

**924.** *An Attempt to Study Reactions of the Free Benzoyl Radical:  
Reactions of Azodibenzoyl and Related Compounds.*

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Oxidation of benzoyl- and dibenzoyl-hydrazine with silver oxide or thermal decomposition of azodibenzoyl in solution gives inconclusive indications of the production of free benzoyl radicals. Much better evidence of the formation of free aroyl radicals has been obtained from studies of the photolyses of both azodibenzoyl and *p*-nitroazodibenzoyl in solution which show that the radicals react by dimerisation and by addition to undecomposed substrate in preference to attacking the surrounding solvent. Reaction schemes are proposed to account for the formation of the main reaction products.

Oxidising actions and Diels–Alder condensations of azodibenzoyl are also reported.

THIS work was planned as a study of the reactivity of the free benzoyl radicals by using processes which, unlike the homolytic chain reaction of benzaldehyde, do not involve competitive reactions of other radicals. Reactions of free alkyl radicals of a single type

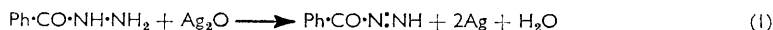
can be examined by pyrolysing symmetrical azo-compounds in the presence of appropriate substrates,<sup>1</sup> but in 1950 it was found (by U. F. M.) in this laboratory that the pyrolysis of azodibenzoyl, Ph·CO·N:N·CO·Ph, does not provide unequivocal evidence for the generation of significant amounts of free benzoyl radicals. Experiments somewhat similar to our unpublished work were later described by Leffler and Bond.<sup>2</sup>

One of us (D. M.) has now attempted to obtain free benzoyl radicals by oxidising benzoylhydrazine with silver oxide (cf. oxidation of phenylhydrazine<sup>3</sup>), but the consequential reactions so closely concern the chemistry of azodibenzoyl that it has been necessary to study comprehensively both this molecule and related compounds. The results of our studies of the products of oxidations of benzoyl- and dibenzoyl-hydrazine and of both thermal and photochemical decompositions of azodibenzoyl are summarised in the Table.

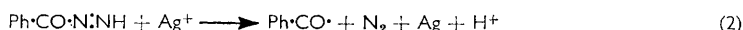
The silver oxide oxidation of benzoylhydrazine in dry benzene gives substantial amounts of benzoic acid and of 2,5-diphenyl-1,3,4-oxadiazole (III) together with a little biphenyl but no benzil. Under these conditions the biphenyl formation may be ascribed to oxidation, by the silver oxide, of benzoyl radicals to benzoyloxy-radicals which could decarboxylate to free phenyl and then attack the solvent. Though some of the benzoic acid appears as silver benzoate, tests showed that the latter does not decompose thermally or photolytically under our conditions. A similar reaction in cumene gave no biphenyl, very little bicumyl, and again very little benzaldehyde, so that positive evidence for the generation of free benzoyl radicals is, from both reactions, inconclusive.

Small amounts of both di- and tri-benzoylhydrazine are formed in each solvent.

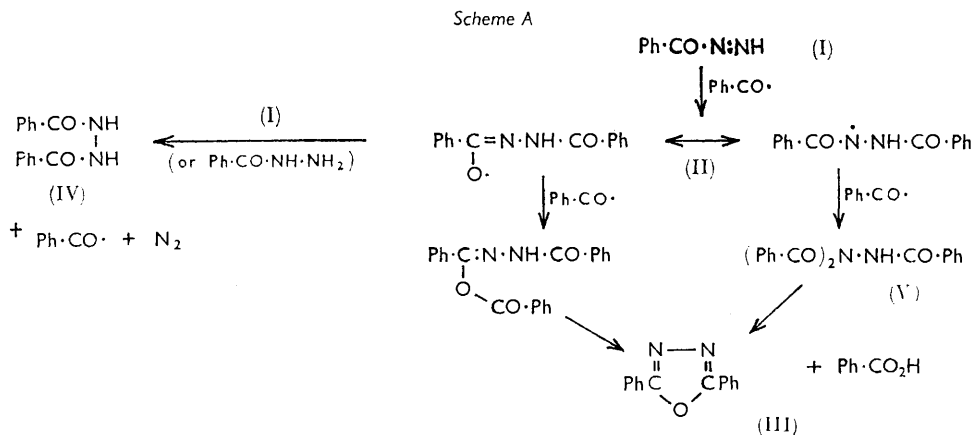
Benzoyl di-imide (I) may be the primary product of oxidation of benzoylhydrazine (cf. Hardie and Thomson<sup>3</sup>) by equation (1) and the precursor of the main reaction products.



It could itself be oxidised to benzoyl radicals as in eqn. (2) and, in homolytic reactions,



be a hydrogen donor. Thus Scheme A can be drawn.



