On the Reproducibility of the Oxidative Bisdecarboxylation Reaction[1]

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In 1952 Doering, Farber, and Sayigh[3] reported a method for the replacement of a 1,2-dicarboxylic anhydride group by a double bond. This method involved an oxidation by lead dioxide in which two molecules of carbon dioxide were eliminated leaving an olefin. The reaction was applied to hexahydrophthalic anhydride, 4,5-dimethylhexahydrophthalic anhydride, bicyclo[2.2.2]octane-2,3-dicarboxylic anhydride, and 1-acetoxy- and 1-carbomethoxybicyclo[2.2.2]octane-2,3-dicarboxylic anhydride, giving the related olefins in yields of 20% to 35% of the theoretical.

Using this method, Beckmann and Schaber[4] reported the conversion of 2-methylbicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride to aposantene in 15% of the theoretical yield. A related reaction has been reported by McElvain[5] in the conversion of nepetonic acid to 1-acetyl-3-methylcyclopentene.

During a study of the solvolysis of some bridgehead bromides the reaction between lead dioxide and 1-acetoxybicyclo[2.2.2]octane-2,3-dicarboxylic anhydride (I) was repeated. In contrast to the previous report[3] various samples of fresh commercial lead dioxide gave at the most only 4% of the theoretical yield in many attempts. An old sample of lead dioxide of unknown origin, while not duplicating the original yield, was considerably more active than the fresh material. The discoverers[3] recalled using only a single ancient sample of lead dioxide of unknown history.

In investigating this mystery, it was found from emission spectra[6] that the bisdecarboxylation was not effected by impurities in the lead dioxide. An X-ray crystal study[7] suggested that the important factor was particle size and not crystal structure. In fact, those samples of larger particle size (as determined roughly by sedimentation rate) were the more effective in the decarboxylation.

Samples of lead dioxide prepared by the aqueous decomposition of lead tetraacetate,[8] by the electrolysis of a lead nitrate solution,[9] and by the hypochlorite oxidation of lead acetate,[10] as well as Mallinckrodt *Analytical Reagent* grade all failed to decarboxylate I. These materials had slower rates of sedimentation than the one active sample and were therefore presumed to have smaller particle sizes.

A modification of the hypochlorite oxidation[10] described below finally led to the production of lead dioxide which was uniformly effective in the bisdecarboxylation reaction. The preparation was reproducible and gave lead dioxide which decarboxylated I consistently in 19% yield. The decarboxylation of 1-acetoxybicyclo[3.2.2]nonane-2,3-dicarboxylic anhydride has been performed consistently in 23% yield[11] using lead dioxide prepared in this manner.

EXPERIMENTAL

Active lead dioxide. A solution of 180 g. of sodium hydroxide in 500 ml. of water was added with stirring to a solution prepared by dissolving lead acetate trihydrate (300 g.) in 600 ml. of warm water. To the resultant suspension was added all at once a mixture of 220 g. of technical calcium hypochlorite (Fisher Scientific Co.). and 1500 ml. of water. The stirred mixture was heated rapidly to boiling and kept there for several minutes. After being cooled, the supernatant liquid was decanted and the yellow precipitate was washed in the following way: five hundred ml. of 1:1 nitric acid was cautiously added (in small portions at first) and the suspension was vigorously stirred. Fifteen hundred ml. of water was then added and after the precipitate settled, the liquid was decanted and the procedure was repeated at least four times. The now brown precipitate was washed once more with water and filtered with suction. It was dried overnight at 110° and ground with a mortar and pestle to yield 132 g. (70%) of dark brown powder.

The reaction of lead dioxide with nepatonic acid exploded at 250°[5]; accordingly the decarboxylation reactions should be conducted with the precautions indicated where explosions are expected.

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(1) Taken from a dissertation submitted by Manuel Finkelstein in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Yale University.

(2) Eastman Kodak Company Fellow, 1953 and Procter and Gamble Summer Research Fellow, 1955.

(3) W. von E. Doering, M. Farber, and A. Sayigh, *J. Am. Chem. Soc.*, **74**, 4370 (1952).

(4) S. Beckmann and R. Schaber, *Ann.*, **585**, 154 (1954).

(5) S. M. McElvain and E. J. Eisenbraun, *J. Am. Chem. Soc.*, **77**, 1599 (1955).

