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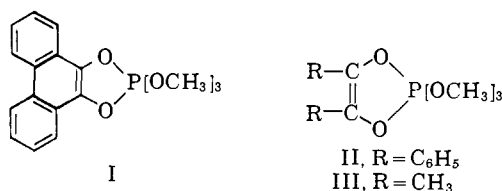
## Reaction of the *o*-Quinone-Trialkyl Phosphite and the $\alpha$ -Diketone-Trialkyl Phosphite 1:1 Adducts with Ozone and with Oxygen. A New Synthesis of Cyclic Diacyl Peroxides via Oxyphosphoranes<sup>1,2</sup>

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Ozonization of the phenanthrenequinone-trimethyl phosphite 1:1 adduct (I) at  $-75^\circ$  in methylene chloride-methanol solution gave the eight-membered cyclic diphenoyl peroxide VII in 80% yield. Close to 1 mole equiv. of ozone was consumed. The peroxide reacts with the adduct and gives phenanthrenequinone, diphenic anhydride, and trimethyl phosphate. Ozonization of the benzil-trimethyl phosphite adduct (II) gave benzoyl peroxide, benzoic anhydride, and benzil. The biacetyl-trimethyl phosphite adduct (III) gave acetyl peroxide, acetic anhydride, and biacetyl. The consumption of ozone by the diketone adducts varied with the rate at which the ozone was supplied. The diketone adducts reacted slowly with pure oxygen and gave anhydride, diketone, and phosphate; the quinone adduct was inert to oxygen.

We have reported<sup>4</sup> the formation of crystalline 1:1 adducts, I, from the reaction of *o*-quinones with trialkyl phosphites.<sup>5</sup>  $\alpha$ -Diketones also form 1:1 adducts, II and III, with trialkyl phosphites.<sup>4,6-9</sup>



These adducts are formulated as cyclic pentaoxyphosphoranes; however, they could exist in equilibrium with relatively small amounts of the open dipolar form IV.<sup>10</sup> The reactions of these adducts, for example, with bromine, hydrogen chloride, water, and carbonyl functions could involve the open dipolar structures.<sup>4,10</sup>

(1) (a) Organic Compounds with Pentavalent Phosphorus, Part XIII. (b) Part XII: F. Ramirez, A. V. Patwardhan, and S. R. Heller, *J. Am. Chem. Soc.*, **86**, 514 (1964).

(2) Preliminary reports of parts of this work have appeared; (a) F. Ramirez, R. B. Mitra, and N. B. Desai, *ibid.*, **82**, 2651 (1960); (b) *ibid.*, **82**, 5763 (1960); (c) F. Ramirez, N. B. Desai, and R. B. Mitra, *ibid.*, **83**, 492 (1961).

(3) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society (Grant 286-A), the National Science Foundation (G 19509), and the National Cancer Institute of the National Institutes of Health (CA-04769) for support of this research.

(4) (a) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960); (b) *ibid.*, **85**, 3252 (1963).

(5) The phosphorus of trialkyl phosphites attacks the oxygen of *p*-quinones to give alkyl ethers of *p*-quinol phosphates. Dialkyl phosphites yield *p*-quinol phosphates. (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 856 (1957); (b) *ibid.*, **22**, 1282 (1957); (c) *ibid.*, **23**, 778 (1958); (d) *J. Am. Chem. Soc.*, **81**, 587 (1959); (e) F. Ramirez, E. H. Chen, and S. Dershowitz, *ibid.*, **81**, 4338 (1959).

(6) G. H. Birum and J. L. Dever, Abstracts, 135th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958, p. 101 P; (b) U. S. Patents 2,961,455 (1960) and 3,014,949 (1961).

(7) V. A. Kukhtin, *Dokl. Akad. Nauk S.S.S.R.*, **121**, 466 (1958); *Chem. Abstr.*, **53**, 1105b (1959).

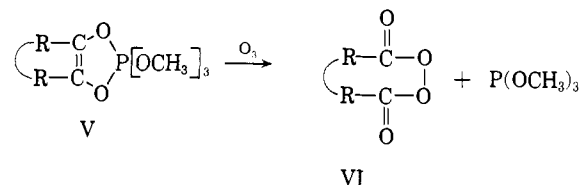
(8) (a) V. A. Kukhtin and K. M. Orekhova, *J. Gen. Chem., U.S.S.R.*, **30**, 1229 (1960); *Chem. Abstr.*, **55**, 358i (1961); (b) V. A. Kukhtin, K. M. Kirillova, and R. R. Shagidullin, *Zh. Obshch. Khim.*, **32**, 649 (1962); *Chem. Abstr.*, **58**, 546h (1963).

(9) (a) V. A. Kukhtin, K. M. Kirillova, R. Shagidullin, Yu. Yu. Samilov, N. A. Lyazina, and N. F. Rakova, *J. Gen. Chem., U.S.S.R.*, **32**, 2020 (1962); *Chem. Abstr.*, **58**, 4543A (1963); (b) V. A. Kukhtin, T. N. Voskoboeva, and K. M. Kirillova, *J. Gen. Chem., U.S.S.R.*, **32**, 2300 (1962); (c) K. M. Kirillova and V. A. Kukhtin, *ibid.*, **32**, 2305 (1962); (d) V. A. Kukhtin and K. M. Kirillova, *ibid.*, **32**, 2755 (1962).

(10) (a) F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3041 (1961); (b) F. Ramirez, N. Ramanathan, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 1317 (1962); (c) F. Ramirez, N. B. Desai, and N. Ramanathan, *Tetrahedron Letters*, No. 5, 323 (1963); (d) F. Ramirez, N. B. Desai, and N. Ramanathan, *J. Am. Chem. Soc.*, **85**, 1874 (1963); (e) F. Ramirez, A. V. Patwardhan, N. B. Desai, N. Ramanathan, and C. V. Greco, *ibid.*, **85**, 3056 (1963); (f) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963).



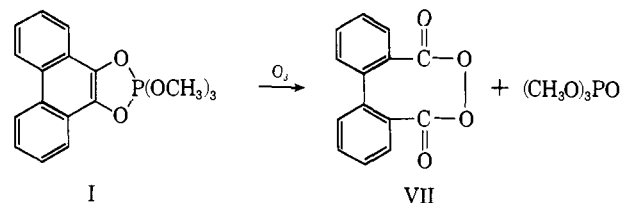
The cyclic unsaturated oxyphosphoranes I, II, and III have infrared and Raman bands which correspond to olefinic double bonds. It appeared of interest to explore the behavior of the adducts toward one of the classical double-bond reagents, namely ozone.<sup>11,12</sup> This reaction might provide a convenient route to certain cyclic diacyl peroxides (V  $\rightarrow$  VI) not obtainable otherwise.<sup>13</sup> This paper<sup>2</sup> describes the action of ozone



and of molecular oxygen on adducts I, II, and III. The ozonization of triphenylphosphine has been reported by Horner, Schaefer, and Ludwig<sup>14</sup>; that of trialkyl and triaryl phosphites by Thompson.<sup>15</sup>

### Results

**Ozonization of the Quinone-Phosphite 1:1 Adduct (I).**—A rapid reaction occurred when a 0.1 *M* solution of the phenanthrenequinone-trimethyl phosphite adduct (I) in methylene chloride was treated with ozone at  $-75^\circ$ . About 0.96 mole of ozone was consumed per mole of adduct. The main products were diphenoyl peroxide (VII, 60%) and trimethyl phosphate (*ca.* 100%; expt. 1, Table I). The ozonization produced



(11) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(12) (a) R. Criegee, *Angew. Chem.*, **71**, 525 (1959); (b) *Ber.*, **93**, 689 (1960).