The addition of benzoyl radicals to the N=N bond of (I) and to both O and N atoms of the mesomeric radical (II) is warranted since Kharasch, Zimmermann, Zimmt, and Nudenberg<sup>4</sup> have shown that benzaldehyde adds to azobenzene in the presence of t-butyl peroxide to give benzoyldiphenylhydrazine, whilst Horner and Naumann<sup>5</sup> have effected

<sup>1</sup> Waters *et al.*, Part I, *J.*, 1950, 764 to Part XII, *J.*, 1958, 4632.

<sup>2</sup> Leffler and Bond, *J. Amer. Chem. Soc.*, 1956, **78**, 335.

<sup>3</sup> Hardie and Thomson, *J.*, 1957, 2512.

<sup>4</sup> Kharasch, Zimmermann, Zimmt, and Nudenberg, *J. Org. Chem.*, 1953, **18**, 1045.

<sup>5</sup> Horner and Naumann, (a) *Annalen*, 1954, **587**, 81; (b) *idem.*, 93.

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radical-catalysed addition of benzaldehyde to azodibenzoyl. Again, benzoyl radicals add to the oxygen atom of benzaldehyde.<sup>6</sup> The reaction (V)  $\longrightarrow$  (III) + PhCO<sub>2</sub>H, which has been put forward by Leffler and Bond,<sup>2</sup> is considered in further detail below.

Scheme A assigns very high, but selective, reactivity to the benzoyl radical, whereas one would anticipate that it would (like free benzyl) be a resonance-stabilised entity prone to dimerise to benzil which is not formed.

(All yields are in moles per hundred moles of starting material.)

Reactants, concentrations, conditions	Gases	PhCO <sub>2</sub> H	PhCHO	(PhCO) <sub>2</sub>	Diphenyl-oxadiazole (PhCONH) <sub>2</sub>	(PhCO) <sub>2</sub> N   PhCONH	Other products	
<b>A. Silver Oxide Oxidations</b>								
PhCO·NH·NH <sub>2</sub> (0.03 mole), benzene (1%)	71 total 3.6 CO <sub>2</sub>	31	5 <sup>a</sup>	12	1	2	4 Ph <sub>2</sub>	
PhCO·NH·NH <sub>2</sub> (0.01 mole), cumene (3%)	76 total	47	<1 <sup>b</sup>	3	1	2	1 bicumyl <sup>b</sup>	
(PhCONH) <sub>2</sub> (0.01 mole), benzene (2%)	71 total	100	trace <sup>b</sup>	22			4 Ph <sub>2</sub>	
<b>B. Photolytic Decompositions of Azodibenzoyl</b>								
0.01 mole, benzene (1%), 7 hr., 80°	51 total 6 CO <sub>2</sub> +ve CO <sup>c</sup>	8	none <sup>b</sup>	29 <sup>b</sup>	22	7	21 Ph <sub>2</sub> <sup>b</sup> <1 PhCOPh <sup>b</sup>	
0.01 mole, cumene (10%), 8 hr., 140–150°		32	trace <sup>b</sup>	10 <sup>d</sup>	25	10	No bicumyl <sup>b</sup>	
0.001 mole, no solvent, 5 hr., 100°	62 total +ve CO <sup>c</sup>	trace	trace	24 <sup>b</sup>	19 <sup>b</sup>	8	No Ph <sub>2</sub> <sup>b</sup> No PhCOPh <sup>b</sup>	
<b>C. Thermal Decompositions of Azodibenzoyl<sup>f</sup></b>								
0.02 mole, toluene (4%), 6 hr., 110°	5.5 CO <sub>2</sub>				9	22	4	7 C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> <sup>e</sup>
0.03 mole, ethylbenzene (7%), 4 hr., 110°						40	6	
0.02 mole, chlorobenzene (4%), 3 hr., 132°	26 CO <sub>2</sub>	5	1 <sup>a</sup>	6	25	6	6	
0.01 mole, chlorobenzene (0.5%), 3 hr., 132°	17 CO <sub>2</sub>	2		5	19	14	2	
0.03 mole, nitrobenzene (4%), 2 hr., 150°	34 CO <sub>2</sub>	+ve		2	2	5		2 PhCONHPh
0.02 mole, tetrachloroethylene (4%), 7 hr., 121°	+ve CO <sub>2</sub>	8			24	2		HCl
0.02 mole, <i>o</i> -dichlorobenzene (5%), 4 hr., 135°	14 CO <sub>2</sub>	7			11			
0.002 mole, no solvent, 2 hr., 200° (by D. M.)		trace		9	24			

<sup>a</sup> Identified as 2,4-dinitrophenylhydrazone. <sup>b</sup> Detected or estimated by vapour phase chromatography. <sup>c</sup> Detected by the colour reaction with dodecamolybdophosphoric acid–palladium chloride reagent. <sup>d</sup> Estimated by chromatography on alumina. <sup>e</sup> M. p. 135°, not depressed in admixture with authentic 3-benzoyl-2,5-diphenyl-2,3-dihydro-1,3,4-oxadiazole (see ref. 18). <sup>f</sup> Experimental work by U. F. M.

