The solution was refluxed for 24 hr. and the sulfide was isolated in the manner described for XVIII; 76 mg. (22%) of light yellow oil which was about 95% pure (by gas–liquid chromatography) was obtained. Microfractionation yielded a colorless liquid.

Anal. Calcd. for $C_{12}H_{24}S$: C, 71.95; H, 12.08. Found: C, 72.08; H, 12.12.

Thiacycloundecane (XXII).—The above procedure duplicated with 11.5 g. (0.038 mole) of 1,10-dibromodecane (XX) (Fisher Scientific Corp.) yielded 850 mg. (13%) of 96+% pure (g.l.c.) thiacycloundecane, b.p. 66–68° (0.2 mm.).

Anal. Calcd. for $C_{10}H_{20}S$: C, 69.72; H, 11.70; S, 18.58. Found: C, 69.82; H, 11.74; S, 18.36.

Thiacyclooctane 1-Oxide[14] (XXIII).—A solution of 130 mg. (1 mmole) of thiacyclooctane in 2 ml. of methanol was treated at 0° with 2 ml. of a 0.52 *M* aqueous solution of sodium metaperiodate during a 10-min. period. The mixture was stirred overnight at 0° and filtered. The precipitate, sodium iodate, was washed with two 5-ml. portions of chloroform. The aqueous-methanol layer was extracted with chloroform and all chloroform portions were joined, dried (magnesium sulfate), and concentrated, first at 100 mm., and then at 0.1 mm., leaving colorless prisms (120 mg., 82%). The product was extremely hygroscopic, liquefying within minutes after exposure to the atmosphere. Sublimation of a portion of the sulfoxide (handled under nitrogen in a glove bag) at 50° (0.5 mm.) yielded fine needles, m.p. 61–62° (sealed capillary). The infrared spectrum of this material (neat) had an intense band at 1025 cm.$^{-1}$ characteristic of sulfoxides.

Anal. Calcd. for $C_7H_{14}OS$: S, 21.87. Found: S, 21.75.

Thiacyclononane 1-oxide (XXIV) was prepared in 89% yield by the procedure used for XXIII. It was much less hygroscopic than XXIII. Sublimation at 50° (0.05 mm.) gave fine colorless needles, melting below 40° apparently due to hydration. The infrared spectrum (Nujol) had an intense band at 1045 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{16}OS$: S, 19.96. Calcd. for $C_8H_{16}OS \cdot 2H_2O$: S, 16.32. Found: S, 16.87.

7,7-Dimethylthiacyclododecane 1-oxide (XXV) was prepared from XVIII in 92% yield by the procedure used for XXIII. Recrystallization from petroleum ether followed by sublimation at 70° (0.05 mm.) gave fine white needles, m.p. 107–108°. The product was not appreciably hygroscopic. The infrared spectrum (carbon tetrachloride) had a strong band at 1047 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{26}OS$: S, 13.89. Found: S, 14.40.

Thiacyclooctane 1,1-Dioxide.—Oxidation of thiacyclooctane (130 mg. in 2 ml. methanol) by 2.5 ml. of 1 *M* sodium metaperiodate[14] yielded colorless needles of sulfone. Recrystallization from petroleum ether gave crystals melting at 55–56° and 74–75° (microscope hot stage). These are dimorphic forms of the same compound, for their gas–liquid chromatograms were identical in shape and retention times; the infrared bands of both were at 1116 and 1285 and 1308 cm.$^{-1}$ (doublet). Müller,[15] who first made this compound, reported a melting point of 61° and apparently did not notice its dimorphism.

Thiacyclononane 1,1-Dioxide.—Thiacyclononane was oxidized by sodium metaperiodate.[14] The sulfone melted at 79.5–80°, lit.[15] 81.5–82°; its infrared spectrum had bands at 1112 and[15] 1280 and 1310 cm.$^{-1}$ (doublet).

6,6-Dimethylthiacyclodecane 1,1-Dioxide.—Oxidation of 6,6-dimethylthiacyclodecane[1] by hydrogen peroxide[16] produced the sulfone as colorless plates, m.p. 86.5–87°. Gas-liquid chromatography indicated a purity of 99+%; infrared absorption bands were at 1115, and 1271, 1287, and 1298 cm.$^{-1}$ (triplet).

