Ionic Peroxide Reactions. The Mechanism of the Reaction of Peroxycarbonates with Trivalent Phosphorus Nucleophiles[1]

WALDEMAR ADAM* AND AGUSTIN RIOS[2]

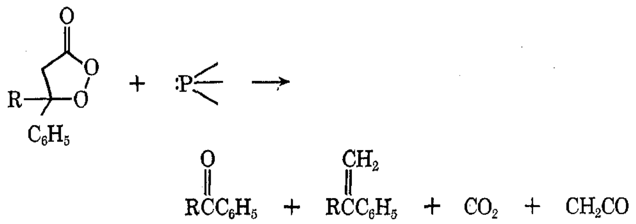
Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

Received July 23, 1970

The reaction of diisopropyl peroxydicarbonate with triphenylphosphine in *n*-pentane affords 65% diisopropyl carbonate, 10% diisopropyl pyrocarbonate, and a quantitative yield of triphenylphosphine oxide. The proportion of carbonate to pyrocarbonate is 6.4, 60.0, and ∞ in the solvents *n*-pentane, benzene, and acetonitrile. A crossover experiment indicates statistical crossing in the carbonate but none in the pyrocarbonate. The rates are insensitive to solvent polarity. A mechanism is proposed in which a phosphorane intermediate is formed in a slow step which is subsequently partitioned into carbonate product *via* an ionic route and into pyrocarbonate *via* a molecular path.

Ionic reactions of peroxides are well documented.[3] Among these the heterolysis of the peroxide linkage by nucleophiles such as the hydride ion,[4] carbanions,[5] olefins,[6] amines,[7] phosphines,[8] phosphites,[9] phenols,[10] sulfides,[11] and iodides[12] are typical examples. On the other hand, electrophiles such as aluminum halides,[13] boron halides,[14] and transition metal halides[15] lead to oxygenation of aromatic substrates by heterolysis of peroxides. Examples of intramolecular migration induced by peroxide bond heterolysis are the Criegée rearrangement,[16] the Baeyer-Villiger oxidation,[17] and the carboxy inversion reaction.[18]

Recently we reported[19] an interesting and novel example of a fragmentation reaction when β-peroxylactones are treated with trivalent phosphorus nucleophiles as shown in the equation



In continuation of our work on ionic reactions of peroxides, we decided to investigate the behavior of peroxydicarbonates toward trivalent phosphorus nucleophiles. Our interest in this system was stimulated by the possibility that the pentacovalent phosphorus intermediate, generated between the peroxide and phosphorus compound, might simply form pyrocarbonate or undergo fragmentation into carbonate and carbon dioxide. Both alternatives would be worthy of study since the former would constitute a convenient preparation of pyrocarbonates,[20] while the latter would be a novel fragmentation. In this paper we report on the mechanism of this reaction.

Results

Products.—When equimolar amounts of diisopropyl peroxydicarbonate and triphenylphosphine in hexane are allowed to react at room temperature, instantaneous gas evolution is observed and a white solid precipitates. The white precipitate, formed in quantitative yield, was identified as triphenylphosphine oxide by mixture melting point with an authentic sample. By means of a gas buret it was established that 75–80% carbon dioxide gas was liberated, using *p*-xylene as solvent in order to minimize vapor pressure corrections.

The supernatant liquid was then analyzed for volatile products on a Varian 202-B Aerograph. The major peak was shown to be diisopropyl carbonate and the minor peak diisopropyl pyrocarbonate, identified by retention times and infrared spectra with the authentic materials. From a semimicro scale sample (0.05 mol) were isolated by fractional distillation 53% carbonate and 4% pyrocarbonate.

The quantitative analysis of the volatile products was carried out by means of infrared spectroscopy and by gas chromatography. From the Beer's law plots it was

---

(1) This work was financed by the National Science Foundation, the A. P. Sloan Foundation, and the Petroleum Research Fund, administered by the American Chemical Society. It was presented at the 5th Caribbean Chemical Symposium, Bridgetown, Barbados, Jan 1969.

(2) Western Fher Fellow, 1967–1970.

(3) A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, Chapters 9 and 10.

(4) H. R. Williams and H. S. Mosher, *J. Amer. Chem. Soc.*, **76**, 3495 (1954); M. Matic and D. A. Sutton, *J. Chem. Soc.*, 2679 (1952); G. A. Russell, *J. Amer. Chem. Soc.*, **75**, 5011 (1953).

(5) S. O. Lawesson and N. C. Yang, *ibid.*, **81**, 4230 (1959).