(13) See F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **82**, 893 (1960), and references therein for discussion on cyclic peroxides.

(14) L. Horner, H. Schaefer, and W. Ludwig, *Ber.*, **91**, 75 (1958).

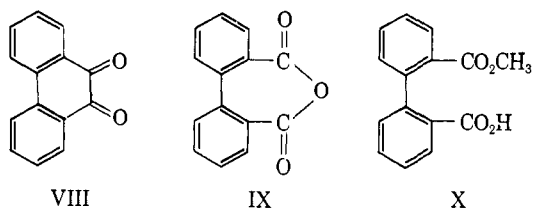
(15) (a) Q. E. Thompson, *J. Am. Chem. Soc.*, **83**, 845 (1961); (b) *Chem. Ind. (London)*, 121 (1959).

TABLE I  
OZONIZATION OF THE PHENANTHRENEQUINONE-TRIMETHYL  
PHOSPHITE ADDUCT (I) TO DIPHENOYL PEROXIDE (VII)<sup>a</sup>  
AT -75°

Expt.	Solvent (v./v.), M	Mmoles O <sub>3</sub> <sup>c</sup> / min.	Moles O <sub>3</sub> <sup>b</sup> / mole add.	Iso- lated <sup>c</sup> per- oxide VII, %	Per- oxide VII by io- dimetry, %
1	CH <sub>2</sub> Cl <sub>2</sub> , 0.11	2.10	0.96	54 <sup>d</sup>	..
2	CH <sub>2</sub> Cl <sub>2</sub> , 0.22	1.20	<1	50 <sup>d</sup>	70
3	CH <sub>2</sub> Cl <sub>2</sub> , 0.10	0.65	0.80	..	44 <sup>d</sup>
4	CH <sub>2</sub> Cl <sub>2</sub> -CH <sub>3</sub> OH (1:10), 0.06	1.90	.92	63 <sup>e</sup>	80
5	CH <sub>2</sub> Cl-CH <sub>3</sub> OH(1:8), 0.11	1.90	.96	50 <sup>e</sup>	75
6	CH <sub>2</sub> Cl <sub>2</sub> -CH <sub>3</sub> OH(1:5), 0.11	2.30	<1	50 <sup>e</sup>	70
7	CH <sub>2</sub> Cl <sub>2</sub> -CH <sub>3</sub> OH(1:2.5), 0.11	2.15	0.82	35 <sup>e</sup>	50
8	CH <sub>2</sub> Cl <sub>2</sub> -CH <sub>3</sub> OH(1:1), 0.13	2.27	0.85	28 <sup>f</sup>	..
9	CH <sub>2</sub> Cl <sub>2</sub> -CH <sub>3</sub> OH(1:10), 0.10	0.80	<1	32 <sup>e</sup>	70

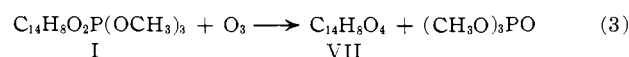
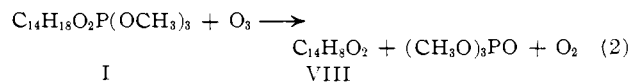
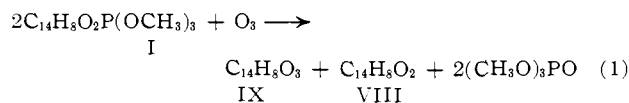
<sup>a</sup> The phosphorus appears as trimethyl phosphate. Other products are phenanthrenequinone and diphenic anhydride (IX). If methanol is used as solvent, the anhydride is converted into monomethyl diphenate (X). All of the starting material was consumed in these experiments. <sup>b</sup> Total O<sub>3</sub> dosage - O<sub>3</sub> found in KI trap. <sup>c</sup> Once recrystallized from CH<sub>2</sub>Cl<sub>2</sub> + CH<sub>3</sub>OH (9 ml. + 10 ml. per g. at 20° followed by cooling at 0°). <sup>d</sup> Peroxide remains in solution. <sup>e</sup> Peroxide precipitates during ozonization. <sup>f</sup> The precipitate which separates during ozonization is anhydride + quinone, not peroxide.

also phenanthrenequinone (*ca.* 25-30%) and diphenic anhydride (IX, 5-10%). The latter appeared as monomethyl diphenate (X) when the product was recrystallized from methylene chloride-methanol.



The diphenoyl peroxide (VII) reacted further with the adduct I and gave equimolar amounts of phenanthrenequinone (VIII) and diphenic anhydride (IX). This explains the lower yields of peroxide at low ozone rates (expt. 3). The best yields of peroxide VII were obtained when the ozonization was carried out in mixtures of methylene chloride and methanol, since the peroxide is sparingly soluble in the alcohol and escapes further reaction with the adduct I (expt. 4).

Some quinone VIII must be produced directly from adduct I and ozone, since there is always more quinone than anhydride among the ozonization products. The stoichiometry of these reactions is

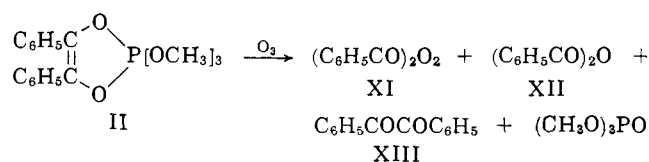


Molecular oxygen had no effect on the quinone-phosphite adduct I.

The structure of diphenoyl peroxide VII follows from the following observations: (1) molecular weight and elemental analysis, including direct oxygen determination; (2) the peroxide oxidizes hydriodic acid to iodine

and is reduced to 2,2-diphenic acid; (3) triphenylphosphine converts the peroxide into diphenic anhydride and is oxidized to the oxide, as found by Denney and co-workers for benzoyl peroxide<sup>16</sup>; (4) diphenoyl peroxide should be compared with phthaloyl peroxide prepared by Greene and Rees.<sup>13</sup> The six-membered cyclic peroxide melts at 126-127° and explodes at 130°; it has a single peak at 5.66 μ. The eight-membered peroxide VII explodes at 70° and has also a single band at 5.66 μ. Dibenzoyl peroxide has two bands at 5.58 and 5.64 μ.

**Ozonization of the Benzil-Trimethyl Phosphite Adduct (II).**—When a 0.1 M solution of the benzil-phosphite adduct II in methylene chloride was ozonized at -75°, benzoyl peroxide (XI, 18%), benzoic anhydride (XII, 20%), benzil (XIII, 62%), and trimethyl phosphate (100%) were produced (expt. 10, Table II). The peroxide was determined by iodimetry and



the figures are considered reliable within 1%. The anhydride and the diketone were estimated from comparisons of the infrared spectrum of the reaction mixture with spectra of mixtures of the four products. The figures are considered significant within 5%.

