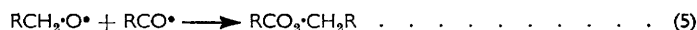
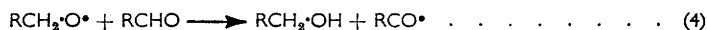


⁵ Rice and Rodowskas, *J. Amer. Chem. Soc.*, 1935, **57**, 350.

Ketones are similarly formed from secondary alkoxy-radicals.⁶⁻⁸ Tertiary alkoxy-radicals, however, decompose to ketones and alkyl radicals.⁸⁻¹⁰ The latter can also be formed, although in much less yield, from the more stable primary and secondary alkoxy-radicals.^{7,8} Nitrosoalkanes are formed in some nitrite pyrolyses from alkyl radicals by direct coupling with nitric oxide, or by abstraction of nitric oxide from alkyl nitrite.¹¹ Abstraction of hydrogen from alkoxy-radicals by nitric oxide is thought to account for the formation of nitrous oxide, which is a decomposition product of many alkyl nitrites.^{3,12}

Pyrolysis of alkyl nitrites in the liquid phase has not been so widely studied. However, the formation of nitric oxide, octan-2-one, and (+)-octan-2-ol from (+)-1-methylheptyl nitrite¹³ accords with the above mechanism, and the intermediate production of alkoxy-radicals during decomposition of t-butyl nitrite and of n-octyl nitrite in hydrogen-atom donor solvents is indicated by high yields of the appropriate alcohols.^{9,14} The slow thermal decomposition of 4-nitrobenzyl nitrite¹⁵ leads to the expected 4-nitrobenzaldehyde and to its acetal with 4-nitrobenzyl alcohol, formed, presumably, from its constituents by the usual ionic mechanism.

Recently, the decomposition of benzyl nitrite has been examined under a variety of experimental conditions.¹⁶ The products from the pyrolysis of the pure liquid included benzyl alcohol, benzaldehyde, benzoic acid, benzyl benzoate, nitric oxide, nitrous oxide, nitrogen, carbon dioxide, and water. The formation of an ester and an acid was previously observed by one of us when studying the decomposition of n-octyl nitrite in butyric acid.¹ In this case the yield of n-octyl octanoate excluded the possibility of its formation by direct esterification of octan-1-ol with octanoic acid, and the following mechanism was suggested:



Despite the concordance of this mechanism with that independently put forward by Gray, Rathbone, and Williams¹⁶ we subsequently became of the opinion that direct combination of $\text{RCO}\cdot$ and $\text{RCH}_2\cdot\text{O}\cdot$ is an improbable process. Moreover, it is one for which there is no analogy in other reactions of alkoxy-radicals. In order to elucidate the mechanism of formation of esters from alkyl nitrites, and also to confirm the absence of aldehyde noted in our earlier experiments, we have now re-examined the thermal decomposition of n-octyl nitrite.

The yields of major products formed by pyrolysis of n-octyl nitrite at 116° and 132° are shown in the Table. There were also obtained small amounts (<2%) of octanal and two unidentified volatile compounds, and a larger quantity (7%) of high-boiling residue. The last had an infrared absorption maximum at 5.82 μ and yielded octan-1-ol and octanoic acid on hydrolysis, indicating the presence of esters. A trace of an alkylamine, tentatively identified as 1-octylamine, was also formed on hydrolysis, suggesting that an aliphatic amide might be present. The origin of strong infrared absorption at 6.50 μ has not yet been elucidated.

A notable feature of these experiments, which confirmed our earlier results, was the very low yield of aldehyde. When considered in conjunction with the high yields of acid and ester, it suggests that aldehydes are very active hydrogen-atom donors, and that reaction (4) is very much faster than the competing reaction (3).

⁶ Steacie and Shaw, *Proc. Roy. Soc.*, 1935, **A**, 151, 686.

⁷ Adler, Gray, and Pratt, *Chem. and Ind.*, 1955, 1517.

⁸ Levy, *Ind. Eng. Chem.*, 1956, **48**, 762.

