the xylene sulfonic acids only moderate yields (46–63%) of isophthalic and terephthalic acids were obtained, and no other organic products were isolated. The relatively low yields are probably caused by partial hydrolysis of the xylenesulfonic acids to xylenes while the reactants were heating to reaction temperature. Considerable amounts of insoluble polymers are formed in the reaction of xylene, sulfur and water.

Both thiacyclopentane (tetrahydrothiophene) and furan react to give succinic acid. The latter reaction is especially interesting as it involves both reduction and oxidation to give the final product. Propylene oxidation gave 12.5 mole per cent. propionic acid and 7.2 mole per cent. acetic acid. It is believed that these are not the optimum conditions for propylene oxidation and that organic sulfides could be recycled.

It can be concluded from these results that oxidation of organic compounds by sulfur and aqueous inorganic hydroxides, or their salts with weak acids, can be used to prepare a variety of carboxylates.

Discussion

One type of reaction in which sulfur and organic compounds react in the presence of additional reagents is the Willgerodt and Kindler reactions and their extensions, which employ aqueous ammonia or organic amines.[3,4] With these reagents, the course of the reaction alters drastically and the principal products are amides. Aqueous ammonia may yield some ammonium salts as well. Historically, these reactions were limited to ketones and were most successful with aryl substituted ketones such as acetophenone. Later work[5] showed that the reaction could be extended to aldehydes and olefins,[3] alkylbenzenes in low yields,[4] and even to paraffins.[6] In the course of such oxidations, carbon chain degradation has been observed in the case of certain ketones[3] and alkylbenzenes.[4] We noted similar effects, as already mentioned. Throughout most examples of the Willgerodt reaction with ketones, concurrent oxidations and reductions have been postulated to explain the products obtained. A further example apparently exists in the oxidation of furan to succinic acid, as shown in Table I. The addition of reagents other than anhydrous or aqueous ammonia or amines, with or without sulfides, to the reaction of sulfur and organic compounds has been little studied. Willgerodt noted that sodium sulfide and sulfur with acetophenone gave only very small amounts of phenylacetic and benzoic acids.[5] This lack of success probably is associated with known condensation reactions of ketones in the presence of strong bases. Our results with both acetophenone and acetone bear this out. However, once the ketone function is no longer present, this need not be a limitation, as illustrated in the present study.

It appears that the oxidation of organic compounds with sulfur is of much broader application than the original Willgerodt reaction. It has been extended far beyond the aryl substituted ketones to include even saturated paraffins. The use of ammonia or amines is not necessary, and amides need not be produced. Where carboxylic acids are desired and this technique is applicable, a sometimes difficult hydrolysis can be avoided.

While there has been considerable speculation about the mechanism of the Willgerodt reaction, none of the schemes appears suitable to explain completely the oxidation of a single methyl group with sulfur and an aqueous base to give a carboxyl group. There is evidence that attack of an activated carbon atom may be the first step.[3j,7] This activation can apparently be supplied thermally where it is otherwise low, as in the case of the alkylbenzenes and lower paraffins.[6]

Although mercaptans have been isolated in some instances, Moreau[8] has shown that in the reaction of diphenylmethane with sulfur to give thiobenzophenone, diphenylmethylthiol does not function as

(3) (a) M. Carmack and M. A. Spielman, "Organic Reactions," Vol. III, Roger Adams, editor, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 83; (b) L. Cavalieri, D. B. Pattison and M. Carmack. This Journal, 67, 1783 (1945); (c) M. Carmack and L. F. DeTar, ibid., 68, 2029 (1946); (d) D. B. Pattison and M. Carmack, ibid., 68,

2033 (1946); (e) J. A. King and F. H. McMillan, ibid., 68, 525, 632, 2335 (1946); (f) E. V. Brown, et al., ibid., 73, 3735 (1951); (g) J. A. Blanchette and E. V. Brown, ibid., 74, 1066 (1952); (h) R. T. Gerry and E. V. Brown, ibid., 75, 740 (1953); (i) Yukawa and Kishi, C. A., 46, 7061 (1952); (j) W. G. Dauben and J. B. Rogan, This Journal, 78, 4135 (1956).