A comparison among expt. 14, 10, 12, 16, and 15, shows that the number of moles of ozone which are consumed by 1 mole of the adduct II varies with the rate of ozonization. At the higher ozonization rates the ozone consumption falls in the range 0.52-0.6 (probably closer to the lower limit). At the lower ozonization rates the ozone consumption falls in the range 0.24-0.27. However, higher figures for the ozone consumption (0.76-0.80) were observed in the presence of methanol (expt. 13), and when the total ozone dosage was increased (expt. 11), both at the high ozonization rates. At 20°, ozone consumption fell in the range 0.2-0.5 mole equiv. at the ozonization rates employed.

The benzil adduct II is attacked by *pure* molecular oxygen. This reaction is very slow under the conditions of the ozonization. However, the low ozone consumption in some of the experiments suggests oxygen involvement during ozonization. In one experiment, the adduct was treated with 0.05 mole equiv. of ozone in methylene chloride at -75°; then pure oxygen was passed and the infrared spectrum was examined. Most of the adduct had disappeared after 2 hr. The products were benzoic anhydride and benzil, with the latter predominating.

Benzoyl peroxide does not react with the benzil adduct II under the conditions of the ozonization. The benzoic anhydride obtained in the experiments of Table II is produced in the ozonization itself, with or without oxygen participation.

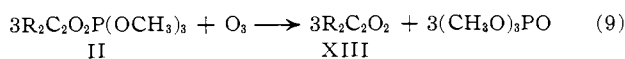
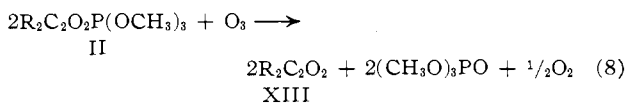
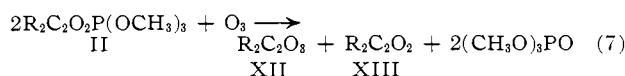
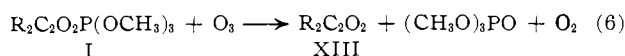
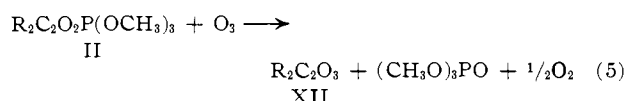
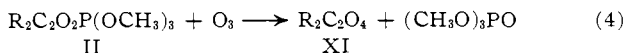
The products can be formed in reactions having the stoichiometry shown in eq. 4-9.

(16) (a) D. B. Denney, W. F. Goodyear, and B. Goldstein, *J. Am. Chem. Soc.*, **82**, 1393 (1960); (b) D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957); (c) D. B. Denney and L. C. Smith, *ibid.*, **82**, 2396 (1960); (d) M. A. Greenbaum, D. B. Denney, and A. K. Hoffmann, *ibid.*, **78**, 2563 (1956).

TABLE II  
 OZONIZATION OF THE BENZYL-TRIMETHYL PHOSPHITE ADDUCT (II) TO BENZOYL PEROXIDE, BENZOIC ANHYDRIDE, BENZIL, AND TRIMETHYL PHOSPHATE

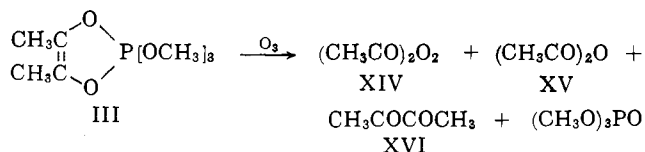
Expt.	Solvent	M	Temp., °C.	Mmoles O <sub>3</sub> /min.	Moles O <sub>3</sub> /mole add. (II)	Peroxide XI, %	Anhyd. XII, %	Benzil XIII, %
10	CH <sub>2</sub> Cl <sub>2</sub>	0.10	-75	1.75	0.54 <sup>a</sup>	18 <sup>b</sup>	20 <sup>c</sup>	62 <sup>c</sup>
11	CH <sub>2</sub> Cl <sub>2</sub>	.13	-75	1.85	.76 <sup>d</sup>	20 <sup>b</sup>	23 <sup>c</sup>	57 <sup>c</sup>
12	CH <sub>2</sub> Cl <sub>2</sub>	.10	-75	1.00	.5-0.6 <sup>e</sup>	25 <sup>b</sup>	10 <sup>c</sup>	65 <sup>c</sup>
13	CH <sub>2</sub> Cl <sub>2</sub> -CH <sub>3</sub> OH(1:2.6)	.10	-75	1.97	.80 <sup>f</sup>	44 <sup>g</sup>	...	...
14	CH <sub>2</sub> Cl <sub>2</sub>	.10	-75	2.03	.52 <sup>h</sup>	25	15	60
15	CH <sub>2</sub> Cl <sub>2</sub>	.10	-75	0.30	.27 <sup>h</sup>	14	20	66
16	CH <sub>2</sub> Cl <sub>2</sub>	.10	-75	0.61	.24 <sup>h</sup>	15	20	65
17	CH <sub>2</sub> Cl <sub>2</sub>	.10	+20	1.0	.26-0.36 <sup>e</sup>	17 <sup>b</sup>	13 <sup>c</sup>	70 <sup>c</sup>
18	CH <sub>2</sub> Cl <sub>2</sub>	.10	+20	0.85	.20-0.35 <sup>e,i</sup>	15 <sup>b</sup>	15 <sup>c</sup>	70 <sup>c</sup>
19	CH <sub>2</sub> Cl <sub>2</sub>	.10	+20	0.92	.5 <sup>e</sup>	20 <sup>c</sup>	15 <sup>c</sup>	65 <sup>c</sup>
20	Hexane <sup>j</sup>	.10	-75	1.0	.55 <sup>e</sup>	30 <sup>b</sup>	...	...

<sup>a</sup> 1.00 mole equivalent of O<sub>3</sub> introduced and 0.46 found in the KI trap; no adduct left in soln. <sup>b</sup> By iodimetry ( $\pm 1\%$ ). <sup>c</sup> From infrared spectra vs. known mixtures ( $\pm 5\%$ ). <sup>d</sup> 1.22 mole equiv. of O<sub>3</sub> introduced and 0.46 found in trap; no adduct left in soln. <sup>e</sup> Moles of O<sub>3</sub> required to cause disappearance of 1 mole of adduct II, by infrared determination. <sup>f</sup> 1.00 mole equiv. of O<sub>3</sub> introduced and 0.20 found in trap. <sup>g</sup> 11% of peroxide precipitated during ozonization; 33% by iodimetry. <sup>h</sup> O<sub>3</sub> appeared in KI trap after passing 0.40, 0.16, and 0.20 mole equiv. of O<sub>3</sub>, respectively, in expt. 14, 15, and 16. Total O<sub>3</sub> dosage was 1.00, 1.00, and 0.60 mole equiv., respectively; O<sub>3</sub> found in trap was 0.48, 0.73, and 0.36 mole equiv., respectively. <sup>i</sup> Infrared bands owing to adduct disappearance after ca. 0.2 mole equiv. of O<sub>3</sub> had been introduced; changes in carbonyl region noted (more benzoyl peroxide) during additional 0.15 mole equiv. of O<sub>3</sub>; no changes in spectrum thereafter. <sup>j</sup> Products are sparingly soluble.