7,7-Dimethylthiacyclododecane 1,1-Dioxide.—Oxidation of XVIII by hydrogen peroxide by the method of Tarbell and Weaver[16] yielded 89% of the crude sulfone. Recrystallization from petroleum ether and sublimation at 50° (0.05 mm.) gave colorless plates, m.p. 147–148°; infrared absorption bands were at 1118, and 1276 and 1292 cm.$^{-1}$ (doublet).

---

[14] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

[15] A. Müller, E. Funder-Fritzche, W. Konar, and E. Rintersbacher-Wlasak, *Monatsh.*, **84**, 1206 (1953).

[16] D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.*, **63**, 2941 (1941).

Ozonation of Substituted Diazomethanes[1]

ARTHUR M. READER, PHILIP S. BAILEY,[2] AND HAROLD M. WHITE

Department of Chemistry, The University of Texas, Austin, Texas 78712

Received July 27, 1964

Ozonation of diphenyldiazomethane, diazofluorene, and azibenzil resulted in cleavage of the carbon–nitrogen bond to give the corresponding ketones in high yield. Depending on the solvent, temperature, and solution concentration, the stoichiometry of the ozonation varied from 1:1 to nearly 2:1 in regard to moles of diazo compound reacting per mole of ozone. Two ozonation routes are proposed, one with 1:1 stoichiometry and resulting in the ketone, nitrogen, and oxygen, and the other involving 2:1 stoichiometry and yielding the ketone, nitrogen, and nitrous oxide.

In two previous papers we have reported the attack of ozone on the carbon–nitrogen double bonds of certain Schiff bases,[3] nitrones,[3] and 2,4-dinitrophenylhydrazones.[4] The major reaction was cleavage of the carbon–nitrogen double bond, although noncleavage products also were obtained in the case of Schiff bases.[3] The suggestion was made that the major type of ozone attack on the carbon–nitrogen double bonds of the substances was nucleophilic.[3,4]

Wibaut and Boon[5] recently reported the attack of ozone on azibenzil (Ic) to give benzil (Vc). Since we had independently discovered the same type of reaction and found a variable stoichiometry, we published a preliminary report concerning the ozonation of diphenyldiazomethane (Ia).[1] The present paper gives the experimental details of the ozonation of Ia, extends the study to azibenzil (Ic) and diazofluorene (Ib), and discusses possible mechanisms for the reaction.

Diphenyldiazomethane (Ia) and diazofluorene (Ib) absorbed ozone quantitatively and gave quantitative, or near quantitative, yields of benzophenone (Va) and fluorenone (Vb), respectively, in carbon tetrachloride, methylene chloride, or methanol solutions. In carbon tetrachloride solution, at the point where the starting material (Ia or Ib) had all reacted, as determined by the disappearance of the red color, the mole ratio of Ia and Ib to ozone reacting was 1.7–1.9 and 1.4–1.5, respectively. Changes in temperature and in concentration of the solution appeared to have little effect on the ratio. With methylene chloride solvent, however,

---

[1] For a preliminary report on a part of this work, see A. M. Reader and P. S. Bailey, *Chem. Ind.* (London), 1620 (1961). A major part of the work presented in the present paper came from the Ph.D. Dissertation of A. M. Reader, The University of Texas, June 1962.

[2] To whom inquiries should be directed.

[3] A. H. Riebel, R. E. Erickson, C. J. Abshire, and P. S. Bailey, *J. Am. Chem. Soc.*, **82**, 1801 (1960).

[4] R. E. Erickson, A. H. Riebel, A. M. Reader, and P. S. Bailey, *Ann.*, **653**, 129 (1962).

[5] J. P. Wibaut and J. W. P. Boon, *Helv. Chim. Acta*, **44**, 1171 (1961).

TABLE I

OZONATIONS OF Ia AND Ib WITH OZONE-OXYGEN[a]