(4) (a) M. A. Naylor and A. W. Anderson, ibid., 75, 5392 (1953); (b) 75, 5395 (1953).

(5) C. Willgerodt and F. H. Merk, J. prakt. Chem., [2] 80, 192 (1909).

(6) M. A. Naylor, U. S. Patent 2,711,134.

(7) (a) T. Asinger, M. Thiel and E. Pallas, Ann., 602, 37 (1957); (b) T. Asinger, M. Thiel and H. Kattwasser, ibid., 606, 67 (1957); (c) P. A. Barrett, J. Chem. Soc., 2056 (1957).

(8) R. C. Moreau, Bull. soc. chim. France, 22, 918, 922, 1014, 1019 (1955).

an intermediate. If, similarly, thiols are not an intermediate in the oxidation of methyl groups but rather thioaldehydes are formed, these could be sufficiently active at reaction temperatures to react in any one of a number of ways. In the absence of other reagents, it could react with itself or with its own precursors. In Moreau's analogous thioketone system[8] tetraphenylethylene or tetraphenylethane was produced. The toluic acids which gave stilbenedicarboxylic acids and bibenzyldicarboxylic acids[1,2] may also proceed by way of thioaldehyde.

Recently Tsurugi,[9] in a somewhat similar study of the diphenylmethane sulfur reaction, proposed a free radical mechanism leading to thiobenzophenone and diphenylmethane polysulfides which might be applied equally effectively to explain the first stages of the oxidations we are reporting.

The manner in which added reagents, such as ammonia, amines and bases, function is open to some question; but we believe it is common to all. Certainly ammonia and amines are not unique for further reaction of the intermediates as argued by Carmack and DeTar,[3c] although they may show specific effects in certain instances. While the use of ammonia can give high yields of iso- and terephthalic acids from m- and p-xylenes, the use of sodium salts of carboxylic or sulfonic acids can give yields close to the maximum theoretical value. Even weak bases, such as calcium or sodium carbonate or sodium borate or sulfide, suffice, as shown in Table II. In the absence of base, however, m-xylene gave a relatively poor yield (29 mole per cent.) of isophthalic acid (Table I), the remainder being non-acidic by-products.

The observed results with no base could be explained as resulting from the poor solubility of both sulfur and xylene in water, and the high solubility of sulfur in xylene at reaction temperature. This in turn would foster reactions without participation of water, to give non-oxygenated products. The use of sufficient base to dissolve carboxylic or sulfonic acids as neutral salts permits high yields, even though sulfur is not in solution. Similarly, the use of enough base to dissolve sulfur in one form or another, even in the absence of solubilizing polar substituents on the organic constituent, can give high yields.

In addition to the above effects, we propose a further generalized effect of bases. Ammonia, amines, hydroxides, sulfides and polysulfides are all nucleophilic agents. It is suggested that it is through their function as electron donors that they divert the usual reactions of sulfur with organic compounds to favor carboxylic salts, amides and thioamides. More research will be required to prove in detail just where and how they participate.

Experimental

All oxidations required pressure equipment to reach reaction temperature. Three sizes of autoclaves were used with total volumes of 260-cc., 2.5 liters or 4.5 liters. These were constructed of type 304 stainless steel and employed gaskets of the same material. The heads were fitted with a thermowell, pressure gage, bursting disk and valve. Heat was supplied by standard Aminco heater jackets mounted on Aminco

(9) Jitsuo Tsurugi, Bull. Univ. Osaka Pref., A5, 161, 169, 173 (1957).

rockers. Reactions were usually conducted by charging the reactants to an autoclave, heating to reaction temperature (with or without agitation), and agitating at temperature either for a definite time or until a constant pressure was attained. After cooling, most of the hydrogen sulfide produced was bubbled into aqueous sodium hydroxide. The autoclave was then opened and the contents treated to recover the products.