The data of Table II suggest that the diketone and the anhydride are formed mainly according to eq. 7, 8, and 9. Evidently, the formation of diketone and phosphate in a reaction with a stoichiometric relationship between adduct II and ozone which is higher than 3:1 must involve molecular oxygen.

**Ozonization of the Biacetyl-Trimethyl Phosphite Adduct (III).**—The yield of acetyl peroxide (XIV) from the ozonization of the biacetyl-phosphite adduct III is relatively small (Table III). Acetic anhydride (XV) is formed also in small amounts; the main product is biacetyl (XVI).



The biacetyl adduct III was completely destroyed when about 0.5 mole equiv. of ozone had been introduced. The reaction of adduct III with pure molecular oxygen is too slow under the conditions of the ozonization to account for the formation of much anhydride and diketone. The adduct III does not

react appreciably with benzoyl peroxide under the conditions of the ozonization. It appears that anhydride and diketone are formed mainly according to equations like 7, 8, and 9, with possible involvement of oxygen during the ozonization.

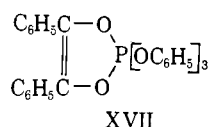
TABLE III  
 OZONIZATION OF THE BIACETYL-TRIMETHYL PHOSPHITE ADDUCT (III) TO ACETYL PEROXIDE (XIV), ACETIC ANHYDRIDE (XV), BIACETYL (XVI), AND TRIMETHYL PHOSPHATE, IN CH<sub>2</sub>Cl<sub>2</sub>

Expt.	M	Temp., °C.	Mmoles O <sub>3</sub> /min.	Moles O <sub>3</sub> /mole add. III	Per. <sup>a,b</sup> XIV, %
21	0.1	-75	0.77	0.57 <sup>c</sup>	16
22	.1	+20	0.77	.50 <sup>d</sup>	16
23	.1	+20	1.02	.4-0.5 <sup>e</sup>	16
24	.2	+20	0.97	.4-0.5 <sup>e</sup>	15
25	.1	+20	.97	.48 <sup>e</sup>	15
26	.1	-75	.92	..	18 <sup>f</sup>
27	.1	+20	.92	..	14 <sup>f</sup>

<sup>a</sup> By iodimetry. <sup>b</sup> Other products: anhydride (14%), biacetyl (70%), trimethyl phosphate (100%) by infrared analysis ( $\pm 5\%$ ). <sup>c</sup> 0.59 mole equiv. of O<sub>3</sub> introduced, 0.02 found in KI trap. <sup>d</sup> 0.52 mole equiv. of O<sub>3</sub> introduced, 0.02 found in trap. <sup>e</sup> Infrared bands of adduct III absent. <sup>f</sup> Ozonization in hexane; products sparingly soluble; I<sub>2</sub> was noted in KI trap after 7.4 and 0.70 mole equiv. of O<sub>3</sub> had been introduced at -75 and +20°, respectively; no adduct left in solution, by infrared.

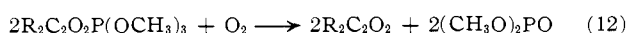
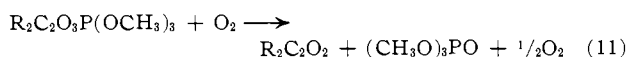
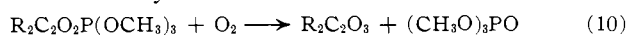
**Reaction of Pure Molecular Oxygen with the  $\alpha$ -Diketone-Phosphite Adducts (II and III).**—When molecular oxygen was passed through a methylene chloride solution of the benzyl-trimethyl phosphite adduct II at -75° very little change resulted in 30 min. (infrared spectrum). Even after 8 hr., the infrared bands of the adduct could be seen. The oxidation of the adduct II was complete in 5 days when a 1.36 M solution of II in benzene was stirred under 1 atm. of oxygen at 20°. The products were benzoic anhydride (XII, 30%), benzil (XIII, 67%), and trimethyl phosphate (ca. 100%).

The reaction of oxygen with the benzyl-triphenyl phosphite adduct, XVII, in benzene at 20° was complete in about 3 days (0.54 M solution). The yield of benzoic anhydride was 25-30%.



The reaction of oxygen with the biacetyl-phosphite adduct III in methylene chloride at  $-75^\circ$  was insignificant after 30 min. The oxidation was complete in 9 days when a 2.0 M solution of the adduct III in benzene was stirred under 1 atm. of oxygen at  $20^\circ$ . The products were acetic anhydride (ca. 15%), biacetyl (XVI, 60%), and trimethyl phosphate. In addition, some of the 2:1 biacetyl-trimethyl phosphite adduct (XVIII) was formed.<sup>10f</sup>

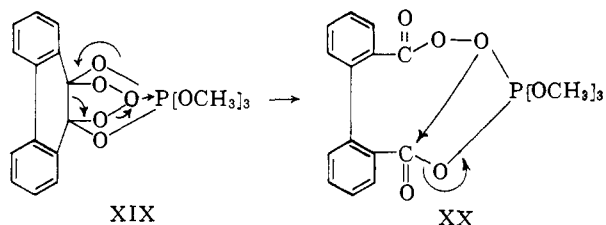
The products can be obtained according to the stoichiometry



**Reaction of Diphenoyl Peroxide (VII) with the  $\alpha$ -Diketone-Phosphite Adducts II and III.**—A nearly instantaneous reaction was observed when the  $\alpha$ -diketone-phosphite adducts II and III were treated with 1 mole equiv. of diphenoyl peroxide (VII) in methylene chloride at  $20^\circ$ . The products were the  $\alpha$ -diketone XIII and XVI, diphenic anhydride (IX), and trimethyl phosphate.

### Discussion

The formation of diphenoyl peroxide (VII) can be explained as



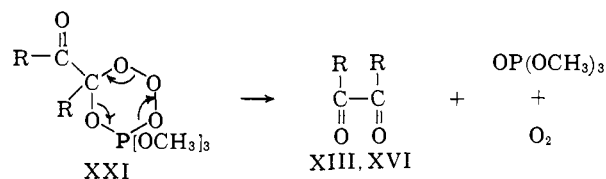
The *primary ozonide XIX* rearranges to an intermediate XX which is well disposed for an intramolecular nucleophilic displacement by the anion of a peroxy acid on the carbonyl function. This process is favored by the nature of the leaving group, a neutral phosphate ester.<sup>2, 4, 10, 17</sup>

The lower yields of acyclic peroxides XI and XIV may reflect the open-chain structure of the intermediates analogous to XX which would be formed from the  $\alpha$ -diketone-phosphite adducts II and III. Other differences in the ozonization of diketone and *o*-quinone adducts become understandable if it is assumed that: (1) there are relatively small amounts of the open dipolar structures (IV) in equilibrium with the cyclic oxyphosphorane structures (I, II, III); (2) these amounts are greater (and/or the equilibration is faster) in the diketone adducts than in the *o*-quinone adducts; (3) ozonization of the cyclic form gives peroxide while ozonization of the open form gives diketone and anhydride; (4) primary ozonides derived from the open form are capable of reacting further with the adducts.