⁹ Joffe, *Research*, 1954, **7**, S44.

¹⁰ Gowenlock and Trotman, *J.*, 1955, 4190.

¹¹ Gray, *Chem. and Ind.*, 1960, 120; Jest and Phillips, *Proc. Chem. Soc.*, 1960, 73.

¹² Gray and Williams, *Nature*, 1960, **188**, 56.

¹³ Kornblum and Oliveto, *J. Amer. Chem. Soc.*, 1949, **71**, 226.

¹⁴ Gingras and Waters, *J.*, 1954, 3508.

¹⁵ Kornblum and Weaver, *J. Org. Chem.*, 1958, **23**, 1213.

¹⁶ Gray, Rathbone, and Williams, *J.*, 1960, 3932.

Product analysis of decomposition of alkyl nitrites, alone, or with
addition of aldehyde.

(The products are expressed in moles/100 moles of initial nitrite.)

| Expt. No. | Temp. | Starting materials | | Products | | | |
|--------------|-------|--|---|----------|---------------------|---------------------|--------------------------|
| | | RO·NO | R'CHO * | ROH † | R'CO ₂ R | R'CO ₂ H | R'CO ₂ ·CO·R' |
| I | 116° | n-C ₈ H ₁₇ ·O·NO | Nil | 39 | 23 | 6 | |
| II | 131 | " | " | 34 | 23 | 7 | |
| III | 116 | " | PhCHO (750) | | 46 | 31 | |
| IV | 116 | " | " | | 53 | 57 | |
| V | 84 | " | " (210) | 49 (9) | 55 | 45 | |
| VI | 116 | " | " | 48 (11) | 52 | 46 | |
| VII | 116 | " | n-C ₅ H ₁₁ ·CHO (240) | 48 (8) | 52 | 38 | |
| VIII | 82 | t-C ₄ H ₉ ·O·NO | PhCHO (230) | 88 | 5·5 | 32 | 32 |
| IX | 82 | " | " | 75 | 5·5 | 41 | 16 |

For experiments I and II, R' = R. In experiments V and IX the reactions did not proceed to completion and the yields are based on unrecovered nitrite.

* The number of moles of added aldehyde per 100 moles of nitrite is shown in parentheses.

† The total yield of alcohol includes that isolated as the acetal, shown separately in parentheses.

Further support for this hypothesis was provided by the decomposition of n-octyl nitrite in an excess of benzaldehyde (experiments III and IV). Octyl benzoate was the only ester formed and there was no identified product whose formation could be ascribed to reaction (3). The isolation of benzoic acid as the only acidic product suggests that the formation of octanoic acid from pure n-octyl nitrite proceeds by way of the aldehyde.

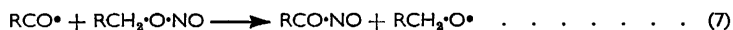
The resinous residue from experiment IV contained esters whose presence was indicated by an infrared absorption maximum at 5·85 μ . On alkaline hydrolysis benzoic acid and octan-1-ol were obtained. Both the residue and the neutral hydrolysis product had infrared absorption maxima at 8·9, 9·3, and 9·6 μ , characteristic of the acetal group.¹⁷ The presence of benzaldehyde diethyl acetal was indicated by acid hydrolysis of the neutral fraction from alkaline hydrolysis, which yielded benzaldehyde and octan-1-ol in the required amounts.

Isolation of volatile products, which were not determined in the earlier experiments, was possible when the decomposition of n-octyl nitrite was carried out in the presence of a smaller excess of benzaldehyde (experiments V and VI). Octanal was not detected: more than 90% of the starting material was accounted for as octan-1-ol, n-octyl benzoate, and benzaldehyde diethyl acetal.

These reactions involving benzaldehyde might represent a special case because of the effect of the aromatic ring on the hydrogen-atom donor properties of the aldehyde. However, the decomposition of n-octyl nitrite in hexanal (experiment VII) yielded products analogous to those obtained in benzaldehyde, thus supporting the suggestion that aldehydes in general undergo hydrogen-atom abstraction more readily than the corresponding nitrites. Hexanal diethyl acetal was isolated from this reaction and was identical with a synthetic specimen.