Sublimed 99.8% active sulfur (Stauffer) was employed for all runs; otherwise C.P. inorganic reagents were used throughout. All p-xylene was Oronite 95% containing 2% m-xylene and 1% o-xylene and 1% ethylbenzene. Two grades of m-xylene were used, 98% m-, 1.3% o-, and 92% m-, 5.9% p-xylene. Other organic reagents were Eastman Kodak Co. white label unless specified to the contrary.

Phthalic Acids from Toluic Acids.—The acid, obtained by catalytic air oxidation of mixed xylenes, and purified by distillation, contained 73.5% m-, 24.5% p- and 2.0% benzoic acids, with 0.09% of foreign matter. Reaction of 136 g. (1.0 mole) of this acid with 1.0 mole of sodium hydroxide, 300 g. water, and 128 g. (4.0 g. atoms) of sulfur at 315° gave a maximum pressure of 150 atm. in 60 minutes. The products were diluted with water to 1300 g., made alkaline with sodium hydroxide, and digested under reflux for several hours. Filtration gave 8.0 g. of black solids, not further identified. Dicarboxylic acids were isolated by acidifying the hot solution with dilute hydrochloride acid, filtering, and extracting the cake with hot water and several portions of boiling xylene to remove sodium chloride, sulfur and toluic acids. There remained a light yellow cake of 144 g. (0.86 mole) of phthalic acids (75% iso-, 25% tere-), neutral equivalent 83.3.

Extraction of the xylene washings with sodium bicarbonate solution with subsequent acidification gave 11.0 g. (0.08 mole) of toluic acids, neutral equivalent 136.5. This represents a 92% conversion of toluic acid. Distillation of the xylene left 19.0 g. of crude sulfur.

A similar oxidation of 136 g. (1.0 mole) of toluic acid with 340 g. (8.5 moles) of sodium hydroxide and 384 g. (12 g. atoms) sulfur in 1000 g. of water at 260–295° over a 4-hour period yielded 153 g. (0.92 mole) of the 75–25 isoterephthalic acid. No unreacted toluic acid was found.

p-Sulfobenzoic and Benzoic Acids from p-Toluenesulfonic Acid.—A maximum pressure of 150 atm. developed upon treating 0.5 mole of p-toluenesulfonic acid hydrate, 0.50 mole of sodium hydroxide, 900 g. water, and 50 g. (1.56 g. atoms) of sulfur at 330° for 70 minutes. Solid products of reaction were extracted with sodium hydroxide solution. Adjustment of the pH of the extract to 7 precipitated sulfur and neutral by-products. Decolorizations with carbon and acidification gave 0.145 mole of benzoic acid, neutral equivalent 122.2. Evaporation and chilling of the original filtrate gave 38.5 g. (0.171 mole) of crude p-sulfobenzoic acid monosodium salt, neutral equivalent 232 (theory 224.6). Further concentration of the filtrate yielded another 6.2 g. (0.027 mole) of p-sulfobenzoic acid monosodium salt, neutral equivalent 227. Caustic fusion of this product yielded p-hydroxybenzoic acid, m.p. 210° (sealed tube).

Use of enough sodium hydroxide to neutralize the sulfobenzoic acid produced decreased loss of the sulfonic group. Reaction of 1.0 mole of p-toluenesulfonic acid monohydrate, 2.0 moles of sodium hydroxide, 100 g. (3.1 gram atoms) of sulfur and 900 g. of water in a 4.5-liter autoclave at 315° for two hours gave a pressure of 141 atm. Steam distillation to remove a trace of oil, decolorization with carbon and evaporation to dryness gave 0.948 mole of disodium sulfobenzoate. Identification was made by conversion of a 5-g. portion of the salt to 3.7 g. of p-sulfobenzoic acid monosodium salt, neutral equivalent 232.

Isophthalic and Terephthalic Acids from Xylenesulfonic Acids.—Reaction of 0.5 mole of sodium p-xylenesulfonate monohydrate and 100 g. (3.1 gram atoms) of sulfur in 1800 g. of water at 315° for two hours developed a maximum pressure of 137 atm. The solid products were filtered and digested with one mole of sodium hydroxide in 500 cc. of water, leaving 44.9 g. of insoluble products (dry weight). The filtrate was neutralized to pH 7 with dilute hydrochloric acid and filtered to recover 15 g. of sulfur. Further acidification and washing gave 20.5 g. of terephthalic acid, neutral equivalent 82.9. The original liquid products from the reaction (pH 5) were decolorized with carbon and acidified to give 17.8 g. of terephthalic acid, neutral equivalent 84.8. Only inorganic salts were recovered on evaporating the filtrates.