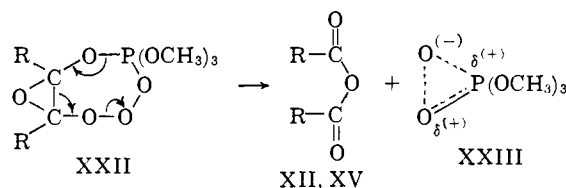
The product of the initial attack by ozone on the open dipolar structure IV should have structure XXI.

(17) F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Am. Chem. Soc.*, **83**, 173 (1961).

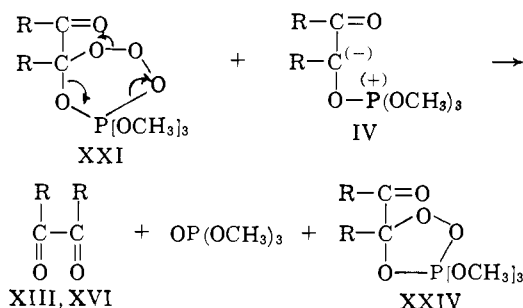
Formation of diketone (or of quinone) from XXI follows readily



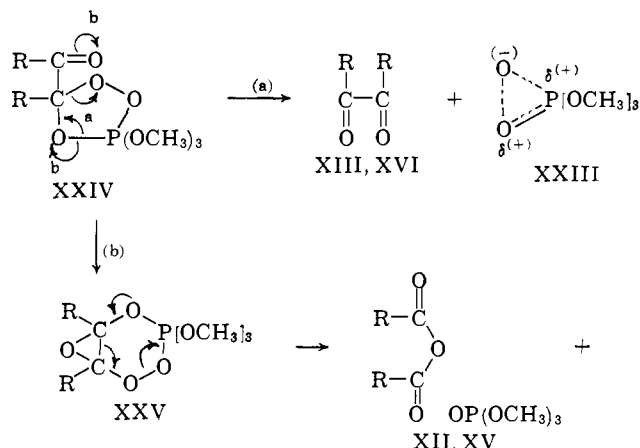
The *peroxonide XXI* can decompose also into anhydride, XII, XV, and a *peroxidic phosphate ester XXIII*, which is the phosphorus analog of a Criegee zwitterion<sup>11, 12</sup>  $[\text{O}^-\text{O}^+(\text{R})_2]$ . This transformation is explained by an intermediate like XXII. The peroxidic phosphate ester XXIII should give phosphate ester and molecular oxygen, for instance through a dimer.



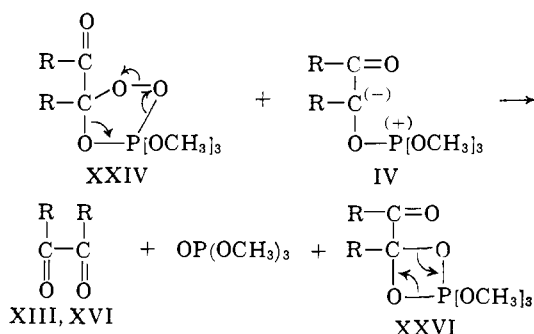
As in other cases of heterolytic cleavage of peroxidic  $-\text{O}-\text{O}-$  bonds,<sup>16</sup> a nucleophilic attack by the carbon of the open form of an adduct, IV, on an oxygen of the peroxonide XXI would result in diketone XIII, XVI, phosphate, and a new fragment XXIV which is essentially the *secondary ozonide of a phosphitemethylene*,  $\text{R}_2\text{C}=\text{P}(\text{OCH}_3)_3$



The secondary ozonide XXIV can explain the formation of diketone, XIII and XVI, by *path a*, and of anhydride, XII and XV, by *path b*, when the adducts II and III react with molecular oxygen. Equations 7 and 8 given above are also accounted for in this manner.

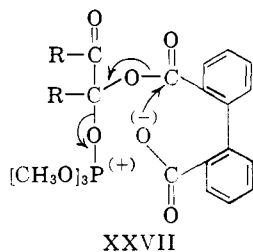


The secondary ozonide XXIV is still an oxidant and may react with a third molecule of the open form of the adduct IV, giving two molecules of diketone, possibly *via* intermediate XXVI (*cf.* eq. 9).

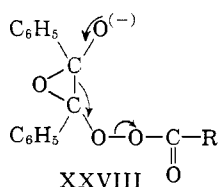


The addition of molecular oxygen to the four-membered intermediate XXVI would regenerate the primary ozonide XXI, making ozone a catalyst in the oxygenation of the adducts II and III.

The attack by an adduct on a peroxidic linkage is demonstrated by the reaction of the adducts I, II, and III with diphenoyl peroxide. These reactions could involve intermediates of type XXVII, in which formation of anhydride and diketone (or quinone) results from the ejection of a neutral phosphate ester.



Intermediates XXII and XXV are similar to the structure XXVIII suggested by Kwart<sup>18</sup> to explain the formation of anhydride from the reaction of peroxyacid anions with  $\alpha$ -diketones. The peroxidic phosphate ester XXIII has been invoked by Thompson<sup>15</sup> to explain his results on the ozonization of phosphite esters. The full report of Thompson's work appeared<sup>16</sup> after the preliminary account of our investigations.<sup>2</sup> Bestman<sup>19</sup> has discussed reactions of phosphinemethylenes with molecular oxygen.



### Experimental

**Ozonization of the Phenanthrenequinone-Trimethyl Phosphite 1:1 Adduct (I) in Methylene Chloride.**—The quinone-phosphite adduct I was prepared as follows<sup>2</sup>: a suspension of recrystallized phenanthrene-quinone in dry benzene was treated with 1.1 mole equiv. of purified trimethyl phosphite. The resulting solution was stirred 6–8 hr. at 20° under N<sub>2</sub>. The solvent was removed under vacuum; the residue was dissolved in hexane and the solution was cooled to –10°. The adduct (90% yield) had m.p. 71–73°. Moisture and oxygen must be excluded at all

times. The reagents should be purified (trimethyl phosphite was kept over sodium ribbon and freshly distilled).

The ozone was generated in a Welsbach T-23 ozonator using 8 p.s.i. of dry oxygen. The rate of ozone production was determined iodimetrically. The ozonizations were carried out in a long narrow column fitted with a fritted glass diffuser and followed by an aqueous KI trap. The amount of ozone found in the trap was subtracted from the total ozone delivered. The cooling bath was Dry Ice-acetone. Peroxide was assayed iodimetrically: 1 ml. of a saturated aqueous KI solution was added to a 200-mg. sample of peroxide in 25 ml. ethanol; 1 ml. of acetic acid was introduced, and the solution was kept 3 min. at 80° and titrated with 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

A solution of 3.80 g. (11.4 mmoles) of quinone-phosphite adduct I in dry methylene chloride (100 ml., *ca.* 0.11 M) was cooled to –75° and treated with ozone at a rate of 2.10 mmoles of O<sub>3</sub> per min. (gas flow 0.16 s.c.f.m.). The solution turned brown initially; the color was discharged toward the end of the reaction. Ozone was passed for 435 sec. ( $\equiv$  15.22 mmoles), the theoretical being 324 sec. The trap was found to contain iodine corresponding to 4.37 mmoles of unutilized O<sub>3</sub>; therefore, somewhat less than 1 mole equiv. of O<sub>3</sub> was consumed (0.96 mole of O<sub>3</sub> per mole of adduct). The infrared spectrum of this solution showed no trace of adduct I.