Expt.	Compd.	Solvent	Temp., °C.	Concn., g. of I/100 ml. of solvent	Molar ratio, I/O_3[b]
1	Ia	CCl_4	0	5.0	1.9
2	Ia	CCl_4	30	5.0	1.9
3	Ia	CCl_4	30	2.0	1.9
4	Ib	CCl_4	0	2.3	1.5
5	Ib	CCl_4	0	2.0	1.4
6	Ib	CCl_4	0	1.3	1.5
7	Ib	CCl_4	25	2.1	1.5
8	Ia	CH_2Cl_2	−78	6.0	1.9
9	Ia	CH_2Cl_2	−78	2.5	1.8
10	Ia	CH_2Cl_2	−78	High dilution[c]	1.6
11	Ia	CH_2Cl_2	−30	5.0	1.8
12	Ia	CH_2Cl_2	0	5.0	1.5
13	Ia	CH_2Cl_2	34	5.0	1.2
14	Ia	CH_2Cl_2	34	3.2	1.1
15	Ia	CH_2Cl_2	34	High dilution[c]	1.0
16	Ib	CH_2Cl_2	−78	1.8	1.8
17	Ib	CH_2Cl_2	0	2.4	1.5
18	Ib	CH_2Cl_2	25	3.7	1.0
19	Ib	CH_2Cl_2	25	1.6	1.1

[a] See Experimental for details. [b] The molar ratio of I reacting to ozone reacting was obtained by dividing the millimoles of starting I by the millimoles of ozone which had reacted at the time of disappearance of the characteristic red color of I. [c] Special technique by which the concentration of I in the reaction mixture was kept at 0.1% or less by adding I to the reaction mixture as needed.

TABLE II

OZONATIONS OF Ia AND Ib WITH OZONE-NITROGEN[a]

Expt.	Compd.	Solvent	Temp., °C.	mmoles of I[b]	mmoles of O_3	Mole ratio,[c] I/O_3	O_2 evolved, mmoles	Calcd. O_3 by path 1, mmoles[d]	% path 1[d]
20	Ia	CCl_4	0	32.1	18.5	1.7	4.7	4.9	15
21	Ia	CCl_4	30	27.2	15.7	1.7	4.4	4.2	15
22	Ib	CCl_4	0	10.7	7.2	1.5	3.3	3.7	35
23	Ia	CH_2Cl_2	−78	33.2	17.3	1.9	1.6	1.4	4
24	Ia	CH_2Cl_2	−30	32.8	18.6	1.8	4.8	4.4	13
25	Ia	CH_2Cl_2	30	11.1	10.4	1.1	2.8	9.7	87
26	Ia	CH_3OH	−78	5.0	5.0	1.0	2.2	5.0	100
27	Ib	CH_3OH	−78	5.2	5.2	1.0	3.6	5.2	100
28	Ib	CH_3OH	−78	15.0	15.0	1.0			

[a] See Experimental for details. [b] In 100 ml. of solvent. [c] The molar ratio of I reacting to ozone reacting was obtained by dividing the millimoles of starting I by the millimoles of ozone which reacted at the time of disappearance of the characteristic red color of I. [d] The millimoles of ozone reacting by path 1, Scheme I, should equal the millimoles of O_2 evolved. This can be calculated from the data obtained, as follows: A = total mmoles of O_3 required to react with Ia or Ib (column 6); B = total mmoles of Ia or Ib reacting at point of color change (column 5); x = mmoles of O_3 reacting by path 1, Scheme I (*i.e.*, 1:1 ratio with 1 mole equiv. of O_2 evolved); $A - x$ = mmoles of O_3 reacting by path 2, Scheme I (*i.e.*, 2:1 ratio without O_2 release). Then $x + 2(A - x) = B$, and $x = 2A - B$; % path 1, Scheme I = $100[(2A - B)/B]$.

the mole ratio of Ia or Ib to ozone reacting at the point of the color change varied from 1.8–1.9, at −78° and normal reaction mixture concentrations, to 1.0 at 25–35° and high dilution of the reaction mixture. Temperature changes appeared to have a greater effect on the ratio than did concentration changes. Using ozone–nitrogen mixtures for the ozonations, it was determined that molecular oxygen was a product[6,7] but the yields were much lower than those of Va and Vb, both with carbon tetrachloride and methylene chloride as the solvent. However, except in methylene chloride solution above 0°, the oxygen yields increased as the mole ratio of Ia or Ib to ozone reacting (at point of color change) decreased. Nitrous oxide was detected in the exit gases, by means of mass spectra, when a high ratio of Ia to ozone reacting was obtained. In methanol solution, 1 mole equiv. of ozone was required for the ozonation of both diphenyldiazomethane (Ia) and diazofluorene (Ib), even at −78°, and, using ozone–nitrogen,[6,7] 0.44 and 0.68 mole equiv. of molecular oxygen was evolved with Ia and Ib, respectively. A mass spectrum indicated the definite presence of carbon dioxide, but not of nitrous oxide. The diphenyldiazomethane (Ia)–methanol ozonation mixture was shown to contain about 0.26 mole equiv. of active oxygen; the corresponding Ib mixture contained considerably less. Much of these data is shown in Tables I and II.