Oxidation of *m*-xylenesulfonic acid was conducted in the same way. The maximum pressure (134 atm.) was reached in 15–20 minutes. The products, treated as described above, yielded 30.9 g. of insoluble solids, 12.2 g. of sulfur and a total of 52.9 g. of isophthalic acid, neutral equivalents 82.4 and 82.2.

Benzoic Acid from Toluene, Sulfur and Calcium Carbonate.—Baker C.P. toluene (1.0 mole), 2.0 moles of calcium carbonate, 96 g. (3.0 g. atoms) of sulfur and 800 g. of water were allowed to react at 315° for three hours (maximum pressure 158 atm.). Solid calcium sulfate (17.9 g.) was filtered from the product. Acidification of the entire product with hydrochloric acid (*p*H 1) and extraction with ethyl ether yielded, on evaporation of the ether, 74.2 g. (0.61 mole) of benzoic acid, neutral equivalent 122.

Isophthalic Acid from *m*-Xylene.—Reaction of 106 g. (1.0 mole) of 92% *m*-xylene, 2.0 moles of calcium carbonate, 192 g. (6.0 g. atoms) of sulfur and 800 g. of water in a 2.5-liter autoclave at 315° for 1.3 hours gave a maximum pressure of 164 atm. The product, consisting of solid and solution, was acidified with hydrochloric acid and filtered. The filter cake was extracted with hot aqueous sodium hydroxide solution. The solution was neutralized (*p*H 7) with hydrochloric acid to liberate sulfur. The filtrate was decolorized with carbon and acidified to *p*H 1. Chloroform extraction of the filtrates and final solid cake yielded 16.4 g. (0.12 mole) of *m*-toluic acid, neutral equivalent 138. The isophthalic acid remaining after the chloroform extraction weighed 18.4 g. (0.11 mole), neutral equivalent 87.0.

Reaction of 106 g. of 92% *m*-xylene with 1.3 moles of sodium carbonate, 256 g. (8 g. atoms) of sulfur and 1500 g. of water in a 4.5-liter autoclave for 65 minutes at 315° gave a maximum pressure of 201 atm. Distilling the product (*p*H 9) with steam and acidification to *p*H 7 yielded 24.6 g. of sulfur. The filtrate was carbon treated and acidified to *p*H 1. Separation of the products with chloroform gave 112.9 g. (0.68 mole) of isophthalic acid and 12.3 g. (0.1 mole) of benzoic acid.

Sodium isophthalate (0.89 mole of Oronite isophthalic acid and 1.8 moles of sodium hydroxide) was treated with 76 g. (0.717 mole) of 92% *m*-xylene, 144 g. (4.5 g. atoms) of sulfur and 770 g. of water in a 2.5-liter autoclave for one hour. Maximum pressure was 144 atm. The reaction mixture had a *p*H of 7–8 and contained some solid crystalline material. The mixture was heated with added sodium carbonate until all the solids dissolved except 19.6 g. (0.61 mole) of sulfur. Carbon treating and acidification of the clear filtrate with aqueous hydrochloric acid yielded 187.6 g. (1.13 moles) of isophthalic acid, neutral equivalent 83.1. A trace of benzoic acid, 0.4 g., was recovered from the filtrate.