Some methylene chloride was removed under vacuum (10 mm., temperature below 10°) until crystals appeared. Methanol (30 ml.) was added and the mixture was kept 30 min. at –75°. The first crop of crude peroxide VII weighed 1.75 g. (after drying in a current of N<sub>2</sub> and then at 0.5 mm. at 20°). The mother liquor was again concentrated at 10 mm. (10°); combined crude peroxide (2.0 g., 76%) assayed as 74% peroxide; the estimated peroxide yield is therefore 56%. This material was dissolved in methylene chloride (*ca.* 20 ml.) and the solution was diluted with methanol (*ca.* 25 ml.). The colorless diphenoyl peroxide (50% yield, over 98% assay) was collected after 2 hr. at 0°.

Diphenoyl peroxide (VII) can be preserved at low temperature but *explodes violently* when heated to *ca.* 70° or under impact. It has a single sharp and strong carbonyl band at 5.66  $\mu$ , with a very slight inflection at 5.72  $\mu$ .

*Anal.* Calcd. for C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>: C, 70.0; H, 3.3; O, 26.7; mol. wt., 240. Found: C, 70.0; H, 3.2; O, 26.5; mol. wt., 219, cryoscopic in benzene (values obtained on freshly prepared samples).

2,2'-Diphenic acid was isolated in over 90% yield from the reaction mixture obtained in the iodimetric assay by the method previously described.

2,2'-Diphenic anhydride was isolated in 80–85% yields when diphenoyl peroxide was treated with triphenylphosphine in benzene solution, or in methylene chloride solution. Triphenylphosphine oxide was also isolated. The diphenic acid and anhydride were identified by direct comparisons with samples of authentic material.

**Recommended Preparation of Diphenoyl Peroxide. Ozonizations in Methylene Chloride-Methanol Solution.**—A solution of 3.88 g. (11.7 mmoles) of quinone-phosphite adduct I in dry methylene chloride (18 ml.) was cooled to –75° and then diluted with methanol (180 ml., precooled to –75°). This solution (*ca.* 0.059 M) was *immediately* treated with ozone at a rate of 1.9 mmoles of O<sub>3</sub> per min. (gas flow: 0.100 s.c.f.m.; 115 v.). Ozone was passed for 400 sec. (theory 369 sec.); iodine corresponding to 1.90 mmoles of O<sub>3</sub> was found in the KI trap; thus 0.92 mole of ozone were consumed per mole of adduct I. The peroxide precipitates out of the solution in this solvent mixture.

The mixture was kept 30 min. at –75° and the peroxide was filtered and dried in a current of nitrogen at 20° (1 hr.; finally at 0.5 mm.). This crude peroxide VII (2.0 g., 72% of theory) was very pale yellow, exploded at 72°, and showed only one carbonyl band in the infrared at 5.66  $\mu$ ; it assayed as 89% peroxide which corresponds to a 63% yield. The crude peroxide was dissolved in 14 ml. of methylene chloride and the solution was diluted with 16 ml. of methanol and cooled 2 hr. at 0°. The purified peroxide (1.75 g., 62% of theory) exploded at 70° and assayed as 98% peroxide.

The original mother liquor was concentrated under vacuum until crystals appeared (0.14 g., *ca.* 5% of theory). From infrared spectra it was estimated that this material is a mixture of peroxide (*ca.* 40%) and phenanthrenequinone (*ca.* 60%).

The second mother liquid was evaporated to dryness (0.5 mm., 15°). The residue (2.16 g.) consisted mainly of trimethyl phosphite (theory 1.7 g.); in addition, the infrared spectrum showed

(18) H. Kwart and N. J. Wegemer, *J. Am. Chem. Soc.*, **83**, 2746 (1961).

(19) H. J. Bestman, *Angew. Chem.*, **72**, 34 (1960).

the 5.66  $\mu$  peroxide band and a broader band at 5.82  $\mu$  owing to monomethyl diphenate. These two bands were of nearly equal intensities. A much weaker band at 5.94  $\mu$  is due to quinone. Iodimetric assay of this material showed 22% peroxide content. No attempt was made to obtain pure diphenoyl peroxide from this fraction, but if this is the only peroxide present then the over-all yield of diphenoyl peroxide from adduct I is about 80% (by iodimetric assay), of which 63% is easily obtained in pure form.

**Effect of Solvent Composition on Peroxide Yield.**—Several ozonization experiments were carried out using various ratios of methanol to methylene chloride. The results are given in Table I. When the proportion of methanol was low (less than 2.4 volumes of methanol per volume of methylene chloride, 0.10–0.13 *M*) the solid which separated during the ozonization (20–30%) was a mixture of diphenic anhydride and phenanthrenequinone, richer in the latter. The mother liquids gave the indicated amounts of diphenoyl peroxide. Monomethyl diphenate was found also in these experiments.

**Slow Ozonization of the Quinone-Phosphate 1:1 Adduct (I).**—An 0.1 *M* solution of the quinone adduct I in pure methylene chloride was cooled to  $-75^\circ$  and treated with ozone at a rate of 1.05 mmoles of  $O_3$  per minute. Aliquots were withdrawn for infrared analysis after 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mole equiv. of ozone had been introduced.

The disappearance of the adduct was followed by noting the decrease of its three sharp bands at 6.07, 7.28, and 10.45  $\mu$ . After 0.6 of a mole equivalent of ozone had been introduced, only the strongest band at 7.28  $\mu$  was detectable, indicating that most of the adduct had reacted. Complete disappearance of the adduct was noted at 0.6–0.8 mole equiv. of  $O_3$ . Further ozone input produced no detectable changes. The solution gave the spectrum of an equimolar mixture of phenanthrenequinone and diphenic anhydride, with sharp bands at 6.62, 6.74, 5.96, and 6.30  $\mu$ . The characteristic bands of trimethyl phosphite were present. *No diphenoyl peroxide was detectable spectrophotometrically in this experiment.*

**Fast Ozonization of the Quinone-Phosphite 1:1 Adduct (I) with 0.5 Mole Equiv. of Ozone.**—An 0.092 *M* solution of adduct I in pure methylene chloride was treated at  $-75^\circ$  with ozone at a rate of 2.27 moles of  $O_3$  per minute. The ozonization was stopped after 0.5 mole equiv. of ozone had been introduced. This solution had the spectrum of an equimolar mixture of phenanthrenequinone and diphenic anhydride. The spectrum was similar to the spectrum obtained in the slow ozonization described above, except that some unreacted adduct was still present in the interrupted fast ozonization. No peroxide was evident spectrophotometrically.

This experiment should be compared with the uninterrupted fast ionization in which 54% of diphenoyl peroxide was isolated; *i.e.*, the quinone-phosphite adduct I reacts competitively with ozone and with diphenoyl peroxide.