All the above results accord with a mechanism involving reactions (4) and (5). However, decomposition of t-butyl nitrite in benzaldehyde afforded a product of a different type. The expected ester, t-butyl benzoate, was obtained in small yield, and the major product was benzoic anhydride. We infer from these results that one or more steps in the reaction sequences leading to ester, acetal, and, probably, to acid, are ionic.

A mechanism which satisfactorily accounts for the features of nitrite decomposition involves formation of RCO·NO:

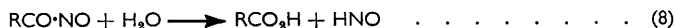


Both reactions (6) and (7) may occur, but the latter appears more probable, as it is

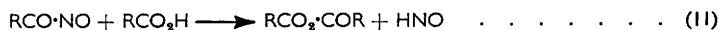
¹⁷ Bergmann and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161; Lagrange and Mastagli, *Compt. rend.*, 1955, **241**, 1947.

analogous to the abstraction of NO from nitrites by alkyl radicals,^{11,18} and, as has been pointed out previously,¹⁶ accounts for the strong catalytic effect of aldehydes on rates of nitrite decomposition.

We suggest that $\text{RCO}\cdot\text{NO}$ readily reacts with water or with alcohols forming acids and esters, respectively:



The subsequent decomposition of HNO accounts for the formation of water and nitrous oxide, previously identified as decomposition products of nitrites. When the alcohol is unreactive, *e.g.* *t*-butyl alcohol, formation of the anhydride may compete with reaction (9):



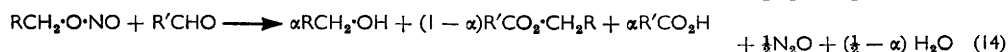
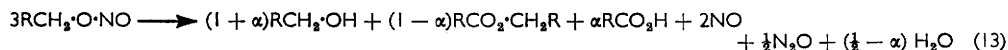
It appears that compounds of the type $\text{RCO}\cdot\text{NO}$ have not been described. However, the oxidation of benzhydroxamic acid by bromine water¹⁹ yielding benzoic acid and nitrous oxide may involve intermediate formation of $\text{PhCO}\cdot\text{NO}$. The formation of methyl benzoate by a similar oxidation in methanol supports this hypothesis.²⁰

The suggested mechanism rests largely on the results of experiments involving *t*-butyl nitrite, and would be invalid if such reactions represented a special case in which production of benzoic anhydride by some unique process competes with ester formation according to step (5). This possibility was excluded by reinvestigation of the reaction of benzaldehyde with *t*-butoxy-radicals derived from di-*t*-butyl peroxide.²¹ *meso*- and racemic 1,2-dibenzoyloxy-1,2-diphenylethane were the only products isolated. Their m. p.s were higher than those previously recorded, but the structures, which had not been rigorously proved by earlier workers,²¹ were confirmed by hydrolysis to the appropriate diols.

Comparison of the reactions involving *t*-butyl nitrite and di-*t*-butyl peroxide, both of which proceed by initial formation of *t*-butoxy-radicals, leads to two important conclusions. First, the absence of *t*-butyl benzoate from the decomposition products of the peroxide in benzaldehyde indicates that *t*-butoxy- and benzoyl-radicals do not couple to form the ester (scheme 5). Secondly, the absence of the easily identifiable *meso*- and racemic-1,2-dibenzoyloxy-1,2-diphenylethane from the reaction involving *t*-butyl nitrite shows that the formation of $\text{Ph}\cdot\text{CO}\cdot\text{NO}$ by abstraction of NO (reaction 7) is more rapid than the addition of benzoyl radical to benzaldehyde:



The yields of products shown in the Table are in accord with the suggested mechanism. If α and $(1 - \alpha)$ represent the number of moles of acid and ester, respectively, formed from one mole of $\text{RCO}\cdot\text{NO}$ by the competing reactions (8) and (9), the overall equations for the decomposition of pure alkyl nitrites, and in the presence of added aldehyde, are as follows:



Equation (15) shows the overall reaction leading to an anhydride where α and $(1 - \alpha)$

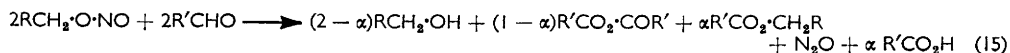
¹⁸ Kharasch, Meltzer, and Nudenberg, *J. Org. Chem.*, 1957, **22**, 37; Gray and Rathbone, *Proc. Chem. Soc.*, 1960, 316.