(6) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961); F. D. Greene and W. Adam, *J. Org. Chem.*, **29**, 136 (1964); H. Kwart, P. S. Starcher, and S. W. Tinsley, *Chem. Commun.*, 335 (1967); T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964).

(7) D. B. Denney and D. Z. Denney, *J. Amer. Chem. Soc.*, **82**, 1389 (1960); W. B. Geiger, *J. Org. Chem.*, **23**, 298 (1958); C. Walling and N. Indictor, *J. Amer. Chem. Soc.*, **80**, 5815 (1958); R. Huisgen and F. Bayerlein, *Justus Liebigs Ann. Chem.*, **630**, 138 (1960).

(8) V. L. Horner and W. Jürgeleit, *ibid.*, **591**, 138 (1955); M. A. Greenbaum, D. B. Denney, and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **78**, 2563 (1956); D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957); D. B. Denney, W. F. Goodyear, and B. Goldstein, *ibid.*, **82**, 1393 (1960); A. G. Davies and R. Feld, *J. Chem. Soc.*, 4637 (1958).

(9) C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **81**, 1243 (1959).

(10) C. Walling and R. B. Hodgdon, Jr., *ibid.*, **80**, 228 (1958); D. B. Denney and D. Z. Denney, *ibid.*, **82**, 1389 (1960).

(11) C. G. Overberger and R. W. Cummins, *ibid.*, **75**, 4250 (1953); D. Swern, L. P. Witnauer, C. R. Eddy, and W. E. Parker, *ibid.*, **77**, 5537 (1955); J. O. Edwards, **78**, 1819 (1956); J. C. Martin, D. L. Tuleen, and W. G. Bentrude, *Tetrahedron Lett.*, 229 (1962).

(12) D. H. Fortmun, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Amer. Chem. Soc.*, **82**, 778 (1960); J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos, *ibid.*, **80**, 5435 (1958); H. Boardman and G. E. Hulse, *ibid.*, **75**, 4272 (1953).

(13) P. Kovacic and M. E. Kurz, *J. Org. Chem.*, **31**, 2459 (1966).

(14) J. D. McClure and P. H. Williams, *ibid.*, **27**, 24 (1962).

(15) J. T. Edward, H. S. Chang, and S. A. Samad, *Can. J. Chem.*, **40**, 804 (1962); G. A. Razuvaev, N. A. Kartashava, and L. S. Boguslavskaya, *J. Gen. Chem. USSR*, **34**, 2108 (1964).

(16) E. Hedaya and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1661 (1967); P. D. Bartlett and J. L. Kice, *ibid.*, **75**, 5591 (1953); H. L. Goering and A. C. Olsen, *ibid.*, **75**, 5853 (1953); R. Criegée and R. Kaspar, *Justus Liebigs Ann. Chem.*, **560**, 127 (1948).

(17) C. H. Hassall, *Org. React.*, **9**, 73 (1957); K. Syrkin and I. I. Moiseev, *Russ. Chem. Rev.*, **29**, 193 (1960).

(18) J. E. Leffler and C. C. Petropoulos, *J. Amer. Chem. Soc.*, **79**, 3068 (1957); D. B. Denney and D. Z. Denney, *ibid.*, **79**, 4806 (1957); F. D. Greene, H. P. Stein, C. C. Chiu, and F. M. Vane, *ibid.*, **86**, 2080 (1964).

(19) W. Adam, J. R. Ramírez, and S. C. Tsai, *ibid.*, **91**, 1254 (1969).

(20) W. Thoma and H. Rinke, *Justus Liebigs Ann. Chem.*, **624**, 30 (1959).

extrapolated that 75.3 ± 1.0% carbonate and 6.21 ± 0.45% pyrocarbonate were formed when diisopropyl peroxydicarbonate was treated with triphenylphosphine in chloroform. Using the calibrated internal standard technique, the gas chromatographic analysis showed that 65.0 ± 2.0% carbonate and 10.1 ± 0.8% pyrocarbonate were formed in *n*-pentane, while in benzene a 92% yield of carbonate was obtained under conditions where the pyrocarbonate was decomposed into carbonate. Since the infrared and the gas chromatographic quantitative results were at such variance, we suspected that the carbonate/pyrocarbonate ratio is solvent sensitive. Indeed, gas chromatographic analysis revealed that the carbonate/pyrocarbonate ratio was 6.4, 60.0, and ∞ in pentane, benzene, and acetonitrile.

Since pyrocarbonates are thermally labile,[20] the possibility exists that the carbonate is a secondary product formed from the decomposition of the pyrocarbonate under the reaction conditions. To exclude this possibility, a control experiment was conducted in which a synthetic reaction mixture was simulated consisting of pyrocarbonate and triphenylphosphine in hexane and stirred at room temperature for 6 hr, several times the usual reaction time. Infrared and gas chromatographic analysis showed that no carbonate was formed from the pyrocarbonate under the reaction conditions.