**Reaction of Diphenoyl Peroxide (VII) with the *o*-Quinone-Phosphite and the  $\alpha$ -Diketone-Phosphite 1:1 Adducts.**—(1) Equimolar amounts of diphenoyl peroxide (VII) and of the phenanthrenequinone-trimethyl phosphite adduct (I) were dissolved in methylene chloride at  $20^\circ$ . The solution became red-brown immediately. The infrared spectrum of this solution was identical with the spectrum of a methylene chloride solution containing equimolar amounts of authentic diphenic anhydride (IX), phenanthrenequinone (VIII), and trimethyl phosphite.

(2) Diphenoyl peroxide (VII) reacted instantaneously with the benzil-trimethyl phosphite adduct (II) and with the biacetyl-trimethyl phosphite adduct (III) in methylene chloride at  $20^\circ$ . The infrared spectra of the resulting solutions were identical with the spectra of solutions made from diphenic anhydride (IX), trimethyl phosphite, and benzil or biacetyl, respectively. No attempt was made to isolate the products, the identification rests on the infrared data.

**Ozonization of the Benzil-Trimethyl Phosphite 1:1 Adduct (II) in Methylene Chloride at  $-75^\circ$ .**—(1) A solution of the benzil adduct<sup>4</sup> II (1.67 g.) in methylene chloride (50 ml., 0.10 *M*) was cooled to  $-75^\circ$  and was treated with ozone at the rate of 1.0 mmole of ozone per min. A pale yellow color (not an orange-brown color as in the quinone adduct case) was noted. Aliquots of the solution were withdrawn at various ozone dosages and the aliquots were examined immediately in the infrared. (a) After 0.25 mole equiv. of  $O_3$  had been introduced, adduct was still present as shown by its bands at 8.75, 10.40, and 12.05  $\mu$ . The benzil was detectable by its band at 5.98  $\mu$ . Benzoyl peroxide

showed its characteristic bands at 5.60 and 5.66  $\mu$ . A very weak band at 5.80  $\mu$  was caused by benzoic anhydride; its second band at 5.60  $\mu$  coincides with one of the peroxide bands. (b) After 0.48 mole equiv. of ozone, small amounts of adduct remained; the amounts of peroxide and benzil had increased, but there was only a small increase in anhydride. (c) All the adduct disappeared at an ozone dosage falling between 0.66 and 0.75 mole equiv. of ozone. The ozonization was stopped at this point and it was verified that 0.73 mole of  $O_3$  had been consumed per mole of adduct from an iodimetric assay of the trap content.

The infrared spectrum of the final solution was compared with the spectra of a series of mixtures of benzoyl peroxide, benzoic anhydride, benzil, and trimethyl phosphite, of known mole %. The ozonization mixture consisted of these substances in 25, 10, 65, and 100%, respectively,  $\pm 5\%$  ( $\pm 1\%$  for peroxide.)

Nitrogen was bubbled through the solution (15 min.) to expel any ozone in it. An aliquot was assayed for peroxide content by iodimetry and was found to contain 26% of peroxide.

(2) The ozonization was repeated in a larger scale. Trimethyl phosphite (*ca.* 90%) was isolated by distillation. Benzoyl peroxide was isolated in *ca.* 10–15% by recrystallization from methanol. Benzil was obtained in about 55% after reduction of the peroxide to benzoic acid.

(3) An 0.13 *M* solution of the benzil adduct II in methylene chloride was treated, at  $-75^\circ$ , with ozone at the rate of 1.85 mmoles per min. After 539 sec. (theory for 1 mole equiv.: 449 sec.) the ozonization was stopped. The trap contained iodine corresponding to 6.2 mmoles of ozone; therefore, 0.76 mole of ozone was consumed per mole of adduct I. The solution was flushed with  $N_2$ , and evaporated to dryness at 25 mm. and finally at 0.2 mm. The residue contained peroxide corresponding to a 20% yield of benzoyl peroxide based on the adduct used. The proportion of other products, estimated from the infrared spectrum, are given in Table II.

**Ozonization of the Benzil-Trimethyl Phosphite Adduct (II) in Methylene Chloride-Methanol Solution.**—The benzil-trimethyl phosphite adduct II (3.626 g., 10.8 mmoles) was dissolved in methylene chloride (30 ml.). The cold solution ( $-75^\circ$ ) was diluted with cold methanol (80 ml.) and treated, *immediately*, with ozone at  $-75^\circ$ . The ozone was introduced at the rate of 1.97 mmoles per min. (115 v., 0.070 s.c.f.m., 8 p.s.i. of  $O_3$ ). After 255 sec. (theory 324 sec.) iodine was noted in the KI trap. A total of 10.8 mmoles of ozone was passed and 2.1 mmoles appeared in the trap; therefore 0.80 mole equiv. of ozone was consumed. The solid (0.30 g.) which precipitated during the ozonization was shown to be benzoyl peroxide of 96% peroxide content by iodimetry (11% yield). The filtrate was assayed by iodimetry and was found to contain 33% of peroxide; total 44% of peroxide.

**Ozonization of the Benzil-Trimethyl Phosphite 1:1 Adduct (II) in Methylene Chloride at  $20^\circ$ .**—(1) Ozone was passed at a rate of 0.92 mmole of  $O_3$  per min. through a 0.10 *M* solution of the benzil-trimethyl phosphite adduct (III) in methylene chloride at  $20^\circ$ . Aliquots were examined in the infrared at various ozone dosages. The bands caused by the adduct disappeared after *ca.* 0.26 mole equiv. of ozone had been introduced. Additional ozone was not utilized. The resulting solution had 17% of benzoyl peroxide by iodimetry. Its infrared spectrum corresponded closely to that of a mixture of benzoyl peroxide (17%), benzoic anhydride (13%), benzil (70%), and trimethyl phosphite (100%), on a molar basis. Similar results were obtained in triplicate runs.

**Ozonization of the Biacetyl-Trimethyl Phosphite Adduct (III).**—The adduct was prepared as described.<sup>4</sup> It is sensitive to moisture and to oxygen. It was redistilled prior to use. The presence of adduct in a methylene chloride solution can be detected by sharp bands at 7.20, 10.00, and 12.15  $\mu$  in the infrared spectrum; these are absent in the spectrum of mixtures of biacetyl + acetyl peroxide + acetic anhydride + trimethyl phosphite (70:20:10:100, 80:16:4:100, 55:40:5:100 mole ratios). A band at 8.70  $\mu$  is strong in the adduct and weak in the products of the ozonization.

(1) A solution of the biacetyl-trimethyl phosphite adduct (III, 1.05 g., 5 mmoles) in dry methylene chloride (50 ml.) was treated with ozone at the rate of 0.77 mmole per min. After 229 sec. ( $\equiv$  2.98 mmoles of  $O_3$ ) iodine was noted in the KI trap. The ozonization was stopped and the trap content was assayed (found  $I_2$  corresponding to 0.12 mmole of  $O_3$ ). The infrared spectrum of the solution showed absence of adduct III. There-

fore, 0.57 mole of ozone sufficed to cause the disappearance of 1 mole of adduct III under these conditions. The solution was flushed with  $N_2$  for 10 min. and then was assayed for peroxide; found: 16% of peroxide ( $\pm 1\%$ ). Comparisons of the infrared spectrum of the solution with the spectra of solutions containing known mole ratios of acetyl peroxide, acetic anhydride, biacetyl, and trimethyl phosphite showed that the ozonization produced 16% peroxide, 14% anhydride, 70% diketone, and 100% phosphite ( $\pm 5\%$  for the anhydride and diketone).