¹⁹ de Paolini, *Gazzetta*, 1926, **56**, 757; *Chem. Abs.*, 1927, **21**, 1100.

²⁰ Beckwith, unpublished work.

²¹ Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 3258; Kharasch and Fono, *J. Org. Chem.*, 1959, **24**, 606.

represent the number of moles of ester and anhydride, respectively, formed from one mole of $\text{RCO}\cdot\text{NO}$ by steps (9) and (11).



We have assumed that the acetals isolated from some reactions were formed by the usual ionic mechanism, subsequent to, and independent of, the main reaction sequence. The yields of alcohols shown in the Table, therefore, include amounts isolated as acetals. Because of the methods used to isolate the products the yields may be subject to considerable experimental error. Nevertheless, in most experiments the results may be fitted satisfactorily to the appropriate overall equation. The variation in the yields of acid and of anhydride from experiments VIII and IX can be attributed to hydrolysis of a part of the anhydride during the working-up.

In one experiment (IV), carried out in a large excess of benzaldehyde, the yield of benzoic acid was somewhat larger than expected. It had been suggested previously that benzaldehyde is oxidised by oxides of nitrogen.¹⁶ Indeed, the production of benzoic acid from benzaldehyde and nitrous oxide occurs in high yield at 250–350° under pressure.²² However, it appears that this reaction did not contribute to our results, for no significant oxidation occurred when nitrous oxide was passed through hot, liquid benzaldehyde: nor was the yield of benzoic acid materially increased by addition of a free-radical initiator.

Our failure to identify octanal as a decomposition product of *n*-octyl nitrite contrasts with the reported formation of aldehydes from benzyl nitrite¹⁶ and from 4-nitrobenzyl nitrite,¹⁵ and requires further comment. The aromatic ring would be expected to activate benzyl nitrites towards hydrogen-atom abstraction as compared with alkyl nitrites: the similar activation of arylalkanes is well known. On the other hand, it has been reported that benzaldehyde reacts less readily than aliphatic aldehydes with hydrogen-atom acceptors.²³ For benzyl nitrite as compared with *n*-octyl nitrite, these combined effects should decrease the rate of reaction (4) relative to that of reaction (3), so that the two become of comparable importance, and benzaldehyde, together with benzyl benzoate, is an end product.

EXPERIMENTAL

Reactions were conducted under nitrogen in a vessel kept at constant temperature by the vapour of a boiling liquid. The vessel was fitted with a reflux condenser and traps (solid carbon dioxide) to prevent loss of volatile products. All procedures for the isolation and identification of products were carried out under nitrogen. Infrared absorption spectra were measured for thin liquid films or Nujol mulls on a Perkin-Elmer "Infracord." Vapour-phase chromatography was carried out in a Griffin and George apparatus. Columns were packed with "Celite" (48–80 mesh B.S.S.) bearing a stationary phase of "Apiezon L". Paper chromatograms were run with butanol–1.5*N*-ammonia (1:1) for carboxylic acids, and with butanol–acetic acid–water (4:1:5) for alkylamines. Microanalyses were determined by the C.S.I.R.O. and University of Melbourne Microanalytical Service.

Materials.—*n*-Octyl nitrite, b. p. 76°/16 mm., prepared by dropwise addition of dilute sulphuric acid to a suspension of purified 1-octanol in aqueous sodium nitrite,²⁴ was purified by fractional distillation (nitrogen) through a helix-packed column. It was stored in the dark in a refrigerator and used within one week of its preparation.

n-Pentyl nitrite, b. p. 104°, and *t*-butyl nitrite, b. p. 63°, were similarly prepared. Each nitrite has strong infrared absorption at 6.10 and 6.25 μ due to the $\text{N}=\text{O}$ group.