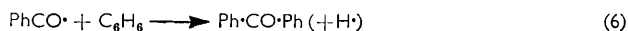
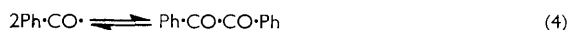
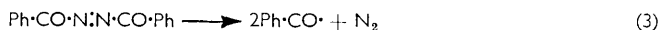
Similar oxidation of dibenzoylhydrazine in benzene, requiring more vigorous conditions, gave the same products (Table, Section A), except that no dibenzoylhydrazine remained unattacked. The first step is probably dehydrogenation to the radical (II) (see scheme A).

Heterolytic schemes for the formation of both (III) and (IV) by oxidation of benzoylhydrazine can be formulated, but support for the free-radical scheme A can be adduced from the study of homolysis of azodibenzoyl (Table, Section B).

The thermal decomposition of azodibenzoyl in solvents at 110–130° (Table, Section C) gives inconclusive evidence for the formation of benzoyl radicals. If produced in significant amount they show little tendency to dimerise unless reversibly (cf. Horner and Naumann<sup>5b</sup>) (very low yields of benzil) or to be hydrogen abstractors; the main reaction products are always the diphenyloxadiazole (III) and dibenzoylhydrazine (IV) together with both nitrogen and carbon dioxide (the evolution of the latter was not noted by Leffler and Bond). However the faster photochemical decomposition of azodibenzoyl clearly shows the initial formation of benzoyl radicals since the yield of benzil then becomes substantial. Moreover, from the decomposition in hot benzene, biphenyl becomes a major

<sup>6</sup> Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 3258.

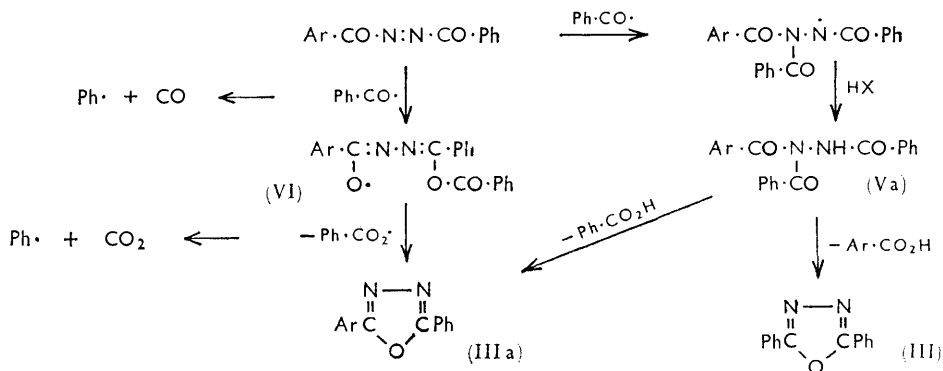
product and a trace of benzophenone is formed, while both carbon dioxide and carbon monoxide were found among the gases evolved (decarbonylation of benzoyl radicals has been previously noted<sup>6</sup>). Thus reactions (3)—(6) can be formulated, but still (III), (IV), and (V) are significant reaction products, whilst only a trace of benzaldehyde is formed. Evidently the benzoyl radical must be a very poor dehydrogenator. In fact, Horner and Naumann<sup>5b</sup> have established that there is some free-radical formation in the photolysis of azodibenzoyl by effecting therewith the polymerisation of vinyl cyanide in benzene.



As they suggest, the re-formation of benzoyl radicals by secondary photochemical decomposition of benzil must not be overlooked and we consider that reactions between benzoyl radicals and undecomposed azodibenzoyl are of major importance.

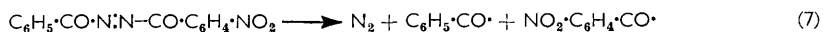
Thus scheme *B*, which accords with scheme *A*, can account for most features of the photochemical decompositions of azodibenzoyl, but to explain the invariable production of dibenzoylhydrazine (IV) it is necessary to conclude that activated azodibenzoyl [the triplet state can be written as  $\text{Ph}\cdot\text{CO}\cdot\dot{\text{N}}-\dot{\text{N}}\cdot\text{CO}\cdot\text{Ph}$  or  $\text{Ph}\cdot\text{C}(\text{O})\cdot\text{N}=\text{N}\cdot\text{C}(\text{O})\cdot\text{Ph}$ ] is a powerful dehydrogenator, as is an activated quinone.