The reaction of diisopropyl peroxydicarbonate with trimethyl phosphite also leads to the formation of carbonate and pyrocarbonate. The interesting finding in this system, however, was that the pyrocarbonate was formed in preference to carbonate. Unfortunately, quantitative product studies were frustrated by the fact that the phosphite and phosphate product severely interfered in the infrared and gas chromatographic work. A number of other trialkyl and triaryl phosphites were tried, but the difficulties persisted.

Kinetics.—Preliminary experiments showed that the phosphines were much too reactive to determine the kinetics by ordinary techniques. Since the trialkyl phosphites and triaryl phosphites led to the same products, and since they are less nucleophilic, the rate studies were carried out for the reaction of tri-*m*-tolyl phosphite with diisopropyl peroxydicarbonate. The reaction was run directly in the thermally equilibrated infrared cell, monitoring the signal output of the decay of the peroxide carbonyl absorption at 1790 cm^{-1} to a Servo-Recorder. Using a 50-fold excess of the phosphite, good pseudo-first-order kinetics through at least three half-lives was observed. The second-order rate constants are 2.78×10^{-4} and 3.76×10^{-4} M^{-1} sec^{-1} at 306.6°K, respectively, in cyclohexane and acetonitrile, at a peroxide concentration of 0.0146 *M* and phosphite concentration of 0.73 *M*.

Crossover Experiment.—In an attempt to capture ionic intermediates by external intervention, diisopropyl peroxydicarbonate was allowed to react with triphenylphosphine in the presence of sodium methyl carbonate. Unfortunately, the peroxydicarbonate reacted vigorously with the carbonate salt, rendering the experiment meaningless. However, when an equimolar mixture of diisopropyl and di-*sec*-butyl peroxydicarbonates was treated with an excess of triphenylphosphine in pentane, gas chromatographic analysis revealed that besides diisopropyl and di-*sec*-butyl carbonate also isopropyl *sec*-butyl carbonate (cross-carbonate) was formed. These carbonates were formed in the proportions 1.00:1.02:1.90, respectively. Therefore, virtually a statistical mixture of carbonates was obtained. Very interesting is the fact that no cross-pyrocarbonate could be detected even at maximum sensitivity, although both the diisopropyl and di-*sec*-butyl pyrocarbonates were formed as minor products.

It is possible that triphenylphosphine might have caused statistical interchange of the diisopropyl and di-*sec*-butyl carbonates. However, a control experiment in which a simulated reaction mixture of the two carbonates and triphenylphosphine in benzene was allowed to stand 3 days at room temperature showed no cross-carbonate on gas chromatographic analysis.