Benzaldehyde and hexanal were each washed with aqueous sodium carbonate, dried, and

²² Brisdon-Jones, Buckley, Cross, and Driver, *J.*, 1951, 2999.

²³ Walling and McElhill, *J. Amer. Chem. Soc.*, 1951, **73**, 2927; Ingles and Melville, *Proc. Roy. Soc.*, 1953, *A*, **218**, 163.

²⁴ Coe and Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516.

fractionally distilled under a reduced pressure of nitrogen. The aldehydes were stored over anhydrous potassium carbonate under nitrogen at 0°.

Nitrous oxide was obtained from Commonwealth Industrial Gases.

Reference Compounds.—The following esters were prepared from the appropriate alcohols and acid chlorides in pyridine solution: *n*-octyl benzoate, b. p. 112–114°/0.2 mm., n_D^{20} 1.4930; *n*-octyl hexanoate, b. p. 92–94°/0.1 mm., n_D^{20} 1.4278; *t*-butyl benzoate, b. p. 58–60°/0.2 mm., n_D^{25} 1.4890.

1,1-Dioctyloxyhexane. This was prepared from hexanal (10 g.) and octan-1-ol (30 g.). Hydrogen chloride (2 g.) was bubbled into the mixture, which was then kept at room temperature for 4 days. The dark product was poured into an excess of aqueous sodium hydroxide, and the organic layer was washed with aqueous sodium hydrogen carbonate, and distilled. The acetal had b. p. 130–131°/0.1 mm., n_D 1.4426 (Found: C, 77.5; H, 13.3. $C_{22}H_{46}O_2$ requires C, 77.1; H, 13.5%).

meso- and racemic 1,2-diphenylethane-1,2-diol were prepared according to the literature.²⁵

Identification of Products.—Liquid products were identified by comparison of b. p.s, refractive indices, and infrared absorption spectra with those of the authentic materials. In addition, alcohols, aldehydes, and acids were converted into suitable solid derivatives. Mixtures of volatile liquids were analysed by vapour-phase chromatography.

Esters were hydrolysed with 10% ethanolic potassium hydroxide, and the neutral and the acidic products were separately identified. Acetals were hydrolysed with 10% sulphuric acid. The products were separated, as formed, by steam-distillation and were analysed by vapour-phase chromatography.

Thermal Decomposition of *n*-Octyl Nitrite.—(a) When *n*-octyl nitrite (16.6 g.) was heated at 116° it gradually became light brown, and a gas containing nitric oxide was evolved. After 80 hr., the reaction mixture in benzene (50 ml.) was extracted with aqueous sodium carbonate. Acidification of the extract gave octanoic acid (0.9 g.). No other acid was detected by paper chromatography. The organic layer, when distilled under reduced pressure, yielded the following fractions: (i) octan-1-ol (5.3 g.), b. p. 100–110°/14 mm.; (ii) *n*-octyl octanoate (6.1 g.), b. p. 110–120°/0.1 mm., which yielded octan-1-ol (3.0 g.) and octanoic acid (3.3 g.) on hydrolysis. There remained a dark, resinous residue (1.1 g.), which was not identified.

(b) *n*-Octyl nitrite (68 g.) was heated at 131° for 24 hr. The crude product (54 g.) was then distilled under reduced pressure. Octan-1-ol (13 g.) and a mixture (2.8 g.) containing water, octanal, and two unidentified constituents were obtained. Octanoic acid (4.3 g.) was extracted from the residue in hexane with aqueous sodium carbonate. The neutral material on distillation yielded octan-1-ol (18.5 g.), b. p. 40–45°/0.2 mm., and *n*-octyl octanoate (24.4 g.), b. p. 105–120°/0.1 mm. The dark nitrogenous residue (4.4 g.) showed strong infrared absorption at 5.82 and 6.50 μ . A sample of the residue was hydrolysed with 10% sulphuric acid. After steam-distillation both octan-1-ol and octanoic acid were isolated from the distillate. The acidic hydrolysis mixture was then made basic with sodium hydroxide and extracted with ether. The extract contained an amine (*ca.* 10 mg.) which gave a positive test with ninhydrin and had an R_F value of 0.85 identical with that of *n*-octylamine.