Scheme B. (For azodibenzoyl itself Ar = Ph.)



The routes of scheme *B* to (III) and (IIIa) by loss of carboxylic acid were established by control experiments. Tribenzoylhydrazine was decomposed to diphenyloxadiazole and benzoic acid when heated or irradiated in benzene (in the latter case the yields were enhanced if benzil was present) but to an extent far too small to account for the amounts of the oxadiazole obtained in the reactions of azodibenzoyl: for this the main pathway is evidently by loss of a benzoate radical from the intermediate (VI) as envisaged by Leffler and Bond.

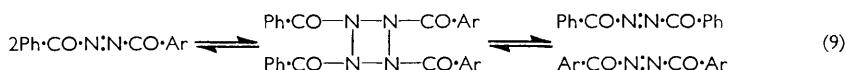
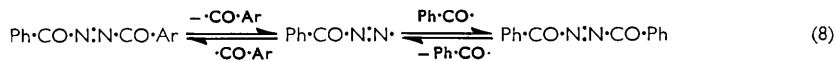
To substantiate reaction scheme *B* the photolysis in benzene of the mixed azo-compound *p*-nitroazodibenzoyl,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , prepared by two routes so as to be sure that it was not contaminated with azodibenzoyl, has been studied. It gave, though in



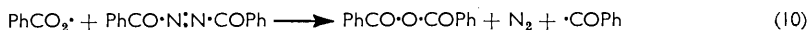
very low yield, the expected products of the direct homolysis (7), *viz.*, biphenyl (1%), *p*-nitrobiphenyl (7%), and *p*-nitrobenzil (0.5%), together with a good yield of 2-phenyl-5-*p*-nitrophenyl-1,3,4-oxadiazole (24%) and *in addition* much smaller amounts of the symmetrical analogues 2,5-diphenyl- and 1,5-di-(*p*-nitrophenyl)-1,3,4-oxadiazoles (3% and 2%). Of the possible di- and tri-aryldiazines only the unsymmetrical compound *p*-nitrodibenzoylhydrazine was isolated (17%) by fractional crystallisation, but others

may have been present in smaller amounts. Again both benzoic and *p*-nitrobenzoic acid were obtained. The low yield of *p*-nitrobenzil, under conditions similar to those of the photolyses listed in the Table, Section B, could be explained by supposing (equation 8, cf. Cohen and Wang <sup>7</sup>) that the elimination of nitrogen requires two consecutive processes and so need not give vicinal benzoyl and *p*-nitrobenzoyl radicals.

The formation of small quantities of the two symmetrical oxadiazoles can be explained by the decomposition of the mixed triaroylhydrazine (Scheme B; e.g., Va  $\rightarrow$  III); as experimentally confirmed this is a minor pathway to the oxadiazoles. Alternatively, fission and recombination processes, e.g., (8), or, dimerisation of the photo-activated azo-compound followed by decomposition of the cyclic intermediate formed, e.g., (9), could cause "scrambling" to give all three azo-compounds, and thence all detected products of scheme B (Ar = *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·), but examination by thin-layer chromatography of a partially decomposed solution of *p*-nitroazodibenzoyl did not show the presence of azo-dibenzoyl. Nevertheless we feel that such mechanisms cannot entirely be rejected.

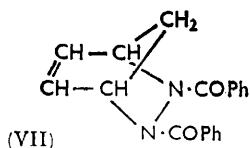


*Other Reactions of Azodibenzoyl.*—The oxidising action of azodibenzoyl, invoked above to account for the invariable production of dibenzoylhydrazine (IV), is indicated for hydrocarbon solvents in the Table, Section C, for the yield of this product is greater in toluene, ethylbenzene, or cumene than in benzene or chlorobenzene. A solution of azodibenzoyl in isopropyl alcohol became colourless after refluxion for an hour and then contained both dibenzoylhydrazine (60%) and acetone (recovery 15%) together with traces of isopropyl benzoate. Again, when heated with phenol, azodibenzoyl gave a 50% yield of dibenzoylhydrazine together with some phenyl benzoate.



The joint decomposition in solution of azodibenzoyl and benzoyl peroxide is complex, but it is clear that the peroxide does not catalyse the homolysis of the azo-compound by an induced decomposition such as (10) or by cross radical combination (11), for benzoic anhydride could not be isolated, though biphenyl and benzophenone were both formed in traces. When cyclohexane was used as the solvent 1,2-dibenzoyl-1-cyclohexylhydrazine was isolated (16%); thus azodibenzoyl acts as a trap for cyclohexyl radicals.