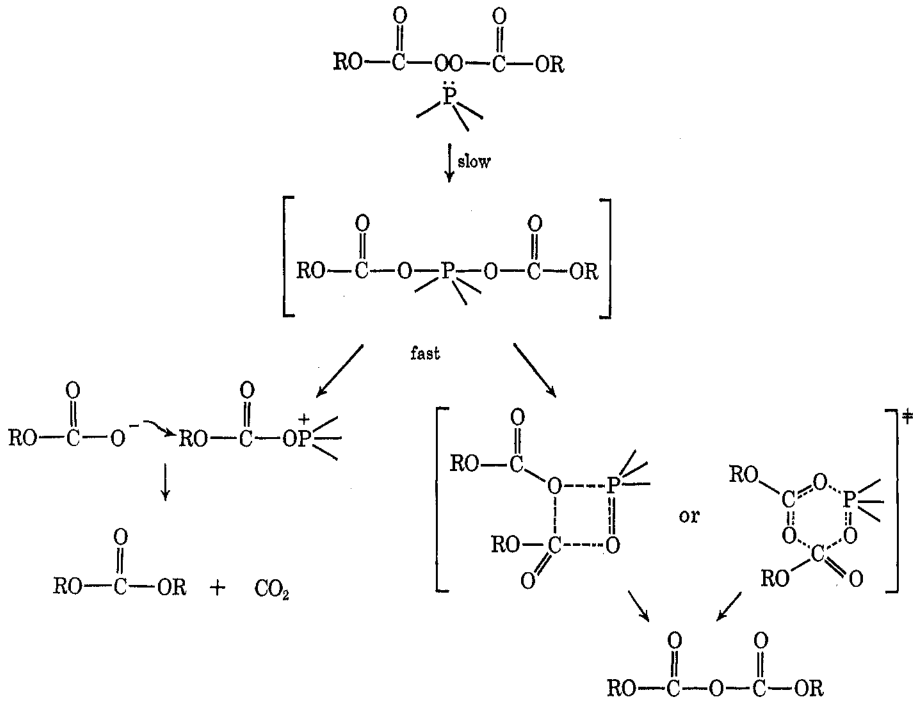
Mechanism.—Let us now construct a reasonable mechanism for this reaction from the above experimental data. To facilitate this task we reiterate the important findings together with their mechanistic implications. (a) The second-order kinetics and the absence of a kinetic solvent effect suggest that a pentacovalent phosphorus intermediate is formed in the rate-determining step,[19,21] which subsequently decays *via* a fast step into the carbonate and pyrocarbonate. (b) The stability of the pyrocarbonate under the reaction conditions implies that both the pyrocarbonate as well as the carbonate are primary products, generated by partitioning of the pentacovalent intermediate *via* distinct paths. (c) The solvent effect on the product ratio of carbonate to pyrocarbonate, *i.e.*, with increasing solvent polarity more carbonate is produced, bespeaks the fact that the pyrocarbonate is formed *via* a molecular path, while the carbonate is formed *via* an ionic path from the pentacovalent intermediate. (d) The presence of a product solvent effect but the absence of a kinetic solvent effect presumes that the kinetic and the product steps are separated into two events. (e) The fact that predominantly carbonate is formed with phosphine, but predominantly pyrocarbonate with phosphite, corroborates the above interpretation since the phosphorus of the phosphite is more electron deficient than the phosphorus of the phosphine and thus the pentacovalent intermediate formed from the phosphite prefers to partition *via* the molecular path rather than the ionic path to avoid depositing a positive charge onto an already desparate phosphorus. (f) The absence of cross-pyrocarbonate but the statistical crossover in the carbonates fortifies the conclusion that the pyrocarbonate is formed *via* a molecular process while the carbonate originates from an ionic path, but both are derived from a common pentavalent phosphorus intermediate.

A reasonable mechanism which accommodates these findings is given by Scheme I. This scheme illustrates that a pentacovalent phosphorus intermediate is generated by rate-determining phosphorus insertion into the peroxide bond. Subsequently the phosphorane is partitioned *via* fast steps into the products. As demanded by the experimental data, the kinetic step and the product step are clearly separated into distinct events. The ionic pathway affords the carbonate by attack of the carbonate ion on the alkyl group of the phosphonium ion, displacing carbon dioxide and the phosphine oxide. The most compelling evidence for

---

[21] D. B. Denney and S. T. D. Gough, *J. Amer. Chem. Soc.*, **87**, 138 (1965).

SCHEME I



R = isopropyl

this interpretation is the statistical crossover in the carbonate product.

The pyrocarbonate, on the other hand, is thought to be produced *via* a molecular route involving either a four- or six-membered cyclic transition state. A more polar solvent would be expected to divert more of the phosphorane *via* the ionic route, while a less nucleophilic phosphorus such as the phosphites compared to the phosphines would channel a greater portion of the intermediate through the molecular path. It is indeed surprising how sensitive the partitioning of the phosphorane into carbonate and pyrocarbonate is toward nucleophilicity and solvent polarity.

It is important to mention that *tert*-butylperoxy isopropyl carbonate behaved normally toward nucleophilic attack by triphenylphosphine. Thus triphenylphosphine oxide was formed quantitatively, but no carbon dioxide gas was evolved. The only volatile product was *tert*-butyl isopropyl carbonate, isolated in 85% yield by distillation.[22] This result suggests that the phosphorane intermediate ROCOOP(<)O-*tert*-Bu either goes *via* a molecular path to give the carbonate product or that the heterolysis proceeds, as we might have been anticipated, exclusively to give the ions $ROCOO^-$ and *tert*-$BuOP<^+$ rather than the ions *tert*-BuO^- and $ROCOOP<^+$. If the latter ions had been formed, some nucleophilic attack by the *tert*-butoxide ion at the alkyl group would have been expected in view of our peroxydicarbonate results. Consequently, alkyl *tert*-butyl ether should have been formed besides the carbonate due to decarboxylation. Alkyl *tert*-butyl carbonates are difficult to make by ordinary methods[23] and we offer this reaction as a convenient synthetic route for these compounds. Similarly the reaction of di-*tert*-butylperoxy carbonate gave di-*tert*-butyl carbonate when treated with excess triphenylphosphine, but no carbon dioxide was liberated.[24]