Reaction of *n*-Octyl Nitrite with Benzaldehyde.—(a) Benzaldehyde (100 ml.) and *n*-octyl nitrite (21.0 g.) were heated at 116°. During the initial vigorous reaction the temperature in the mixture rose to 130° but after approximately 1 hr. it fell to 116°. A gas containing nitric oxide was evolved, and the mixture darkened. After 20 hr. benzaldehyde and volatile products were removed by distillation *in vacuo* and the residue was dissolved in hexane. Benzoic acid (5.0 g.) was extracted with aqueous sodium carbonate. The ether-soluble material showed ester carbonyl absorption at 5.85 μ . A portion (5.0 g.), when hydrolysed, yielded octan-1-ol (3.3 g.) and benzoic acid (2.1 g.). The yield of *n*-octyl benzoate was thus estimated to be 14 g.

(b) The reaction was conducted as in (a) and the mixture, diluted with benzene (50 ml.), was extracted with aqueous sodium carbonate to remove benzoic acid (8.8 g.). Distillation of the organic layer yielded benzaldehyde, octan-1-ol, and *n*-octyl benzoate (15.5 g.), b. p. 112–120°/0.2 mm. A sample (4.0 g.) of the ester, upon hydrolysis, yielded octan-1-ol (2.3 g.) and benzoic acid (2.2 g.). Octanoic acid was not detected by paper chromatography of the

²⁵ Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, 3rd edn., 1955, pp. 175, 188.

hydrolysis product. The distillation residue had infrared absorption maxima at 5.85, 8.9, 9.3, and 9.6 μ . Hydrolysis of a sample (2.0 g.) yielded benzoic acid (0.6 g.), and a neutral oil (1.6 g.) which contained octan-1-ol, detected by vapour-phase chromatography. The neutral hydrolysis product was hydrolysed with dilute sulphuric acid to a mixture of octan-1-ol and benzaldehyde.

(c) Benzaldehyde (28 g.) and n-octyl nitrite (20 g.) in benzene (100 ml.) were heated under reflux for 48 hr. Benzoic acid (3.7 g.) was then extracted with aqueous sodium carbonate and the organic layer was distilled. The following fractions were obtained: (i) A mixture, b. p. 74—84°/20 mm., estimated by vapour-phase chromatography to contain benzaldehyde (6.5 g.) and n-octyl nitrite (9.5 g.); (ii) a mixture, b. p. 40—60°/0.3 mm., estimated by vapour-phase chromatography, and by treatment with 2,4-dinitrophenylhydrazine, to contain benzaldehyde (10.5 g.) and octan-1-ol (3.4 g.); (iii) n-octyl benzoate (8.5 g.), b. p. 110—126°/0.3 mm.; (iv) a dark residue (2.5 g.), estimated by acid hydrolysis to contain benzaldehyde diethyl acetal (1.0 g.).

(d) Benzaldehyde (28 g.) and n-octyl nitrite (20 g.) were heated at 116° for 30 hr. After dilution with benzene the following products were isolated as in (c): benzoic acid (7.1 g.), octan-1-ol (6.1 g.), n-octyl benzoate (15.2 g.), and benzaldehyde diethyl acetal (2.4 g.).