As expected from previous reports,<sup>8,9</sup> azodibenzoyl is a dienophile. Shabarov, Vasil'ev, and Levina<sup>9</sup> have reported that with cyclopentadiene an adduct, m. p. 127.5—128°, is formed, but in excess of cyclopentadiene, or with benzene as the solvent we have isolated both a labile product, m. p. 131—132°, and, in smaller yield, a stable isomer, m. p. 130—131°. Only the stable isomer could be isolated from a reaction in chloroform, and correspondingly the labile isomer could be converted into the stable isomer by heat or by crystallisation from polar solvents. The two isomers had different infrared nuclear magnetic resonance spectra. Both isomers showed absorption indicative of C=C and C=O groups but not of N-H. The labile isomer had a nuclear magnetic resonance spectrum consistent with the symmetrical adduct (VII), depressed the melting point of the stable isomer, and gave a dibromide, m. p. 144—145°, whereas the stable isomer, which from its n.m.r. spectrum has non-equivalent phenyl groups, gave a different dibromide, m. p. 145—147°. Only one adduct has been isolated from the



<sup>7</sup> Cohen and Wang, *J. Amer. Chem. Soc.*, **1955**, **77**, 3628.

<sup>8</sup> Shabarov, Vasil'ev, and Levina, *Doklady Akad. Nauk S.S.S.R.*, **1959**, **129**, 600.

<sup>9</sup> Shabarov, Vasil'ev, and Levina, *Zhur. obshchei. Khim.*, **1962**, **32**, 2806.

combination of *p*-nitroazodibenzoyl and cyclopentadiene, whilst the adduct of azodibenzoyl and butadiene, m. p. 163—164.5°, seems, from its n.m.r. spectrum, to be the symmetrical adduct and identical with known dibenzoyl-1,2,3,6-tetrahydropyridazine.<sup>10</sup>

### EXPERIMENTAL

Purified, dry, fractionated solvents were used throughout; the light petroleum had b. p. 40—60° unless otherwise stated. M. p.s were taken on a Kofler block and are uncorrected.

Azodibenzoyl was prepared by oxidising dibenzoylhydrazine, m. p. 242°, by a modification of Stollé's method,<sup>11</sup> which is described fully below for *p*-nitroazodibenzoyl, and after crystallisation from carbon tetrachloride formed orange-red needles, m. p. 119—120° (slight decomp.) (lit.,<sup>2</sup> m. p. 119.5—121.5°) (yield 50—70%),  $\lambda_{\text{max}}$  (CHCl<sub>3</sub>) 4740 Å ( $\epsilon$  47).

*p*-Nitrodibenzoylhydrazine.—(a) Benzoylhydrazine, m. p. 113°, was refluxed for 30 min. with *p*-nitrobenzoyl chloride in pyridine and the product was precipitated by pouring on ice. It crystallised from acetic acid in cream needles, m. p. 231—232° (lit.,<sup>12</sup> 236°). (b) An identical product, m. p. 231—233°, was obtained similarly from *p*-nitrobenzoylhydrazine (m. p. 211—212°) and benzoyl chloride. Di-*p*-nitrobenzoylhydrazine, m. p. 286—288° (lit., 288, 291°<sup>13</sup>), was prepared similarly from *p*-nitrobenzoylhydrazine and *p*-nitrobenzoylchloride.

*p*-Nitroazodibenzoyl.—To a solution of *p*-nitrobenzoylhydrazine (7.8 g.) in hot ethanol were successively added, with stirring, sodium ethoxide (2.0 equiv.) in ethanol (20 ml.) and mercuric chloride (7.9 g., 1.1 mol.) in the same solvent (40 ml.). After 1 hr. the insoluble yellow mercuric salt was collected (11.2 g.), dried, suspended in dry carbon tetrachloride (80 ml.) and treated dropwise with stirring with dry bromine (1.33 ml., 1.0 mol.) in the same solvent (25 ml.). The azo-compound was kept in solution by heating the mixture to 50°; this was filtered and the filtrate was concentrated and cooled. The rose-coloured product (5 g.) crystallised from ether in plates, m. p. 123.5—124.5° (decomp.),  $\lambda_{\text{max}}$  (CHCl<sub>3</sub>) 4780 Å ( $\epsilon$  46) (Found: C, 59.6; H, 3.2; N, 14.4. C<sub>14</sub>H<sub>9</sub>N<sub>3</sub>O<sub>4</sub> requires C, 59.4; H, 3.2; N, 14.8%).