After all of the diphenyldiazomethane (Ia) had been used up in the ozonation, as seen by the color changes, ozone absorption continued in all three solvents, quantitatively for a period in methylene chloride (even at −78°) or carbon tetrachloride (until about 1 mole equiv. had been absorbed), after which it continued slowly; ozone absorption was not quantitative after the color change in methanol at −78°. We believe that these results are due to ozone attack on benzophenone (Va), which was shown to occur readily. This was verified by infrared spectra. At the point of the color change, the spectrum of the carbon tetrachloride reaction mixture was identical with that of pure benzophenone. After further reaction with ozone the reaction mixture was slightly peroxidic and additional carbonyl peaks had appeared in the infrared spectrum.

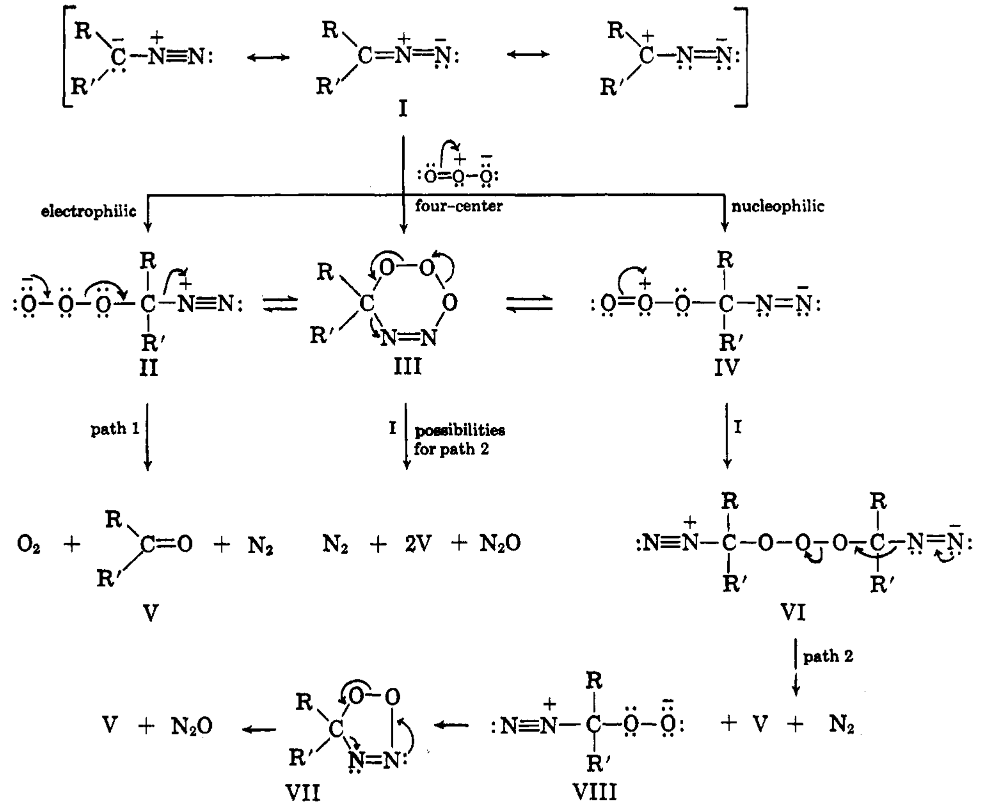
It appears from these results that there are two principal competing reactions in the ozonation of Ia and Ib, one with 1 mole of ozone reacting with 1 mole of the diazo compound (I) with release of 1 mole equiv. of molecular oxygen, and the other involving 1 mole of ozone reacting with 2 moles of diazo compound without release of molecular oxygen. Nitrous oxide must be a product of the second reaction. The degree to which each of these reactions occurs can be calculated as shown in Table II, which also shows excellent agreement between the calculated millimoles of ozone reacting by the 1:1 route and the millimoles of molecular oxygen evolved, except in expt. 25–27, which will be discussed later.

---

(6) P. S. Bailey and A. M. Reader, *Chem. Ind.* (London), 1063 (1961).