Related Work.—The existence of pentacovalent phosphorus compounds is well documented.[25] They are conveniently prepared through the reaction of peroxides with trivalent phosphorus nucleophiles.[26] In most cases the pentacovalent adducts are unstable[25] and undergo the oxygen extrusion reaction[8]

$$R{-}OO{-}R + :P< \longrightarrow R{-}O{-}R + O{=}P<$$

The novel feature of the reaction of peroxydicarbonates with trivalent phosphorus nucleophiles is that the intermediary phosphorane is partitioned into two products, namely pyrocarbonate and carbonate. A related case of competitive partitioning concerns the cyclic phosphorane produced from β-peroxylactones and trivalent phosphorus compounds,[19] shown in Scheme II. Two possible dipolar ions A and B are produced from the cyclic phosphorane, which subsequently suffer ionic push–pull triggered fragmentation to yield the products. Also in this case solvent polarity, phosphorus nucleophilicity, and β-alkyl group structure control the relative partitioning of the phosphorane into the dipolar ions A and B. In fact, this novel ketene elimination and decarboxylation reactions stimulated us to look for other examples of competitive partitioning of pentacovalent phosphorus intermediates. Indeed, the phosphorane formed from peroxydicarbonates and phosphines undergo competitive partitioning, but, unlike the cyclic phosphorane produced from β-peroxylactones which is partitioned into two distinct dipolar ions, the partitioning competes between a molecular route (pyrocarbonate) and an ionic route (carbonate).

---

[22] W. Adam and J. Sanabia, unpublished results.

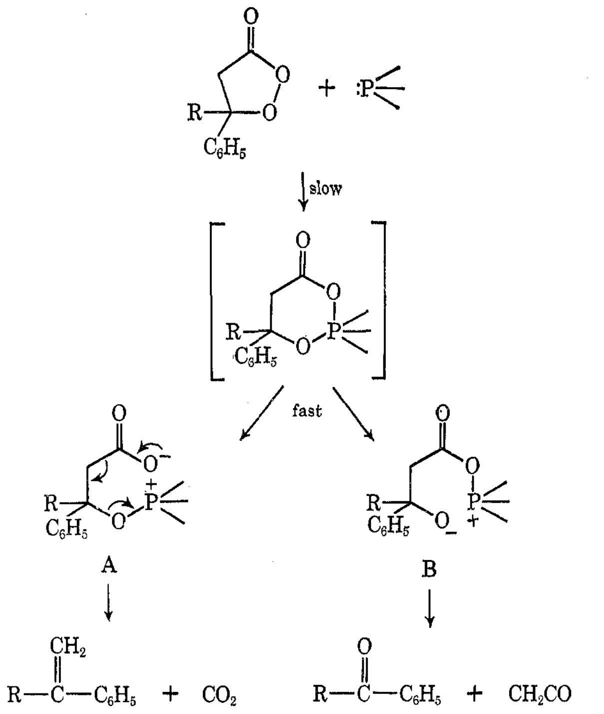
[23] W. Klee and M. Brenner, *Helv. Chim. Acta*, **44**, 2151 (1961); H. A. Staab, *Ber.*, **95**, 1284 (1962).

[24] W. Adam, B. S. Ramaswamy, and P. Rullan, unpublished results.

[25] F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

[26] D. B. Denny and N. G. Adin, *Tetrahedron Lett.*, 2569 (1966); D. B. Denney and S. T. D. Gough, *J. Amer. Chem. Soc.*, **87**, 138 (1965).

SCHEME II



An alternative mechanistic interpretation of the experimental data of the peroxydicarbonate–triphenylphosphine reaction is to propose that solvent-caged ion pairs are formed. Some of the caged ion pairs collapse to produce the pyrocarbonate; the remainder diffuse apart and finally generate the carbonate and carbon dioxide. For the moment we prefer competitive partitioning between the molecular and ionic paths; however, oxygen-18 labeling experiments and the use of optically active substrates are in progress to provide information on the more subtle aspects of the mechanism of this reaction.

Finally it is worthy to point out that the reaction of tertiary arylamines with diisopropyl peroxydicarbonate has been studied.[27] A free-radical-chain mechanism has been proposed in this case. This contrasting behavior of the tertiary amines compared to the phosphorus nucleophiles has been noted previously.[28]

Experimental Section

Diisopropyl Peroxydicarbonate.[29]—In an open 125-ml erlenmeyer flask were placed 20.6 g (0.17 mol) of isopropyl chloroformate. While the mixture was cooled with an ice bath and stirred magnetically a chilled suspension of 6.63 g (0.085 mol) of sodium peroxide octahydrate, freshly prepared from 9.6 ml of 30% aqueous hydrogen peroxide and 51.8 ml of 11.1% aqueous sodium hydroxide, was added by means of a medicine dropper, keeping the reaction temperature at 5–10°. After the reaction mixture was stirred for 30 min at 5–10°, the organic layer was taken up in ether, washed well with water, and dried over anhydrous magnesium sulfate. Removal of the drying agent and evaporation of the solvent at reduced pressure, keeping the temperature below 5–10°, gave 16.4 g of oily product. Repeated recrystallization from *n*-pentane at −70° afforded 12.4 g (72% yield) of diisopropyl peroxydicarbonate, mp 8–10° (lit.[30] mp 9–10°). Iodometric titration showed that this material had a purity of 98.9%.

