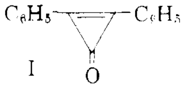
propenone seemed attractive as additional demonstration of the validity of such analogies.[2]

We considered that the interesting reaction between a carbene and a ketene acetal to furnish a cyclopropanone ketal, which has been described by McElvain,[3] could be adapted to this purpose. Since diphenylcyclopropenes are formed readily by base-catalyzed eliminations from appropriately substituted cyclopropanes,[4] we selected the reaction of phenyl ketene dimethyl acetal[5] with benzal chloride and potassium *t*-butoxide. The expected product was the dimethyl ketal of diphenylcyclopropenone (I), but we find that with neutral aqueous processing, this hydrolyzes,[6] the only crystalline product isolated being (I) itself, m.p. 121–121.5° from cyclohexane–benzene. Calcd. for $C_{15}H_{10}O$: C, 87.35; H, 4.89; mol. wt., 206. Found: C, 87.71, 87.52; H, 4.87, 4.93; mol. wt. (cryoscopic, CBr_4), 198. In the ultraviolet the compound shows maxima (CH_3CN) at 297 (4.3), 282 (4.25), 226 (4.13), and 220 (4.16) mμ, with a shoulder at 310 mμ (4.04). Its infrared spectrum (in CCl_4) is in striking agreement with the proposed structure, with weak absorption at 3.4 μ (aromatic C–H), a strong band at 5.40 μ (C=O stretching), and rather strong bands at 6.1 (conjugated C=C), 6.7 and 6.9 (benzene ring) and 7.45 μ (C=O bending). The only other major absorptions are two bands (in CS_2) at 13.0 and 14.5 μ (monosubstituted benzene).

As further evidence, we have studied thermal decomposition. While the melting at 121° is reversible, heating to 130–140° causes evolution of a gas which we have identified as carbon monoxide.[7] From the residue one can isolate, in 20% yield, diphenylacetylene identical with authentic material. This mode of decomposition is not surprising for (I), but the relatively high temperature at which it occurs, and the fact that (I) can be isolated from hydroxylic medium, show that the cyclopropenone system must have strong resonance stabilization indeed to compensate for its high angle strain.



I

---

[2] The stable *s*-triphenylcyclopropenyl cation, reported by R. Breslow and Chin Yuan, THIS JOURNAL, in press, furnishes a similar analogy to tropylium ion.

[3] S. M. McElvain and P. L. Weyna, Amer. Chem. Soc. Meeting Abstracts, Chicago, Sept., 1958, p. 1-P.

[4] S. F. Darling and E. W. Spanagel, THIS JOURNAL, **53**, 1117 (1931).

[5] S. M. McElvain and J. T. Venerable, *ibid.*, **72**, 1661 (1950).

[6] The ready hydrolysis must occur because the intermediate in the reaction is a derivative of a cyclopropenyl cation.

[7] E. G. Voiret and A. L. Bonaimé, *Ann. chim. anal.*, **26**, 11 (1944).

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, N. Y.

RONALD BRESLOW
ROBERT HAYNIE
JOSEPH MIRRA

RECEIVED NOVEMBER 29, 1958

RESOLUTION OF A NON-HETEROCYCLIC QUATERNARY PHOSPHONIUM IODIDE

Sir:

We wish to report the first completely successful resolution of a quaternary phosphonium salt in which the phosphorus atom is not a member of a heterocyclic ring. Both enantiomorphs of methylethylphenylbenzylphosphonium iodide have been obtained by way of the *d*(−)-dibenzoylhydrogentartrate and *l*(+)-dibenzoylhydrogentartrate salts. The iodides were found to be optically stable even in solution, and this fact disposes of the suggestion that the numerous previous failures[1] to resolve asymmetric phosphonium salts of the type $RR_1R_2R_3P^+,X^-$ were attributable to their rapid racemization in solution by a dissociation-equilibrium mechanism[2]

$$RR_1R_2R_3P^+,X^- \rightleftarrows RR_1R_2P + R_3X$$

The only previous successful resolutions of phosphonium salts have been with compounds in which the phosphorus atom was a member of a heterocyclic ring. Holliman and Mann,[3] proceeding through the *d*-camphorsulfonate, were on one occasion able to isolate pure crystalline dextrorotatory 2-phenyl-2-*p*-hydroxyphenyl-1,2,3,4-tetrahydroisophosphinolinium bromide, but later they were unable to repeat their initial success. Recently, Hart and Mann[4] accomplished the resolution of P-spiro - bis - 1,2,3,4 - tetrahydrophosphinolinium iodide into its dextro and levo isomers *via* the *d,l*-phosphonium *l*-menthoxyacetate.