(7) P. S. Bailey, P. Kolsaker, B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee, *J. Org. Chem.*, **29**, 1400 (1964).

SCHEME I



a, R = R′ = C_6H_5
b, R, R′ = $-C_6H_4C_6H_4-$
c, R = $-COC_6H_5$; R′ = C_6H_5

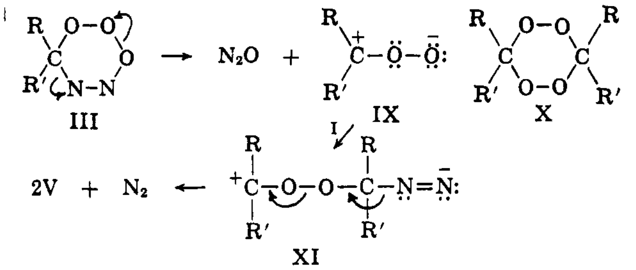
The results can be rationalized by the mechanisms proposed in Scheme I. The first step is the same for both path 1 (1:1 diazoalkane–ozone ratio) and path 2 (2:1 diazoalkane–ozone ratio) and involves the attack of ozone on the carbon atom of the carbon–nitrogen bond of I. The ozone attack could, conceivably, be electrophilic (to give II), nucleophilic (to give IV), or four-center (to give III); all three structures are reasonably represented as being in equilibrium with each other. Since, however, the carbon atom of the carbon–nitrogen bond of diazomethane derivatives is much more susceptible to attack by electrophilic than by nucleophilic reagents,[8] the electrophilic ozone attack seems more probable. Nucleophilic reagents, if they attack at all, generally attack the terminal nitrogen atom of the diazomethane derivative.[8]

Path 1, then, would be completed by loss of molecular oxygen and molecular nitrogen from II, III, or IV to give the cleavage product, ketone V. Path 2 could be represented either by nucleophilic attack of II or by electrophilic attack of IV on a second diazoalkane molecule, both of which would yield VI. The electrophilic attack of IV seems preferable for reasons already stated. Decomposition of VI to VIII, cyclization of VIII to VII, and decomposition of VII, as shown, would complete path 2, resulting in the utilization of 2 moles of diazoalkane I by 1 mole of ozone and the release of molecular nitrogen and nitrous oxide rather than molecular nitrogen and oxygen. Another possibility would be an electrophilic attack of III on I to give V, nitrogen, and nitrous oxide directly.

The suggestion of the formation of intermediates such as II, III, and IV and the attack of these on the starting material, by which two, or all three, atoms of the original ozone molecule are utilized in product formation, is not without analogy. Thompson[9] has established the existence of such an ozone adduct from the ozonation of phosphite esters, and has shown that the adduct will oxidize one or two additional mole equivalents of phosphite to phosphate, or convert sulfides to sulfoxides and sulfones. Ramirez[10] has made similar observations with oxyphosphoranes.

An alternative mechanism for path 2 is shown in Scheme II; this, however, apparently does not occur to any appreciable extent, as would be expected since it involves a nucleophilic attack on the carbon atom of the carbon–nitrogen bond of I (which is unlikely for

SCHEME II



a, R = R′ = C_6H_5
b, R, R′ = $-C_6H_4C_6H_4-$
c, R = $-COC_6H_5$; R′ = C_6H_5

---

(8) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 102-110.

(9) Q. E. Thompson, *J. Am. Chem. Soc.*, **83**, 845 (1961).

(10) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *ibid.*, **86**, 4394 (1964).

reasons already given). Thus, we have been unable to isolate any of dimer Xa of zwitterion IXa[11] from ozonation of diphenyldiazomethane (Ia) and we have not found any benzoic acid or anhydride from ozonation of azibenzil (Ic), as would be expected from rearrangement of zwitterion IXc.[12]

The effect of changes in solvent, temperature, and concentration on the molar ratio of diazoalkane (I) to ozone reacting is understandable in terms of the competition between paths 1 and 2 of Scheme I. Tables I and II show that in carbon tetrachloride, a nonpolar solvent, path 2 is highly favored under all conditions tried, whereas with methanol, a protonic and nucleophilic solvent, path 1 appears to occur exclusively. With moderately polar methylene chloride a competition between paths 1 and 2 occurs, affected by temperature and concentration changes. These results are reasonably explained by the interaction of a nucleophilic solvent such as methanol with intermediate II (or at least solvation of II), which would prevent II from cyclizing to III and/or attacking I, thus causing path 1 to be favored. Such would occur to a lesser extent with methylene chloride and not at all with carbon tetrachloride.