Di-*sec*-butyl peroxydicarbonate was prepared in 75% yield as a viscous oil giving a peroxide titer (iodometric) of 90.2%. All attempts to crystallize the oil failed. The infrared spectrum showed a clean double carbonyl band at 1790 and 1815 cm^{-1} similar to that of the diisopropyl peroxycarbonate.

Diisopropyl Pyrocarbonate.—To a mechanically stirred suspension of 35.0 g (0.28 mol) of sodium isopropyl carbonate, freshly prepared by carbonation of sodium isopropoxide in isopropyl alcohol, in 30 ml of methylene chloride was added a solution of 30 g (0.30 mol) of phosgene in 75 ml of methylene chloride over a period of 90 min, maintaining the reaction temperature at 0–5°. During the phosgene addition carbon dioxide gas was evolved spontaneously. After the reaction mixture stirred overnight at room temperature, the reaction flask was flushed with dry nitrogen gas to remove unreacted phosgene. The solids were collected on a Büchner funnel and washed several times with methylene chloride. The solvent was evaporated from the combined filtrates at reduced pressure and the liquid residue vacuum distilled. The fraction collected at 44–45° (0.5 mm), corresponding to 4.1 g (7.7% yield) of diisopropyl pyrocarbonate, had n^{25}D 1.3985 [lit.[31] bp 44–46° (0.3 mm), n^{25}D 1.3982].

Diisopropyl Carbonate.—To a solution of 4.75 g (0.06 mol) of freshly distilled pyridine in 5 ml of isopropyl alcohol was added slowly while stirring magnetically 6.13 g (0.05 mol) of isopropyl chloroformate. After 2-hr total reaction time the solution was diluted with a large excess of water and the organic layer taken up in ether. The organic layer was dried over magnesium sulfate and, on removal of the solvent, the crude product was rectified by distillation. The pure carbonate, 4.2 g (57% yield), was collected at 73° (57 mm), n^{22}D 1.3920 [lit.[32] bp 146–147° (760 mm), n^{20}D 1.3906].

Di-*sec*-butyl carbonate was prepared *via* the above procedure in 53% yield, bp 70–72 (15 mm), n^{22}D 1.4028 [lit.[33] bp 73–74° (18 mm), n^{22}D 1.4039].

Isopropyl *sec*-butyl carbonate was prepared *via* the above procedure in 37% yield, bp 80–82° (40 mm), n^{22}D 1.3960.

Triphenylphosphine was purchased from Matheson Coleman and Bell Co. and recrystallized from ethanol, mp 79–80°.

Tri-*m*-tolyl phosphite was obtained from Mr. S. C. Tsai and fractionated at reduced pressure, bp 182° (0.05 mm) [lit.[34] bp 188° (1.0 mm)].

Solvents were purified according to standard procedures.[35]

The Reaction of Diisopropyl Peroxydicarbonate with Triphenylphosphine.—A 250-ml round-bottom flask, provided with a magnetic stirring bar and a 250-ml pressure-equalized dropping funnel, was charged with 10.25 g (0.0498 mol) of the peroxydicarbonate, dissolved in 40 ml of pentane. While the solution was stirred magnetically, a solution of 15.72 g (0.06 mol) of triphenylphosphine dissolved in 175 ml of pentane was added dropwise from the funnel. Spontaneous gas evolution and precipitation of a white solid was observed. After a total of 14-hr reaction time, the solid was collected on a Büchner funnel and washed several times with pentane, affording 13.7 g (98.9% yield) of triphenylphosphine oxide, mp 156–156.5°, mmp 156–156.5°. The solvent was removed from the combined filtrates and the oily residue fractionated at reduced pressure. The first fraction, identified as diisopropyl carbonate by its carbonyl band at 1735 cm^{-1} and comparison with the authentic material, was collected at 48.2° (18 mm), n^{26}D 1.3900, and weighed 3.85 g (53% yield). The second fraction, identified as diisopropyl pyrocarbonate by its characteristic carbonyl bands at 1825 and 1765 cm^{-1} and comparison with the authentic material, was collected at 64–72° (0.30 mm), n^{26}D 1.3988, and weighed 0.36 g (3.8% yield).