Reaction of 1-Octyl Nitrite with Hexanal.—Hexanal (30 g.) and n-octyl nitrite (20 g.) were heated at 116°. The temperature of the reaction mixture rose rapidly to 128°, but fell to 116° after approximately 1.5 hr. After 20 hr. unchanged hexanal was distilled under reduced pressure from the deep red mixture. Hexanoic acid (5.6 g.) was extracted from the residue in benzene, which was then distilled, yielding (i) octan-1-ol (6.5 g.), b. p. 95—105°/10 mm.; (ii) n-octyl hexanoate (14.9 g.), b. p. 85—95°/0.05 mm.; (iii) 1,1-diethoxyhexane (1.5 g.), b. p. 110—130°/0.05 mm. A sample (5 g.) of the ester was hydrolysed with ethanolic potassium hydroxide to octan-1-ol (2.7 g.) and hexanoic acid (2.4 g.). Octanoic acid was not detected. When treated with 2,4-dinitrophenylhydrazine in ethanolic hydrochloric acid, the acetal yielded hexanal, 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 103°. Hydrolysis of the acetal with aqueous sulphuric acid yielded hexanal and octan-1-ol, detected by vapour-phase chromatography.

Reaction of t-Butyl Nitrite with Benzaldehyde.—(a) Benzaldehyde (35 g.) and t-butyl nitrite (15 g.) were heated under reflux (internal temperature 82°) for 18 hr. and t-butyl alcohol (8.1 g.) was then distilled off. A further quantity (1.4 g.) of the alcohol was in the cold trap. No acetone was detected. After removal of benzoic acid (5.6 g.) with aqueous sodium carbonate the mixture was distilled. Benzaldehyde (17 g.) and t-butyl benzoate (1.5 g.), b. p. 50—60°/0.1 mm., were obtained. The dark, low-melting residue (10.5 g.) consisted substantially of benzoic anhydride. It had infrared absorption maxima at 5.65 and 6.0 μ , and was hydrolysed with hot aqueous potassium hydroxide to benzoic acid in quantitative yield.

(b) The above experiment was repeated with heating for 8 hr. Distillation yielded a mixture of t-butyl alcohol (5.7 g.) and t-butyl nitrite (4.3 g.), which were estimated by vapour-phase chromatography. To minimise hydrolysis of benzoic anhydride the residue in hexane was rapidly extracted with aqueous sodium hydrogen carbonate to remove benzoic acid (2.1 g.), washed immediately with dilute sulphuric acid, and dried. Distillation then gave t-butyl benzoate (1.0 g.) and benzoic anhydride (9.5 g.), b. p. 138—142°/0.1 mm., m. p. and mixed m. p. 42°.

Reaction of Di-t-butyl Peroxide with Benzaldehyde.—Benzaldehyde (80 g.) and the peroxide (20 g.) were heated at 132° for 72 hr. During this time the temperature in the mixture fell slowly to 100° and a precipitate formed. The cooled mixture was then filtered and the residue of meso-1,2-dibenzoyloxy-1,2-diphenylethane (12.6 g.) was washed with ether. It formed needles (from toluene), m. p. 253—254° (Found: C, 79.6; H, 5.4. Calc. for $C_{28}H_{22}O_4$: C, 79.6; H, 5.25%). The filtrate and washings were extracted with aqueous sodium carbonate to remove benzoic acid (2.4 g.), and distilled under reduced pressure. Only benzaldehyde was obtained and no t-butyl benzoate was detected. The residue (30 g.) was a viscous, amber oil which slowly solidified to a glass. A portion (3 g.) when chromatographed on neutral alumina yielded racemic 1,2-dibenzoyloxy-1,2-diphenylethane (1.3 g.) which crystallised from hexane in laths, m. p. 132° (Found: C, 79.8; H, 5.3%).

The meso-diester (1 g.) was hydrolysed with methanolic potassium hydroxide to benzoic acid (0.5 g.) and meso-1,2-diphenylethane-1,2-diol (0.45 g.), m. p. and mixed m. p. 136°. Hydrolysis of the racemic diester yielded the racemic diol, m. p. and mixed m. p. 121°.

Reaction of Benzaldehyde with Nitrous Oxide.—Nitrous oxide (11 g.) was bubbled into benzaldehyde (40 ml.) at 132° during 10 hr. Extraction of the product in benzene with aqueous sodium carbonate yielded benzoic acid (0.45 g.). The reaction, when repeated at 100° in the presence of t-butyl perbenzoate (1.0 g.), yielded benzoic acid (0.9 g.).

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