A 2.5-liter autoclave was charged with 42.5 g. (0.4 mole) of *m*-xylene (98%), 243 g. of 28% aqueous ammonia (4 moles NH₃), 250 g. of water (23.6 moles total H₂O) and 96 g. (3.0 g. atoms) of sulfur, and heated to 316° before shaking was begun. After 30 minutes, the maximum pressure of 176 atm. was obtained, indicating completion of the reaction. Shaking continued an additional five minutes. Steam distillation of the product removed hydrogen sulfide and ammonia and reduced the *p*H to 7. No xylene was recovered. Sulfur from the polysulfide decomposition was filtered off and 2 moles of sodium hydroxide was added to saponify amides. The solution was steam distilled until the vapors tested neutral to moist *p*H paper, and the remaining solution of non-volatiles was adjusted to *p*H 7 with dilute hydrochloric acid and carbon treated. Further acidification gave, after thorough washing and drying, 57.0 g. (0.343 mole) of isophthalic acid, neutral equivalent 82.9.

Terephthalic Acid from *p*-Xylene.—A 2.5-liter autoclave was charged with 74 g. (0.7 mole) of *p*-xylene, 425 g. of 28% aqueous ammonia (7 moles NH₃), 250 g. of water (31 moles total H₂O) and 180 g. (5.6 g. atoms) of sulfur. The bomb was heated to 260° before starting shaking. The temperature was raised to 304° where reaction continued for one hour. The pressure rose to a maximum of 196 atm. after 20 minutes at temperature. The products were isolated by the procedure just described to give 108.5 g. (0.653 mole) of terephthalic acid, neutral equivalent 83.2.

Isophthalic and Terephthalic Acids from Xylene—Effects of Bases.—A series of runs were made in a 2.5-liter autoclave, utilizing different sodium bases in varying proportions with either *p*-xylene or 98% *m*-xylene. One run was made in the absence of any base. All of the reactants except the xylene, which was placed in a glass tube wired to the

thermowell, were charged directly. The autoclave was heated to reaction temperature, 330°, without agitation, to prevent mixing of the xylene and the oxidizing solution below the reaction temperature. After reaction and removal of the products, the materials were steam distilled to remove volatile materials. In the run where no base was present, the solid cake was extracted with boiling xylene to remove the sulfur, and the acids were dissolved in aqueous ammonia. When base was present the solutions were carefully neutralized to decompose the polysulfides. The solutions were filtered through Celite and decolorized with carbon. The phthalic acids were precipitated by acidifying the hot solutions with mineral acids, washed and dried. They were identified by their neutral equivalents.

The reactants, conditions and results are summarized in Table II.

TABLE II

m- AND *p*-XYLENE OXIDATIONS WITH SODIUM BASES

Type	Moles	Xylene, mole	Water, moles	Sulfur, moles	Time, min.	Phthalic acid, mole
NaOH	2.0	*m*- 1.0	40	6.5	60	0.61
NaOH	2.0	*p*- 0.95	60	8.0	70	.73
Na₂S	1.1	*p*- .95	49	8.0	90	.75
Na₂CO₃	1.67	*p*- .79	50	6.7	90	.68
Na₂B₄O₇	1.06	*p*- .95	50	8.0	90	.72
None	..	*m*- .5	40	3.5	60	.14

Benzoic Acid from Acetophenone.—Reaction of 0.05 mole of acetophenone, 0.05 mole of sodium hydroxide, 8 g. (0.25 g. atom) of sulfur and 45 g. of water in a 250-ml. autoclave at 260–300° for one hour gave a maximum pressure of 96 atm. The product consisted of a light yellow, turbid aqueous phase with a separate phase of black tar. The autoclave was rinsed with 4 g. of sodium hydroxide in 50 cc. of water, and this was combined with the products. The aqueous phase was separated, acidified with hydrochloric acid to *p*H 7 and filtered hot to remove a trace of neutral water-insoluble products, including free sulfur. The hot filtrate was decolorized with 0.2 g. of carbon, acidified to *p*H 1 with dilute hydrochloric acid, cooled and filtered to remove precipitated acids. After washing and drying the cake, 1.7 g. (0.14 mole) of benzoic acid, neutral equivalent 122.4, was isolated. No unreacted acetophenone was found.