Racemic methylethylphenylbenzylphosphonium iodide, m.p. 166–167°, was prepared by the method of Meisenheimer, *et al.*[1f,5] Treatment with silver *d*(−)-dibenzoylhydrogentartrate,[6] in methanol gave the phosphonium *d*(−)-dibenzoylhydrogentartrate, which was crystallized several times from *n*-propyl alcohol. There was obtained a diastereoisomer of m.p. 142–143°, $[\alpha]^{25}_D$ − 54.0° (*c* 1.281 in methanol).

Anal. Calcd. for $C_{34}H_{33}O_8P$: C, 68.00; H, 5.67; P, 5.17. Found: C, 68.21; H, 5.73; P, 5.48.

By treatment of the dibenzoylhydrogentartrate with ammonium iodide in absolute methanol there was obtained dextrorotatory methylethylphenylbenzylphosphonium iodide, m.p. 159–160°, $[\alpha]^{25}_D$ +24.0° (*c* 0.824 in methanol).

Anal. Calcd. for $C_{16}H_{20}PI$: C, 51.90; H, 5.39; P, 8.38; I, 34.35. Found: C, 51.67; H, 5.65; P, 8.44; I, 34.38.

By the action of silver *L*(+)-dibenzoylhydrogentartrate on racemic methylethylphenylbenzylphosphonium iodide the dextrorotatory dibenzoylhydrogen tartrate, m.p. 142–143°, $[\alpha]^{25}_D$ +54.0° (*c* 1.100

---

[1] (a) A. Michaelis, *Ann.*, **315**, 19 (1901); (b) A. Michaelis, *ibid.*, **315**, 43 (1901); (c) E. Wedekind, *Ber.*, **45**, 2933 (1912); (d) W. J. Pope and C. S. Gibson, *J. Chem. Soc.*, **101**, 735 (1912); (e) L. G. Radcliffe and W. H. Brindley, *Chemistry and Industry*, **42**, 64 (1923); (f) J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt and W. Samuel, *Ann.*, **449**, 213 (1926); (g) G. Kamai, *J. Gen. Chem. (U.S.S.R.)*, **2**, 524 (1932); (h) G. Kamai and L. A. Khismatullina, *Doklady Akad. Nauk. S.S.S.R.*, **92**, 69 (1953); (i) G. Kamai and L. A. Khismatullina, *J. Gen. Chem. (U.S.S.R.)* (in English Translation), **26**, 3815 (1956). It should be pointed out that Kamai and Khismatullina[1h] reported that they had achieved some concentration of the diastereoisomers of allylbutylphenylbenzylphosphonium *d*-bromocamphorsulfonate, but attempts to prepare the enantiomorphic optically active bromides by metathesis with potassium bromide failed.

[2] F. G. Mann, *J. Chem. Soc.*, 65 (1945).

[3] F. G. Holliman and F. G. Mann, *ibid.*, 1634 (1947).

[4] F. A. Hart and F. G. Mann, *ibid.*, 4107 (1955).

[5] These authors were unable to resolve the cation *via* the *d*-bromocamphorsulfonate.

[6] D. M. Coyne, W. E. McEwen and C. A. VanderWerf, THIS JOURNAL, **78**, 3061 (1956).

in methanol) was obtained. (*Anal.* Found: C, 68.19; H, 5.64; P, 5.07). Metathesis with ammonium iodide gave the levorotatory phosphonium iodide, m.p. 158–159°, $[\alpha]^{25}\text{D}$ −23.8° (*c*, 0.927 in methanol). (*Anal.* Found: C, 51.75; H, 5.18; P, 8.34; I, 34.35.)

The availability of the enantiomorphic phosphonium iodides will enable studies on the stereochemical course of important reactions, including the conversion of the corresponding phosphonium hydroxides to asymmetric phosphine oxides and reductions by lithium aluminum hydride, to be carried out. Studies in these areas are in progress in this Laboratory.

Acknowledgment.—This investigation was supported in part by a research grant, RG-4215, from the National Institutes of Health, Public Health Service.