(6) Kindly determined by Mr. William Milligan, Metallurgy Dept., Yale University.

(7) Kindly performed by Mr. Kurt Servos, Geology Dept., Yale University.

(8) R. Kuhn and I. Hammer, *Chem. Ber.*, **83**, 413 (1950).

(9) W. C. Pierce and E. L. Haenisch, *Quantitative Analysis*, John Wiley and Sons, Inc., New York, 1948, p. 446.

(10) H. S. Booth *et al.*, *Inorganic Syntheses*, vol. 1, McGraw-Hill Book Co., New York, 1939, p. 45.

(11) James N. Tilley, Department of Chemistry, Yale University, unpublished results.

Chloroacetyl Chloride from Ketene and Chlorine

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This investigation was undertaken to determine the suitability of adding chlorine to ketene as a preparative method for chloroacetyl chloride. It

TABLE I

REACTION OF KETENE WITH CHLORINE TO PRODUCE CHLOROACETYL CHLORIDE

Run[a] No.	Solvent Type, G.	Ketene, Mole/ Hr.	Chlorine, Mole/ Hr.	Temp., °C.	Time, Hr.	Low[b] Boiler, G.	Product Fraction Wt., G.	Product Fraction DCAC[e] content, %	Product Fraction CAC yield, %	High Boiler, G.
1	AcCl (150)	0.3	0.3	6 to 14	2.0	142.5	30.7	30.4	32	22.7
2	$C_6H_5NO_2$ (150)	0.54	0.53	16 to 22	1.5	13.9	51.5	23.1	44	166.0[c]
3	CH_2Cl_2[d]	0.35	0.35	ca. −50	1.0	—	14.7	45.5	20	16.0
4	CAC[e] (150)	0.54	0.53	12 to 16	2.5	15.7	197.4[f]	18.5	7	41.0
5	CAC (150)	0.54	0.53	17 to 30	2.0	18.8	181.1[f]	12.0	7	35.4
6	CAC (150)	0.67	0.67	16 to 24	1.5	16.6	201.4	15.2	19	20.7
7	CAC (150)	0.35	0.35	10 to 14	1.5	15.3	171.6	10.1	7	22.6
8	SO_2 (214)	0.35	0.34	−24 to −10	1.5	3.4	43.6[j]	None	75	7.8
9	SO_2 (725)	[g]	[g]	−20 to −12	3.0	2.3	102.7[j]	None	75	15.2
10	[h]	[i]	[i]	−14 to −12	2.1	21.0	169.2[f,j]	2.65	23	36.2

[a] Additives were employed as follows: Run 4, chloranil, 1.5 g.; Run 5, copper acetate, 1.5 g.; Run 6, Norite, 2.0 g.; Run 7, diphenyl amine, 1.0 g. [b] Low boiler (mostly acetyl chloride), b.p. up to 103°; product fraction (CAC and DCAC), b.p. 103–107°; high boiler, b.p. above 107°. [c] Included the nitrobenzene charged. [d] Solutions (0.35 mole each) of ketene and of chlorine in 350 ml. of methylene chloride were prepared, then the chlorine solution was added to the ketene solution. [e] Chloroacetyl chloride (CAC) and dichloroacetyl chloride (DCAC). [f] Included the CAC charged. [g] Ketene generator erratic, chlorine flow adjusted throughout run so as to maintain a slight yellow color in the reaction mixture—86 g. of chlorine was introduced. [h] 142 g. (1.26 mole) of CAC and 19.8 g. (0.31 mole) of SO_2 charged. [i] Same procedure as under g.—50 g. of chlorine was introduced. [j] The CAC product from Runs 8, 9, and 10 contained respectively 0.64, 0.75, and 1.26% SO_2; 0.42, 0.47, and 0.75% S; and 0.40, 0.39, and 0.42% SO_2Cl_2 assuming that all the sulfur was present as SO_2 and SO_2Cl_2. Infrared shows the presence of a very small amount of an unidentified component in CAC from Run 8 in addition to the SO_2 and SO_2Cl_2.

had been reported[1] that "chloroacetyl chloride is easily prepared by the addition of chlorine to ketene, either in the vapor phase or in solution". Another report[2] mentioned yields of up to 37% in absolute ether.