In methylene chloride solution it is reasonable that at low temperatures the stability of the equilibrium mixture, II $\rightleftharpoons$ III $\rightleftharpoons$ IV, would be greater and would allow IV (or II or III) to attack the starting material (I) according to path 2, rather than to decompose according to path 1. High concentrations of the diazoalkane also would favor path 2. At higher temperatures, however, the stability of II, III, and IV would decrease, and it is to be expected that decomposition of these (path 1) would increase at the expense of path 2. This also would be the case at high dilutions, where there would be less chance of contact between IV (or II or III) and I.

Tables I and II show that at room temperature in methylene chloride path 1 is predominant, but Table II, expt. 25, shows that the oxygen yield is too low. This appears to be due to attack on the solvent by II and/or IV, resulting in reduction of these intermediates and the oxidation of the solvent. This, probably, also is the reason for the low yields of oxygen in expt. 26 and 27. Evidence for this is the mass spectrogram of the exit gas from ozonation of Ia in methanol at −78°, which indicated the presence of carbon dioxide. Further, although the methanolic reaction mixture was peroxidic, a quantitative yield of crude benzophenone (Va) was obtained upon evaporation. Thus, the peroxidic content must have been due to oxidation of the solvent. This would have to be by IIa, or some other reactive intermediate, since exactly 1 mole equiv. of ozone reacted in the case of both Ia and Ib in methanol. By analogy, Slomp[13] has observed an adduct between pyridine or pyridine oxide and ozone and has presented evidence for its oxidation of methylene chloride. The fact that a lower molecular oxygen yield was obtained with Ia than with Ib (*cf.* expt. 26 and 27) also is reasonable, since IIa should be more stable than IIb (for steric reasons), thus allowing oxidation of the solvent by II to compete more favorably with its decomposition to V in the case of IIa than in the case of IIb. This greater stability of IIa than IIb also shows up in the fact that Ia reacted by path 2 to a greater extent than did Ib in carbon tetrachloride or in methylene chloride at low temperatures (Tables I and II).

Azibenzil (Ic) reacted more slowly with ozone than did Ia or Ib, but good yields of benzil (Vc) were obtained. The molar ratio of azibenzil (Ic) to ozone reacting was 1.3 in methylene chloride at −78° and 1.2 in carbon tetrachloride at 0°, indicating that the mechanisms of Scheme I are in force, although, as might be expected, intermediates IIc, IIIc, and IVc are not as stable as those arising from Ia and Ib. The lower reactivity of Ic is to be expected, since the electron-attracting benzoyl group would decrease the ease of attack by electrophilic reagents on Ic, in comparison to electrophilic attack on Ia or Ib.[14]

Diazomethane derivatives of type $RCHN_2$ also have been studied. The reactions are more complicated, however, involving a competing ozone attack on the carbon–hydrogen bond. They will be reported in a later publication, along with another paper on carbon–hydrogen bond cleavages by ozone.

Experimental

The ozonation set-up and procedures were described in earlier publications.[6,7,15] Solvents were pure and anhydrous unless otherwise stated. Diphenyldiazomethane[16] (Ia), diazofluorene[17,18] (Ib), and azibenzil[17] (Ic) were synthesized by published methods and possessed physical properties identical with those recorded in the literature.