DEPARTMENT OF CHEMISTRY KARL F. KUMLI
UNIVERSITY OF KANSAS WILLIAM E. MCEWEN
LAWRENCE, KANSAS CALVIN A. VANDERWERF

RECEIVED NOVEMBER 19, 1958

THE HIGH TEMPERATURE REACTION BETWEEN SULFUR DIOXIDE AND BENZENE

Sir:

The principal volatile decomposition products in the pyrolysis of diphenyl sulfone are sulfur dioxide and benzene.[1] When the decomposition is carried to completion at temperatures of 500° and higher there is a noticeable decrease in the concentrations of these products This communication reports the results of a short experimental investigation of the reaction between sulfur dioxide and benzene.

Equimolar mixtures of sulfur dioxide and benzene reacted in sealed Pyrex bulbs between 400 and 540°. The principal decomposition products are not volatile at room temperature. Yellow and white crystals were separated from a dark polymeric residue by distillation under vacuum at 450°. The yellow product was identified as sulfur by melting point determination and the white crystals as dibenzothiophene by infrared analysis. The volatile products were analyzed by standard high-vacuum techniques. Results in the accompanying table show a significant reaction between sulfur dioxide and benzene at temperatures above 480°.

With the exception of Run 7, all of the reactions were carried out for 15 hours so that a preliminary investigation of the reaction kinetics might be attempted. If one assumes from the data that sulfur dioxide and benzene react by a second-order process, then for an equimolar mixture the consumption of either reactant is expressed as

$$1/C - 1/C_0 = kt$$

Since time was constant for these runs, the term $(1/C - 1/C_0)$ is proportional to the rate constant for the reaction, if the kinetics are independent of extent of reaction. One can then determine the temperature dependency or apparent activation energy by plotting the log $(1/C - 1/C_0)$ against $1/T$. An apparent activation energy calculated on this basis is approximately 88 kilocalories per mole. Since the dissociation energy of the S–O bond in sulfur dioxide[2] is 92 kcal./mole and the C–H bond in benzene is 102 kcal./mole,[3] the activation energy for this reaction may be representative of the breaking of an S–O bond in sulfur dioxide.

TABLE I

THE REACTION OF SO_2 AND C_6H_6

			Concentration, cc.-atm., STP					
			Reactants		Products			
Run	Temp., °C.	Time, hr.	SO_2	C_6H_6	SO_2	C_6H_6	Other condens-ables	Non-condens-ables
1	540	15	20.5	20.5	5.8	7.2	2.2[a]	NA
8	540	15	20.3	20.3	8.6	NA	0.9	0.1
7	528	2	20.2	20.0	20.4	19.3	0.2	0.1
4	510	15	20.5	20.5	17.8	15.5	0.3	0
6	493	15	20.2	20.2	18.7	17.2	0.4	0
5[b]	490	15	20.9	20.9	15.6	17.7	0.3	0
5	481	15	20.5	20.5	20.0	20.0	0.3	0
2	400	15	20.5	20.3	20.5	19.9	. . .	0

[a] Mass spectrometer analysis of this fraction in %: CO_2 53.35; COS, 39.0; SO_2 3.5; O_2, 1.3; C_6H_6, 0.9; CS_2, 0.7; H_2S, 0.2; H_2O, 0.5–1.0. [b] This reaction was run in the presence of polymeric residue obtained from a previous decomposition of diphenyl sulfone.

Summarizing, sulfur dioxide and benzene are shown to react at approximately 500° by a process compatible with second order kinetics forming sulfur, dibenzothiophene, a polymeric residue, carbon dioxide, carbonyl sulfide, oxygen, and traces of carbon disulfide, hydrogen sulfide, and water.

BATTELLE MEMORIAL INSTITUTE ARTHUR LEVY
COLUMBUS 1, OHIO CHARLES J. AMBROSE

RECEIVED OCTOBER 16, 1958

---

(1) This research is part of a research program on the pyrolysis kinetics of several perphenylated compounds. It is being supported by the United States Air Force under Contract No. AF 33(616)-5217 monitored by Aeronautical Research Laboratory, WCLJC, Wright Air Development Center.

(2) L. P. Blanchard and P. LeGoff, *Can. J. Chem.*, **35**, 89 (1957).

(3) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955, p. 15.