At the outset the formation of dichloroacetyl chloride was not considered to be a problem since chloroacetyl chloride had been reported[3] not to chlorinate appreciably at 25°, which fact was also observed in the current work. This investigation was not very old however, before it was recognized that the major problem was the concurrent formation of dichloroacetyl chloride. This was later verified by Porai-Koshits, *et al.*[4], who concluded that the reaction of ketene with chlorine is a good method for the preparation of mixtures of chloroacetyl chloride and dichloroacetyl chloride. Whether the dichloroacetyl chloride results from direct chlorination of chloroacetyl chloride induced by the addition of chlorine to ketene (analogous to the induced chlorination of dichloroethane during the addition of chlorine to ethylene as reported by Stewart and Smith[5]) or from attack by chlorine on some intermediates formed during the addition of chlorine to ketene is a moot question at this point.

As a consequence of dichloroacetyl chloride formation, acetyl chloride is produced by addition of the by-product hydrogen chloride to ketene.

Dichloroacetyl chloride formation is undesirable not only because it reduced the yield of chloroacetyl chloride but more importantly, separation of chloroacetyl chloride and dichloroacetyl chloride by distillation is impracticable because of the proximity of their boiling points. Therefore, the preparation of pure chloroacetyl chloride from ketene and chlorine would be practical only by complete elimination of dichloroacetyl chloride formation.

The production of dichloroacetyl chloride can be completely eliminated in the liquid phase in sulfur dioxide as solvent. Of the various solvents tried, sulfur dioxide is uniquely specific in this respect (Table I). Under all other conditions tried, dichloroacetyl chloride was produced. The runs summarized in Table I were chosen as representatives from the many made during this investigation.

If the concentration of chloroacetyl chloride in sulfur dioxide becomes high enough, some dichloroacetyl chloride will be formed. Charging a mixture of chloroacetyl chloride and sulfur dioxide (3:1 molar ratio) as solvent resulted in the production of dichloroacetyl chloride (Run 10). Thus, there should be some particular concentration of chloroacetyl chloride in sulfur dioxide below which no dichloroacetyl chloride will be formed.

In a dilute solution of chloroacetyl chloride in sulfur dioxide, under conditions that should enhance the chances for dichloroacetyl chloride production, *i.e.*, excess chlorine present (Run 9), no dichloroacetyl chloride was formed. This is in con-

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(1) A. B. Boese, Jr., *Ind. Eng. Chem.*, **32**, 16 (1940).

(2) B. N. Dashkevich, *Sbornik Trudov Leningrad. Tekh. Inst. USPK*, No. 3, 12–16 (1940); *Khim. Referat. Zhur.*, **4**, No. 3, 30 (1941). *Chem. Abstr.*, **37**, 4363 (1943).

(3) H. B. Watson and E. M. Roberts, *J. Chem. Soc.*, 2779 (1928).

(4) B. A. Porai-Koshits, L. S. Etros, and K. Yu. Maryanouskaya, *J. Gen. Chem. USSR*, **26**, 426 (1956).

(5) T. D. Stewart and D. M. Smith, *J. Am. Chem. Soc.*, **52**, 2869 (1930).

trast to the only reported[6] preparation of chloroacetyl chloride free of dichloroacetyl chloride from ketene and chlorine. In this case chlorine reacted in the vapor phase with an 80% or greater excess of ketene.

Chloroacetyl chloride was tried as the solvent in a number of runs. In all cases, dichloroacetyl chloride was produced as evidence by the isolation of acetyl chloride from the reaction mixture.

EXPERIMENTAL[7]

Ketene source. The ketene used was prepared by the pyrolysis of acetic anhydride[8] in a modification of the apparatus described by Fisher, *et al.*[9] In the present apparatus the acetic anhydride was fed to the evaporator from a reservoir under nitrogen pressure through a Fisher and Porter "Tri-Flat Flowrater Meter" (tube No. 02F). The rate of flow was controlled with a suitable needle valve. The evaporator, connecting to the top of the cracker and tilting a few degrees from the horizontal was constructed of 14 mm. Pyrex tubing 53 cm. long with a 38-cm. heated section. Heat was supplied by a winding of Nichrome ribbon. Operating temperatures were as described by Fisher *et al.*

Reaction of chlorine in ketene. The reactor or flask was charged with the solvent, cooled to the desired temperature and ketene and chlorine were introduced for the specified time. In the reactor the chlorine entered the mixture from the bottom through a 2-mm. capillary. A sintered glass disperser was used in the runs conducted in the 500-ml. flask. In both cases ketene was introduced through a hollow stirrer (Ace Glass "Mini-Lab" stirrers modified to fit a 34/45 standard taper joint).