A control experiment was carried out by preparing a solution of 59.9 mg (0.31 mmol) of pyrocarbonate and 79.2 mg (0.31 mmol) of triphenylphosphine in 1.0 ml of benzene and letting it stand 6 hr. No gas was evolved and infrared and gas chromatographic analysis showed the absence of diisopropyl carbonate.

Quantitative Determination of Carbon Dioxide Gas.—A 3-ml round-bottom flask, provided with a magnetic stirring bar and a

---

[27] J. C. Crano, *J. Org. Chem.*, **31**, 3615 (1966).

[28] R. Huisgen, W. Heydcamp, and F. Bayerlein, *Ber.*, **93**, 363 (1960).

[29] Utmost care should be exercised when working with peroxydicarbonates since a sample allowed to stand at room temperature underwent violent decomposition. All safety measures should be taken.

[30] F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. T. de Witt, H. C. Stevens, and J. H. Langston, *J. Amer. Chem. Soc.*, **72**, 1254 (1950).

[31] J. H. Howe and L. R. Morris, *J. Org. Chem.*, **27**, 1901 (1962).

[32] K. Sabathy, *Monatsh. Chem.*, **72**, 308 (1939).

[33] R. L. Frank, H. R. Davies, Jr., S. S. Drake, and J. B. McPherson, Jr., *J. Amer. Chem. Soc.*, **66**, 1509 (1944).

[34] E. N. Walsh, *ibid.*, **81**, 3023 (1959).

[35] K. B. Wiberg, "Laboratory Techniques in Organic Chemistry," McGraw-Hill, New York, N. Y., 1960.

2-ml pressure-equalized dropping funnel, whose outlet was connected to a 50-ml gas buret, was equilibrated at 29°. The flask was charged with a solution of 377.6 mg (1.83 mmol) of diisopropyl peroxydicarbonate in 0.5 ml of xylene and the dropping funnel with a solution of 602.6 mg (2.30 mmol) of triphenylphosphine in 1.4 ml of xylene. With the mercury level at zero and stirring magnetically the phosphine solution was added dropwise, always maintaining the mercury levels at equal heights in the buret and the leveling bulb. After complete addition (about 15 min) the reaction mixture was stirred until no change in the mercury level was observed (about 30 min). A total volume of 40.6 ml of gas was produced, corrected for xylene vapor pressure,[36] representing 1.42 mmol of carbon dioxide (77.6% yield).

Quantitative Infrared Analysis of Diisopropyl Pyrocarbonate and Carbonate.—Standard solutions of the carbonate (0.01–0.06 M) and pyrocarbonate (0.01–0.03 M) were prepared in chloroform. Their absorbances were then determined in 0.2-mm sodium chloride cells at 1735 cm^{-1} for the carbonate and 1820 cm^{-1} for the pyrocarbonate on the Perkin-Elmer 237-B Infracord. For maximum accuracy the above concentrations were chosen so that the absorbance reading were within the range 0.10–0.70. The The Beer's law plots from these data were good straight lines with molar extinction coefficients of 12.96 and 14.58 for the carbonate and pyrocarbonate, respectively. The reaction mixture resulting from 0.386 mmol of proxycarbonate and 0.405 mmol of triphenylphosphine in 3.0 ml of chloroform was transferred to a 10-ml volumetric flask, diluted to the calibration mark, and its absorbance measured at 1735 and 1820 cm^{-1} using the same sodium chloride cells. The respective values were 0.382 and 0.035, which on extrapolation from the Beer's law plots indicated that 76.2% carbonate and 6.5% pyrocarbonate had formed.

Quantitative Gas Chromatographic Analysis of the Volatile Products.—The analyses were performed on a Varian 202-B Aerograph using a 2.5-ft copper column (0.25-in. diameter), packed with 20% SE-30 and 2% NaOH on Chromosorb W, and operated at a helium flow rate of 100 ml/min, an injector temperature of 96°, a detector temperature of 154°, and a column temperature of 83°. Under these conditions, which are extremely critical, the thermally labile pyrocarbonate undergoes less than 1% decomposition, maintaining good base lines, excellent separation, and symmetrical peaks.