All the 2,5-diaryl-1,3,4-oxadiazoles (III) were prepared by refluxing the appropriate di-aryloxyhydrazine for several hours in thionyl chloride and then evaporating the solvent. 2,5-Diphenyl-1,3,4-oxadiazole formed prisms, m. p. 141° (lit.,<sup>14</sup> 140°), from ethanol; 5-*p*-nitrophenyl-2-phenyl-1,3,4-oxadiazole formed yellow plates, m. p. 207—208° (lit.,<sup>12</sup> 209°) from benzene-light petroleum (Found: N, 16.1. Calc. for C<sub>14</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub>: N, 15.7%); 2,5-di-*p*-nitrophenyl-1,3,4-oxadiazole formed deep yellow needles, m. p. 308—310° (lit.,<sup>15</sup> 302°) from dioxan (Found: C, 54.1; H, 2.7; N, 17.4. Calc. for C<sub>14</sub>H<sub>8</sub>N<sub>4</sub>O<sub>5</sub>: C, 53.9; H, 2.6; N, 17.9%).

1,2-Dibenzoyl-1-cyclohexylhydrazine.—Cyclohexanone benzoylhydrazone, m. p. 162° (lit.,<sup>16</sup> m. p. 161°) (1.0 g.), in methanol (10 ml.) was treated dropwise with a solution of sodium borohydride (0.5 g.) in methanol (5 ml.). After evaporation of the methanol the residue was decomposed with dilute acetic acid and the resulting 2-benzoyl-1-cyclohexylhydrazine (85%) was crystallised from aqueous ethanol, m. p. 120°;  $\nu$  (Nujol) 3315, 3240, 1645 cm.<sup>-1</sup> (NH doublet, C=O) (Found: C, 71.3; H, 8.4; N, 13.0. C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>O requires C, 71.5; H, 8.3; N, 12.8%). Treatment of this with benzoyl chloride in pyridine gave 1,2-dibenzoyl-1-cyclohexylhydrazine which crystallised from aqueous methanol in prisms, m. p. 199—199.5° (lit.,<sup>17</sup> m. p. 195°) (Found: C, 74.5; H, 6.7; N, 8.6. Calc. for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.5; H, 6.9; N, 8.7%).

*Silver Oxide Oxidations of Benzoyl- and sym.-Dibenzoyl-hydrazines.*—The oxide (3 mol.) was added in portions to stirred suspensions, at room temperature, of the hydrazine in the chosen solvent (see Table): benzoylhydrazine reacted immediately but dibenzoylhydrazine reacted only after heating. Free silver and water were formed and gas was evolved; this was in some cases measured. Finally the mixtures were refluxed, filtered from silver residues, cooled, and washed (NaHCO<sub>3</sub> aq.) till free from benzoic acid. Solvents were removed by fractionation and examined by vapour-phase chromatography for the presence of benzaldehyde. The organic

<sup>10</sup> Baranger, Levisalles, and Vuidart, *Compt. rend.*, 1953, **236**, 1365.

<sup>11</sup> Stollé, *Ber.*, 1912, **45**, 273.

<sup>12</sup> Stollé and Leverkus, *Ber.*, 1913, **46**, 4076.

<sup>13</sup> Sattler and Zarban, *J. Amer. Chem. Soc.*, 1948, **70**, 873; Dann and Davies, *J.*, 1929, 1050.

<sup>14</sup> Pinner, *Annalen*, 1897, **297**, 221.

<sup>15</sup> Stollé and Bambach, *J. prakt. Chem.*, 1906, [2], **74**, 22.

<sup>16</sup> Grammaticakis, *Bull. Soc. Chim. France*, 1950, 690.

<sup>17</sup> Kost and Grandberg, *Zhur. obshchei Khim.*, 1955, **25**, 719.

<sup>18</sup> Stollé, *J. prakt. Chem.*, 1904, **70**, 396.



residues were treated with ether, or ether-light petroleum; this was filtered from insoluble tribenzoylhydrazine and diphenyloxadiazole, and the various components were separated chromatographically, on neutral alumina. Benzoic acid was recovered from the alkaline washings and from the insoluble silver residues.

*Control experiments.*—(i) Benzaldehyde was easily oxidised to benzoic acid by refluxion, in wet benzene solution, with silver oxide. (ii) Dibenzoylhydrazine gave no trace of diphenyloxadiazole after refluxion for 4 hr. in wet benzene. (iii) No diphenyloxadiazole was formed when benzaldehyde and benzoylhydrazine were refluxed together in benzene.

*Decomposition of Azodibenzoyl in Solution.*—(a) *Thermal.* The solutions in dried solvents were refluxed until nearly colourless in a stream of nitrogen which was then passed through baryta for the estimation of carbon dioxide.