(2) Other ozonizations were carried out in methylene chloride at  $20^\circ$ . The results are summarized in Table III. Examination of the infrared spectra of solutions after various ozone dosages showed that between 0.4 and 0.5 mole of ozone caused the disappearance of 1 mole of adduct. Examinations of the KI trap showed that this value also corresponds to the ozone which was utilized in the reaction.

(3) Ozonizations were carried out in hexane. The results are given in Table III. The products of the ozonization are sparingly soluble in hexane.

Biacetyl, acetyl peroxide, and acetic anhydride can be recognized by infrared bands at 5.82, 5.60, and 5.52  $\mu$ , respectively.

**Attempted Reaction between Benzoyl Peroxide and the  $\alpha$ -Diketone-Phosphite Adducts.**—The infrared spectrum of a solution containing equimolar amounts of benzoyl peroxide and the benzil adduct II in methylene chloride was examined at various times. After 3 hr. at  $20^\circ$ , there was little evidence for the formation of anhydride and  $\alpha$ -diketone. After 28 hr., the bands caused by these reaction products were detectable. The reaction was not investigated further; it appeared to be incomplete even after 28 hr.

**Reaction of the Benzil-Trimethyl Phosphite 1:1 Adduct (II) with Oxygen in Benzene Solution.**—(1) A solution of the benzil-phosphite adduct II (14.3 g.) in dry benzene (30 ml., 1.36  $M$ ) was stirred at  $20^\circ$  under an atmosphere of dry oxygen. After 5 days, the benzene was removed under vacuum and the residue was examined in the infrared: bands caused by benzoic anhydride (XII), benzil (XIII), and trimethyl phosphite were observed.

(a) A 3.02-g. aliquot of the residue was treated with saturated aqueous sodium bicarbonate and the mixture was kept 17 days at  $20^\circ$ . Benzil (1.21 g., 67%, m.p.  $87$ – $92^\circ$ ) was filtered off, and the filtrate was made acidic with concentrated HCl. Benzoic acid (0.49 g., m.p.  $118$ – $119^\circ$ ) was filtered off and the filtrate was extracted with ether. From the ether additional benzoic acid (0.11 g.) was obtained; total yield of benzoic acid: 30%.

(Benzil was recovered unchanged after 17 days in contact with saturated aqueous bicarbonate.)

(b) A 4.4-g. aliquot of the original residue was distilled under vacuum and gave 1.65 g. (94%) of trimethyl phosphite ( $114$ – $118^\circ$  at 60 mm.).

(c) A 1.21-g. aliquot of the original residue was treated with 0.2 g. of aniline. The mixture was kept 15 min. at  $90^\circ$ , diluted with water, kept 2 hr. at  $20^\circ$ , and extracted with ether. The ether solution gave 0.13 g. of benzanilide, m.p.  $161$ – $162^\circ$  (corresponds to 19% of benzoic anhydride).

**Reaction of the Benzil-Triphenyl Phosphite 1:1 Adduct (XVII) with Oxygen.**—A solution of the benzil-triphenyl phosphite adduct (7.2 g.) in benzene (25 ml., 0.54  $M$ ) was stirred at  $20^\circ$  under an atmosphere of oxygen. After 3 days the reaction seemed complete (the phenyl phosphite adduct appears to react faster than the methyl phosphite adduct). Benzanilide corresponding to 25% of benzoic anhydride was obtained by the procedure (1c) indicated above for the methyl phosphite adduct.

**Reactions of the Biacetyl-Trimethyl Phosphite 1:1 Adduct (III) with Oxygen in Benzene Solution.**—A solution of the biacetyl-phosphite adduct III (12.0 g.) in dry benzene (25 ml., 2.0  $M$ ) was stirred at  $20^\circ$ , under an atmosphere of dry oxygen, for 9 days. The mixture was submitted to fractional distillation. Benzene and most of the biacetyl were removed first. The second fraction was acetic anhydride (10–15%) identified by infrared spectrum and by conversion to acetanilide. The third fraction was trimethyl phosphite (70–75%). The fourth fraction (ca. 15%) was the adduct formed from biacetyl and the 1:1 biacetyl-trimethyl phosphite adduct (III), *i.e.*, the 2:1 biacetyl-trimethyl phosphite adduct XVIII (*meso*- and *rac*-2,2,2-trimethoxy-4,5-dimethyl-4,5-diacetyl-1,3-dioxaphospholane).<sup>10</sup>

The presence of biacetyl (about 60%) among the reaction products was determined by formation of the bis-2,4-dinitrophenylhydrazone.

**Attempts to Oxidize the Phenanthrenequinone-Trimethyl Phosphite 1:1 Adduct (I) with Molecular Oxygen.**—A solution of the quinone adduct I in dry benzene was stirred under 1 atm. of dry oxygen for 7 days. The adduct was recovered unchanged.

The pure adduct I was kept 4 days at  $110^\circ$  under an oxygen atmosphere. The product consisted of phenanthrenequinone (ca. 40%) and recovered adduct I (ca. 40%, separated by ether extraction.)

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, N. Y.]

## The Addition of Silylamines and Silazanes to Isocyanates

By J. F. KLEBE, J. B. BUSH, JR., AND J. E. LYONS

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Addition reactions of secondary and tertiary silylamines and of silazanes with isocyanates were studied. Silylamine-isocyanate adducts (1:1) were obtained with secondary and tertiary silylamines. Spectroscopic evidence favors N-silylurea structures for these thermally stable, hydrolytically sensitive adducts. Silylureas containing at least one proton on nitrogen were found to undergo a rapid silyl-proton exchange. Reactions of disilazanes with isocyanates led to disilyl-substituted ureas and biurets. Isothiocyanates and silylamines formed analogous adducts which reverted to the starting materials at elevated temperatures.

### Introduction

The rapidly growing literature on the chemistry of silicon-nitrogen compounds contains a remarkably small number of reports dealing with an important type of reaction, the addition of silylamines to reactive functional groups and activated double bonds. No extensive study of any specific silylamine addition reaction, *e.g.*, to activated carbon-carbon double bonds, to isocyanates, etc., has been published. In several publications dealing with reactions of this kind, the silicon-nitrogen bond has been regarded as being analogous to a carbon-nitrogen bond; only structures of addition products have been considered which may be derived by cleavage of a hydrogen-nitrogen bond also con-

tained in the molecule. A few authors, however, report silylamine addition products whose structures show that cleavage of a Si-N bond has indeed taken place; this suggests that this bond may resemble in its reaction the H-N rather than the C-N bond. The factors governing the structure of addition products of secondary silylamines, R-N-Si≡, in which cleavage

H

of either Si-N or H-N can apparently occur, have not previously been investigated.

Additions of secondary silylamines to acrylonitrile,<sup>1</sup>

(1) V. G. Mironov, A. D. Petrov, and N. A. Pogonkina, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 768 (1955).