Ozonations of Diphenyldiazomethane (Ia) and Diazofluorene (Ib) with Ozone–Oxygen.—In all of these experiments solutions of 1–6 g. of Ia or Ib in 100 ml. of carbon tetrachloride or methylene chloride were used at temperatures of 0° to 30° in carbon tetrachloride and of −78° to 34° in methylene chloride. Similar ozonator settings were used in all cases so that ozone was delivered at a known concentration between 1.25 and 1.50 mmoles/l. at a gas flow rate of 0.01 ft.^{3}/min. Ozone absorption was quantitative and the ozonation was allowed to proceed until the red color of the diazo compound disappeared. Essentially quantitative yields of benzophenone (Va) and fluorenone (Vb) were obtained following work-up. The results are shown in Table I. A typical experiment (12) is described in detail. A solution of 5.03 g. (25.9 mmoles) of Ia in 100 ml. of methylene chloride was ozonized at 0°, as described above, with an ozone–oxygen stream containing 1.44 mmoles of ozone/l. The red color of Ia disappeared when 17.3 mmoles of ozone had reacted. The ratio of moles of Ia reacting per mole of ozone reacting, therefore, was 1.5. The volume of the reaction mixture was reduced to 50 ml. by evaporation at room temperature under reduced pressure. An infrared spectrum of this solution was identical with an infrared spectrum of authentic benzophenone taken on a solution 10% by weight in methylene chloride. The identity of the product was further confirmed by evaporation of the reaction mixture to dryness under reduced pressure, dissolving the residue in a small volume of ethanol, and converting to the 2,4-dinitrophenylhydrazone (DNP) with 10 g. of 2,4-dinitrophenylhydrazine in sulfuric acid–ethanol–water. A 100% yield of the crude DNP was obtained; recrystallization from ethanol–ethyl acetate gave a 95% yield of material melting at 238–239°, no depression in a mixture melting point with an authentic sample.

About one-third of the runs in Table I were carried out by isolation of Va as the DNP as just described, and isolation of

---

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

(12) P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *J. Am. Chem. Soc.*, **82**, 6136 (1960).

(13) G. Slomp, Jr., *J. Org. Chem.*, **22**, 1277 (1957).

(14) P. Yates, B. L. Shapiro, N. Yoda, and J. Fugger, *J. Am. Chem. Soc.*, **79**, 5756 (1957).

(15) P. S. Bailey and S. S. Bath, *ibid.*, **79**, 3120 (1957).

(16) L. I. Smith and K. L. Howard, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 351.

(17) C. D. Nenitzescu and E. Solomonica, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 496.

(18) R. Baltzly, N. B. Mehta, P. B. Russell, R. E. Brooks, E. M. Grivsky, and A. M. Steinberg, *J. Org. Chem.*, **26**, 3669 (1961).

fluorenone (Vb) as such, m.p. 83–84°, rather than as a DNP. Since in these experiments near quantitative yields of Va or Vb were always found, the identity and quantitative yields of Va and Vb were simply verified in the remaining two-thirds of the experiments by the infrared technique described above.

Expt. 10 and 15 (Table I) were performed by slowly dropping a concentrated solution of the diazo compound, contained in a pressure-equalizing dropping funnel fitted to the top of a standard ozonation vessel, into the reaction mixture at such a rate that a very pale pink color was maintained in the reaction mixture. In this manner a low concentration of Ia (estimated to be less than 0.1%) was maintained throughout the run.

Ozonations of Ia and Ib with Ozone–Nitrogen.—Solutions of 1.0–6.5 g. of Ia or Ib in 100 ml. of solvent were employed at the temperatures shown in Table II. Although the technique using ozone–nitrogen has been described previously,[6,7] additional details are given below. We neglected to state earlier[6] that the oxygen analyzer is calibrated with a mixture of 10% oxygen and 90% nitrogen supplied by The Matheson Co., Inc. The silica gel[6] is cooled to −78° and exposed to the required volume of ozone–oxygen from the previously calibrated Welsbach T-23 ozonator. It is best to use excess silica gel so that less than 50% saturation by ozone is required.[6] The system is purged with nitrogen at −78° to remove molecular oxygen; essentially no ozone is lost during this process. Ozone desorption by nitrogen is brought about by allowing the temperature of the silica gel to increase slowly. In the standard procedure the ozone–nitrogen mixture is passed through the ozonation vessel to a potassium iodide trap which is followed by the thermometer well, rotameter, and oxygen analyzer in said order. In the present case the system was modified by inserting a three-way stopcock in the line between the silica gel vessel and the ozonation vessel, and attaching an auxiliary iodide trap to the side arm of the stopcock. As soon as the red color of the diazo compound disappeared the gas flow was directed through this side arm into the auxiliary iodide trap. In this way use of excess ozone by reaction with the product and/or the solvent was prevented, and accurate determinations of the amount of ozone which actually reacted with I were facilitated (amount on silica gel minus amount which reacted in the iodide trap). During this period the analyzer recorder was turned off and the analyzer outlet was closed. When all of the excess ozone had been desorbed and swept into the auxiliary trap, the analyzer recorder was turned back on, and the gas flow was redirected through the ozonation vessel and oxygen analyzer until a zero reading was obtained on the recorder. The reaction mixture was then allowed to come to room temperature while being swept with nitrogen, and in no case was any additional oxygen detected by the oxygen analyzer. Calculations of the molecular oxygen yield were as described previously.[7] Data are given in Table II.