(b) *Photochemical.* Decompositions were carried out in Pyrex flasks exposed to a Hanovia 250 w. ultraviolet lamp, the heat of which caused the solutions to boil, and were much more rapid than the purely thermal ones. Thus irradiation at 4 cm. of a solution of azodibenzoyl (0.10 g.) in refluxing cumene (5 ml.) caused complete decomposition (disappearance of the N=N absorption band at 4740 Å) in 15 min.; without irradiation decomposition took 40 min. Similarly a solution in refluxing benzene was decomposed on irradiation in 25 min., but without it there was little decomposition in 16 hr. Decomposition products were separated by crystallisation supplemented by chromatography and were identified by mixed m. p. and infrared spectra. The photolysis of *p*-nitroazodibenzoyl (3.4 g.) in benzene (400 ml.) took 5 hr. for completion (disappearance of the N=N absorption at 4780 Å). The yellow solution was evaporated and the solid residue, which had a faint odour of benzaldehyde, was extracted with hot light petroleum. This removed a yellow solid (14 mg.) which after crystallisation from ether-light petroleum had m. p. 128—135° and proved, by identity of infrared spectra to be *p*-nitrobenzil (yield 0.5 mole %). The undissolved residue was separated by cold ether (100 ml.) into two fractions (A and B). The insoluble portion (A) dissolved in hot acetone apart from a small residue (64 mg.) which after crystallisation from hot acetic acid proved to be 2,5 di-*p*-nitro-1,3,4-oxadiazole (m. p. and mixed m. p. 307—309° and identical infrared spectra: yield 2 moles %). The acetone-soluble material, after crystallisation from ethanol, gave 5-*p*-nitrophenyl-2-phenyl-1,3,4-oxadiazole, m. p. and mixed m. p. 204—207°, and more soluble *p*-nitrodibenzoylhydrazine m. p. and mixed m. p. 231—233°.

The ether-soluble fraction B was chromatographed on neutral alumina giving successively biphenyl, m. p. and mixed m. p. 68—70° (1 mole %), *p*-nitrobiphenyl, m. p. and mixed m. p. 114—115° (7 mole %), 2,5-diphenyl-1,3,4-oxadiazole (m. p. and mixed m. p. 139—140° and identical infrared spectra; 3 moles %), further 5-*p*-nitrophenyl-2-phenyl-1,3,4-oxadiazole (to total 24 moles %), further *p*-nitrodibenzoylhydrazine (to total 17 moles %) and eventually, by acetic acid extraction, a mixture (0.5 g.) of benzoic and *p*-nitrobenzoic acids some of which could have come from hydrolysis of aroylhydrazines.

*Control experiment.* Irradiation of a suspension of tribenzoylhydrazine (200 mg.) in refluxing benzene (10 ml.) for 8 hr. gave benzoic acid (1 mg.) and diphenyloxadiazole (2 mg.); when benzil (200 mg.) was present a higher yield of both acid (10 mg.) and oxadiazole (8 mg.) was obtained.

*Reaction of Azodibenzoyl with Isopropyl Alcohol.*—A boiling solution of azodibenzoyl (0.3 g.) in purified isopropyl alcohol (2 ml., v.p.c. showed under 0.02% acetone) became colourless in 1 hr. The solvent was distilled off and collected and a further 1 ml. of isopropyl alcohol was added, distilled off and added to the first distillate, which then on treatment with Brady's reagent gave acetone-2,4-dinitrophenylhydrazone (45 mg., 15%), m. p. 122—123° after crystallisation from methanol. The involatile residue was extracted with hot light petroleum (10 ml.) and left insoluble dibenzoylhydrazine (0.18 g., 60%). Evaporation of the petroleum left a waxy solid (70 mg.), vapour-phase chromatography of which showed the presence of isopropyl benzoate (3%).

*Reaction of Azodibenzoyl with Phenol.*—Azodibenzoyl (0.5 g.) and phenol (1.0 g.) were fused together at 100° for 8 hr. and the resulting dark gum was triturated with ether (25 ml.) to leave insoluble dibenzoylhydrazine (0.26 g., 57%). Potassium hydrogen carbonate extraction of the ether solution yielded benzoic acid (8 mg., 3%) whilst extraction with cold 4*N*-sodium hydroxide left a residue which after crystallisation from light petroleum proved to be phenyl benzoate, m. p. and mixed m. p. 66—67° (58 mg., 14%).

*Reaction of Azodibenzoyl with Benzoyl Peroxide.*—Azodibenzoyl (0.48 g.) and benzoyl peroxide

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(0.51 g., 1 mole) were refluxed together in cyclohexane (20 ml.). After 24 hr. the red colour of the solution had disappeared and on cooling 1,2-dibenzoyl-1-cyclohexylhydrazine separated (0.1 g., 16%), m. p. and mixed m. p. 196—197° after two crystallisations from benzene. Bicarbonate extraction of the cyclohexane solution gave benzoic acid (0.27 g.). Neutral material which remained was distilled to 250°/1.5 mm., and the distillate, which crystallised, was shown to consist substantially of diphenyloxadiazole, together with traces of biphenyl and benzophenone, (detected by v.p.c.). Similar volatile products were obtained from a reaction carried out in petroleum of b. p. 100—120°.