Acetic Acid from Acetone.—Reaction of 4.0 moles of acetone, 5 moles of sodium hydroxide, 160 g. (5 g. atoms) of sulfur and 1800 cc. of water in a 4.5-liter autoclave at 177° for two hours gave a pressure of 18 atm. Steam distillation of the product gave 16.5 g. of neutral organic sulfur compounds, not further identified. The residue, acidified with dilute sulfuric acid, gave 61.7 g. of a dark red-brown cake of crude sulfur. The filtrate was neutralized to *p*H 7, evaporated to a small volume, and ether extracted. Evaporation of the ether left no residue. The aqueous phase was reacidified with sulfuric acid and extracted with five 200-cc. portions of ether. Distillation of the ether left 26.1 g. of residue which was fractionally distilled in a one-foot helices packed column to give a total of 10.8 g. (0.18 mole) of acetic acid, identified by Duclaux constants in the fraction boiling 60–119°. The amount of unconverted acetone was not determined.

Aliphatic Acids from 1-Butanol.—Three separate experiments were made to determine the effect of temperature. The procedure was otherwise the same in each. A 4.5-liter autoclave was charged with 2 moles of 1-butanol, 256 g. (8 g. atoms) of sulfur, 2.5 moles of sodium hydroxide, and 1500 cc. of water. The autoclave was heated with shaking to the temperature indicated in Table III for two hours. The products were handled in the same manner as with acetone. Unreacted butanol was recovered by salting out the steam distillate.

Succinic Acid from Furan.—Reaction of 1.0 mole of furan, 64 g. (2.0 g. atoms) of sulfur, 6 moles of ammonia and 1300 g. of water in a 4.5-liter autoclave at 232° for four hours gave a maximum pressure of 59 atm. after 2.1 hours. The product was steam distilled to remove ammonia and hydrogen sulfide and treated with decolorizing carbon. Any amides were saponified by steam distilling after addition of 2 moles of sodium hydroxide. The *p*H was adjusted to 6 with hydrochloric acid, the solution was concentrated by evaporation,

TABLE III

OXIDATION OF 1-BUTANOL WITH SULFUR AND AQUEOUS CAUSTIC

Reaction temperature, °C.	180	230	290
Butanol recovd., moles	1.66	1.25	0.61
Sulfur recovd., g. atoms	3.25	....	.0
Acetic acid, mole	} 0.056	0.10	.272
Propionic acid, mole		0.26	.228

acidified to pH 1 and extracted with ethyl ether. From the ether extract, 1.7 g. (0.03 mole) of acetic acid was recovered. The aqueous solution then was evaporated to dryness and extracted with hot ethanol from which was obtained 35.4 g. (0.30 mole) of succinic acid, neutral equivalent 59.

Succinic and Acetic Acids from Thiacyclopentane.— Reaction of 1.0 mole of thiacyclopentane (tetrahydrothiophene), 6 moles of ammonia, 128 g. (4 g. atoms) of sulfur and 1300 g. of water in a 4.5-liter autoclave at 232° for 3 hours gave a maximum pressure of 72 atm. Ether extraction of the condensate obtained by steam distilling the product gave 3.8 g. of thiacyclopentane. The liberated sulfur (11.3 g.) was filtered from the product, and the amide saponified by addition of sodium hydroxide and continued steam distillation. Ether extraction of the acidified product yielded 5.4 g. (0.09 mole) of acetic acid (Duclaux constant) plus some succinic acid, neutral equivalent 59. The aqueous solution was evaporated to dryness and extracted with acetone. Total yield of succinic acid was 23 g. (0.19 mole).

Acetic and Propionic Acids from Propylene.—Propylene (5 moles) was treated with 5.5 moles of potassium hydroxide, 396 g. (12.4 g. atoms) of sulfur and 810 cc. of water at 230° for 90 minutes in a 2.5-liter autoclave. Gases were withdrawn through a caustic scrubber which gained 210 g. The remaining gas (3410 cc.) contained 2.4 volume per cent. of propylene. The product was worked up by the same procedure as for acetone oxidation products. Steam distillation gave 203.9 g. of neutral organic oil, d_4^{20} 0.886, containing sulfides which were not further characterized. A crude sulfur cake of 384.6 g. was obtained at pH 7. Fractional distillation of ether extracts yielded a mixture of acids which analyzed as consisting of 0.361 mole of acetic and 0.630 mole of propionic acid.