Work-up and yields were as described earlier. In ozonations of Ia in carbon tetrachloride at 0 and 30° an infrared spectrum of the reaction mixture, taken at the time the red color had just disappeared, was identical with that of pure benzophenone. Ozonation was then continued and ozone absorption was quantitative until a total of nearly 1 mole equiv. had been passed through, after which absorption was slower. An infrared spectrum of the reaction mixture after absorption of 0.9–1.0 mole equiv. of ozone was nearly identical with that of pure benzophenone. However, the benzophenone carbonyl peak had decreased in intensity slightly and additional weak carbonyl peaks had appeared. An active oxygen determination on the reaction mixture showed 0.1 equiv. Under the same conditions a carbon tetrachloride solution of benzophenone quantitatively absorbed 1 mole equiv. of ozone; absorption had not slowed down at this point. The infrared spectrum of the reaction mixture was similar to that of overozonized Ia; about 80% of the benzophenone remained unchanged.

A methylene chloride solution of Ia also continued to absorb ozone nearly quantitatively after the color change occurred, even at −78°. Ozone absorption by methanol solutions of Ia was slow at −78° after the color change occurred (1 mole equiv. of ozone). An active oxygen determination on the cold methanolic reaction mixture immediately after the color change gave 0.26 equiv. There was essentially no change after the reaction mixture had come to room temperature.

Mass Spectroscopy Experiments.—During ozonations of diphenyldiazomethane (Ia) in carbon tetrachloride at 0 and 34° and methanol at −78° with ozone–nitrogen, samples of the outgas were collected midway in the runs. This was done both by ordinary techniques and by trapping at −112°. The mass spectra of the gases from the carbon tetrachloride runs had a large peak at mass number 44 and no peak at mass number 12, showing that carbon dioxide was not contributing to the mass 44 peak. Other peaks appropriate to nitrous oxide (*e.g.*, mass 30) were present. Since no other compound of mass number 44 could reasonably be assumed to be present, and since no compounds of higher mass number were found which could give rise to mass 44, these experiments indicate that nitrous oxide was a product of the ozonations. The spectrum from ozonation in methanol at −78° showed a large peak at mass 44, but no other peaks characteristic of nitrous oxide. It, therefore, is indicative of carbon dioxide.

Ozonation of Azibenzil (Ic).—In a typical experiment a solution of 1.72 g. (7.7 mmoles) of azibenzil (Ic) in 60 ml. of methylene chloride was ozonized at −78° with an ozone–oxygen mixture containing 1.27 mmoles of ozone/l. Absorption of ozone was slow, with some passing into the iodide trap almost from the begining of the ozonation. Because azibenzil is yellow-orange and benzil is yellow, the end point of the reaction could not be determined by the color of the reaction mixture. Ozone passage was continued until 8.9 mmoles of ozone had been delivered. Titration of the iodide trap showed that only 5.5 mmoles of ozone had reacted with Ic. The reaction mixture was reduced to a volume of 17 ml. by evaporation under reduced pressure, and an infrared spectrum of this solution was compared with spectra of 10% solutions of azibenzil and benzil in methylene chloride. Application of the Lambert–Beer law indicated 6% unchanged azibenzil and an 83% yield of benzil (Ve, 88% yield based on Ic reacting). Some very weak foreign bands also were present in the spectrum of the reaction mixture. Based on the amount of diazo compound reacting, the molar ratio of azibenzil to ozone reacting was 7.8/5.5 or 1.3. The reaction mixture was evaporated to dryness under reduced pressure and the residue was recrystallized from ethanol–water, giving an 86% yield (based on Ic reacting) of benzil melting at 94–95°; identification by infrared spectrum and mixture melting point (with an authentic sample). From a similar ozonation, carried out in carbon tetrachloride at 0°, a Ic:O_3 ratio of 1.2 was obtained, and the yield of benzil was 83% (infrared spectrum) and 78% (isolated).

Acknowledgment.—The authors are grateful for grants from the Robert A. Welch Foundation, the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, and the Public Health Service, which made this work possible. A fellowship from the Public Health Service (to A. M. R.) is also gratefully acknowledged.