*Diels-Alder Reactions of Azodibenzoyl.*—(i) Buta-1,3-diene was bubbled into a refluxing solution of azodibenzoyl (0.48 g.) in benzene (25 ml.) and after 9 hr. the colour had disappeared. Evaporation left crystals (0.56 g., 95%) of 1,2-dibenzoyl-1,2,3,6-tetrahydropyridazine which crystallised from ethanol in prisms, m. p. 163—164.5° (lit.,<sup>10</sup> m. p. 160.5°),  $\nu$  (Nujol) 1668 and 1654  $\text{cm}^{-1}$  (C=O doublet)  $\tau$  5.83 p.p.m. (3,6-H), 4.20 p.p.m. (4,5-H), 2.61 p.p.m. (Ph) (Found: C, 74.3; H, 5.5; N, 9.3. Calc. for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$ : C, 74.0; H, 5.5; N, 9.6%).

(ii) *Cyclopentadiene.* (a) *Stable adduct.* The freshly prepared diene (2 ml.) was added to azodibenzoyl (0.30 g.) in dry chloroform (10 ml.) and the solution became colourless within 5 min. Evaporation left a solid which crystallised when rubbed with light petroleum, and after two crystallisations from ethanol this formed fine prisms, m. p. 130—131°,  $\nu$  (Nujol) 1652 and 1635  $\text{cm}^{-1}$  (C=O doublet),  $\tau$  7.64 p.p.m. (1 proton, group of four broad bands), 6.85 p.p.m. (1 proton, group of four broad bands), 4.99 p.p.m. (2 protons, multiplet), 3.78 p.p.m. (2 protons, triplet, olefinic-H), 2.65, 2.52 (6 protons, *m*- and *p*-phenyl-H of non-equivalent phenyl groups) and 2.33, 2.20 p.p.m. (4 protons, *o*-phenyl-H) (Found: C, 74.8; H, 5.1; N, 9.2%; *M*, 281.  $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_2$  requires C, 75.0; H, 5.3; N, 9.2%; *M* 304). The *dibromide*, prepared from equimolar amounts of adduct and bromine in dry chloroform, at room temperature, crystallised from aqueous methanol in prisms, m. p. 144.5—147°,  $\nu$  (Nujol) 1660 and 1632  $\text{cm}^{-1}$  (C=O doublet) (Found: C, 49.3; H, 3.5; Br, 33.4.  $\text{C}_{19}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_2$  requires C, 49.2; H, 3.5; Br, 34.4%).

(b) *Labile adduct.* Azodibenzoyl (0.2 g.) was shaken with cyclopentadiene (10 ml.) alone, or in benzene (5 ml.), until a colourless solution was obtained (10 min.). Evaporation gave a gum which slowly crystallised and two recrystallisations from benzene-light petroleum gave 1,2-dibenzoyl-3,6-methylene-1,2,3,6-tetrahydropyridazine (VII) as prisms, m. p. 131—132°, this being depressed by admixture with the isomer (a) above. When heated above its m. p. or refluxed for  $\frac{1}{2}$  hr. in aqueous methanol or in solvents containing a trace of a mineral acid, this compound was irreversibly converted into the isomer (a). The labile compound had  $\nu$  (Nujol) 1682, 1658  $\text{cm}^{-1}$  (C=O doublet),  $\tau$  8.27 (doublet,  $J = 9$  c.p.s.) and 7.99 p.p.m. (doublet,  $J = 9$  c.p.s.) ( $\text{CH}_2$ ), 4.81 p.p.m. (3,6-H), 3.55 p.p.m. (4,5-H), 2.55 (*m* and *p*-phenyl-H, phenyl groups equivalent) and 2.25 p.p.m. (*o*-phenyl-H). (Found: C, 75.2; H, 5.7; N, 9.2%; *M* 319).

Its *dibromide*, prepared as above, crystallised from benzene-light petroleum in prisms, m. p. 144—145°, but strongly depressed the m. p. of the dibromide of the stable adduct,  $\nu$  (Nujol), 1680, 1648  $\text{cm}^{-1}$  (C=O doublet) (Found: C, 49.8; H, 3.72; Br, 33.6%).

(iii) *p*-Nitroazodibenzoyl (0.4 g.) and cyclopentadiene (10 ml.) slowly reacted to give a pale yellow solution which on evaporation left a partly crystalline gum, crystallisation of which from aqueous methanol gave the *adduct* as yellow needles, m. p. 207—210°,  $\nu$  (Nujol) 1660  $\text{cm}^{-1}$  (C=O) (Found: C, 65.5; H, 4.4.  $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_4$  requires C, 65.3; H, 4.3%).

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