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Synthesis of Compounds Related to Segments of Synthetic Sulfhydryl Polymers[1]

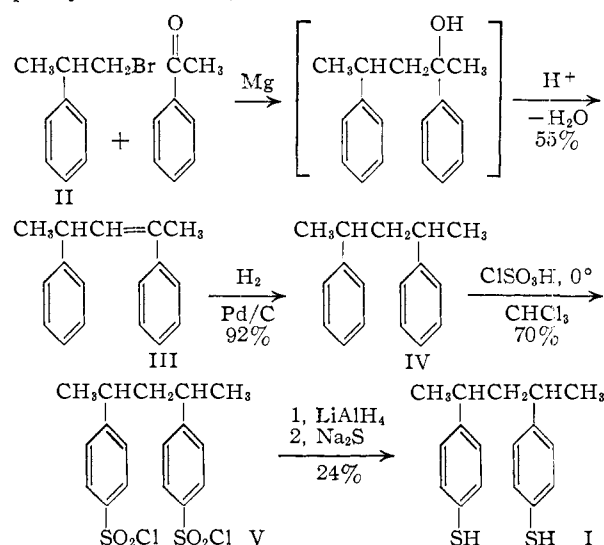BY C. G. OVERBERGER AND P. V. BONSIGNORE[2]

The synthesis of a 2,4-di-(p-mercaptophenyl)-pentane is described. This compound served as a model compound representing a segment of a hydrolyzed polymer of p-vinylphenyl thioacetate. The synthesis of methyl 2,2-dimethyl-4-phenylvaleric ester, a precursor of a model compound representing a segment of a hydrolyzed copolymer of p-vinylphenyl thioacetate and methyl methacrylate is also described. Pyrolytic cracking of the ethyl ester of 2,2-dimethyl-3-acetoxy-4-phenylvaleric acid, which was first investigated as an intermediate in the latter model compound, was found to undergo a facile cleavage of the carboxyethyl and acetate groups to give 2-methyl-4-phenylpentene-2. A mechanism for the latter is proposed. An improved procedure for the preparation of ethylene dithiocarbonate is also described.

Recently, Overberger and Lebovits have reported the synthesis of p-vinylphenyl thioacetate.[3] Free radical polymerization of this monomer alone and copolymerization with methyl methacrylate gave macromolecules which on saponification contained free sulfhydryl groups and were soluble in aqueous base. A solution of the hydrolyzed copolymer was found effective in reactivating urease, a natural sulfhydryl enzyme, which had been inactivated by oxidation with iodine.[4]

A study of the relative ease of oxidizability and the alkylation reactivity of the sulfhydryl groups of these hydrolyzed polymers of p-vinylphenyl thioacetate was undertaken in order to determine the effects imposed on the reactivity of the sulfhydryl group by the restraints of a polymeric carbon–carbon chain and the presence of various functional groups introduced by copolymerization, such as the carboxyl group of methyl methacrylate in the hydrolyzed copolymer. The results of the oxidation and alkylation studies will be reported separately; this paper is concerned with the synthesis of compounds related to the segments of the hydrolyzed

(1) This is the 16th in a series of papers on new monomers and polymers. For the previous papers in this series see C. G. Overberger, H. Biletch and R. G. Nickerson, *J. Polymer Sci.*, **27**, 381 (1958).

(2) This paper comprises a portion of a dissertation submitted by P. V. Bonsignore in partial fulfillment of the requirements of the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) C. G. Overberger and A. Lebovits, THIS JOURNAL, **77**, 3675 (1955).

(4) C. G. Overberger and A. Lebovits, *ibid.*, **78**, 4792 (1956).

homopolymer of p-vinylphenyl thioacetate and its copolymer with methyl methacrylate which were needed for comparison purposes.

The scheme adopted for the preparation of 2,4-di-(p-mercaprophenyl)-pentane, a representative segment of the hydrolyzed homopolymer of p-vinylphenyl thioacetate, is

2-Phenylpropyl bromide (II) was synthesized in 50–55% yield by reduction with lithium aluminum hydride in refluxing ether, of 1,2-dibromo-2-