A preliminary gas chromatographic run showed that the carbonate/pyrocarbonate ratio was approximately 10. Standard solutions of the products were then prepared in pentane at the ratios 1:8, 1:10, and 1:12 of pyrocarbonate to carbonate, by weighing the respective liquids into appropriate volumetric flasks, the total weight of carbonate and pyrocarbonate being maintained constant. An equal weight of internal standard (*p*-dichlorobenzene) was weighed into the volumetric flask, and the contents were diluted to the calibration mark with pentane. Each standard solution was analyzed by adjusting the injection volume and attenuator setting so that maximum needle deflection was secured. The peak areas were disk integrated, taking in each case an average of three injections. Calibration charts of the peak area ratio of each component to the internal standard against the known concentrations were then prepared, yielding good straight lines with slopes near unity.

A reaction mixture in pentane, prepared at the same concentrations and conditions as the standard solutions, was then analyzed on the above column and the peak area ratio of each component to the internal standard determined. With the help of the calibration charts the percentages of carbonate and pyrocarbonate were found to be 65.0 ± 2% and 10.1 ± 0.8% in pentane. In benzene the total yield was 92%.

Crossover Reaction between Diisopropyl and Di-*sec*-Butyl Peroxydicarbonates with Triphenylphosphine.—In a 10-ml round-bottom flask were placed 103 mg (0.5 mmol) of diisopropyl and 117 mg (0.5 mmol) of di-*sec*-butyl peroxydicarbonate, dissolved in 2 ml of benzene. While the mixture was stirred magnetically and kept at reaction temperature at 25° by means of a water bath, there was added dropwise a solution of 524 mg (2.0 mmol) of triphenylphosphine, dissolved in 2 ml of benzene. After 90 min of reaction time the appropriate amount of internal standard was added; the contents were diluted to the calibration mark and then analyzed for carbonates. The relative proportions of diisopropyl, isopropyl *sec*-butyl, and di-*sec*-butyl carbonates were 1.00:1.90:1.02, respectively.

A control experiment was conducted by allowing an equimolar mixture of diisopropyl and di-*sec*-butyl carbonate in benzene in the presence of excess triphenylphosphine to stand several days. Gas chromatographic analysis of the reaction mixture showed the absence of isopropyl *sec*-butyl carbonate.

Rate Measurements.—The kinetics of the reaction were studied directly in a 0.5-mm sodium chloride cell, using a Perkin-Elmer 237-B Infracord. This instrument was equipped with an ordinate scale accessory which permitted locking the wavelength drive mechanism at the desired wavelength, relaying the signal output to a variable drive Heath Servo-Recorder. The reaction rate was followed automatically as a continuous absorbance–time plot on the recorder. The temperature of the reaction cell was regulated by means of a constant-temperature accessory (Barnes Engineering Co.), situated directly in the sample beam. Temperature control was within ±0.1° during a kinetic run. The reduction of the light intensity of the sample beam was compensated by means of a matched sodium chloride cell and an attenuator.

After the empty sample cell was thermally equilibrated at the desired temperature (usually 30 min), it was externally loaded with the reaction mixture whose kinetics were to be determined. For this purpose the inlet and outlet ports of the sample cell were each extended through the top of the constant-temperature compartment with 22-gauge Teflon tubing, provided with the appropriate Luer lock fittings. The external loading process was accomplished by means of Luer lock syringes. One syringe containing the reaction solution was attached to the inlet port and the empty syringe to the outlet port of the sample cell. Quick and efficient loading without introducing air bubbles into the sample cell was achieved by synchroneous push–pull action of the respective syringes.

The reaction solution was prepared by dissolving quickly about 0.0146 mmol of peroxydicarbonate and 0.73 mmol of phosphite in 2.0 ml of solvent, using a calibrated volumetric flask. This solution was charged into the sample cell, while the solvent cell was charged with a solution of 0.73 mmol of phosphite in 2 ml of solvent. The wavelength drive mechanism was set at 1790 cm^{-1}, the Servo-Recorder set at a convenient rate, and the absorbance of the reaction mixture recorded through three half-lives. The kinetic runs were analyzed in terms of pseudo-first-order kinetics giving good straight-line plots. The second-order rate constants are 2.78×10^{-4} and $3.76 \times 10^{-4}\ M^{-1}\ \mathrm{sec}^{-1}$, respectively, in cyclohexane and acetonitrile.

Registry No.—Diisopropyl peroxydicarbonate, 105-64-6; di-*sec*-butyl peroxydicarbonate, 19910-65-7; diisopropyl pyrocarbonate, 24425-00-1; diisopropyl carbonate, 6482-34-4; di-*sec*-butyl carbonate, 623-63-2; isopropyl *sec*-butyl carbonate, 27040-99-9; triphenylphosphine, 603-35-0; tri-*m*-tolyl phosphite, 620-38-2.

---

[36] "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, p D-124.