At the completion of the run the mixture was distilled through a 10-in. helix-packed column. When sulfur dioxide was used as solvent it was first removed through an ice-cooled condenser. Three fractions were taken during the distillation—low boiler (mostly acetyl chloride), b.p. up to 103°; product fraction (chloroacetyl chloride and dichloroacetyl chloride), b.p. 103–107°; and high boilers, b.p. above 107°.

Analysis. The product fraction was analyzed either by determining its neutral equivalent and calculating its chloroacetyl chloride content, assuming that only chloroacetyl chloride and dichloroacetyl chloride were present or by hydrolyzing the dichloroacetyl chloride to oxalic acid and titrating with permanganate. The former was used as a screening analyses; when the dichloroacetyl chloride content was indicated to be low it was determined directly by the latter procedure.

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[6] R. N. Lacey and A. E. Blades, Brit. Pat. **735,902** (to Distillers Co.) Aug. 31, 1955.

[7] Analyses were conducted by Mrs. Geneva Kratzer and Mrs. Dawn Knight.

[8] When ketene prepared from acetone was employed large quantities of sulfuryl chloride and residue were obtained which resulted in a low yield of chloroacetyl chloride. Apparently some by-products in this ketene stream catalyzed the combination of chlorine and sulfur dioxide. The chloroacetyl chloride produced contained only a small amount of dichloroacetyl chloride, however.

[9] G. J. Fisher, A. F. MacLean, and A. W. Schnizer, *J. Org. Chem.*, **18**, 1055 (1953).

Mixed Anhydrides of *S*-Phenylthiocarbonic Acid and Carboxylic Acids

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In a previous communication[1] it was suggested that an intermediate mixed anhydride of *S*-phenylthiocarbonic acid, *i.e.*, $C_6H_5SCO_2H$, and *N,N'*-carbonyl-bis-DL-phenylalanine was formed and was responsible for the observation that an unlimited amount of *S*-phenylthiocarbonyl chloride could be hydrolyzed in a biphasic aqueous system initially containing the relatively water-insoluble acid chloride, an unlimited amount of base and a relatively small amount of DL-phenylalanine whereas when the latter compound was absent, or was replaced by a simple amine, the excess *S*-phenylthiocarbonyl chloride was hydrolyzed either very slowly or not at all.

In order to provide more direct evidence that a mixed anhydride could arise by the reaction of *S*-phenylthiocarbonyl chloride with a carboxylic acid in the presence of a base, an attempt was made to demonstrate mixed anhydride formation by allowing the acid chloride to react with acetic acid in the presence of aqueous ethanolic triethylamine and subsequently adding aniline to the reaction mixture to obtain the expected acetanilide. However, the only amide isolated was *N,S*-diphenylthiocarbamate which could have been formed by the reaction of aniline with the acid chloride.[1] Since it was presumed that any mixed anhydride that may have been formed had been hydrolyzed prior to the addition of the amine, the above reaction was then conducted in anhydrous dioxane. Under these conditions, the principle reaction product was found to be acetanilide, thus demonstrating that a mixed anhydride of *S*-phenylthiocarbonic acid and acetic acid had been formed and that its principle reaction product when treated with aniline is acetanilide. A similar experiment conducted with hippuric acid and aniline gave hippurylanilide.

While the above experiments demonstrate the existence of mixed anhydrides of *S*-phenylthiocarbonic acid and carboxylic acids and thus generalize the observation made previously with *N,N'*-carbonyl-bis-DL phenylalanine[1] to include all carboxylic acids, it should be noted that the other suggestion made earlier[1] that such mixed anhydrides may be useful as intermediates in the synthesis of derivatives of carboxylic acids has lost much of its force. While further investigation could result in improved conditions for the preparation of mixed anhydrides of *S*-phenylthiocarbonic acid and carboxylic acids, the experience gained in this investigation has shown that such mixed anhy-

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[1] D. G. Crosby and C. Niemann, *J. Am. Chem. Soc.*, **76**, 4458 (1954).