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Nitramines and Nitramides. Part XV.¹ Some Novel Nitro-compounds prepared during a Search for N-Nitrohydrazines

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Nitration of NN'-dibenzoylhydrazine does not yield NN'-dibenzoyl-NN'-dinitrohydrazine, PhCO·N(NO2)·N(NO2)·-COPh as reported in the literature, and our evidence shows that the produce is aa-dinitrobenzyl benzoate, PhC-(NO₂)₂·O₂CPh. Four other examples of this type have been prepared; we also report a molecular compound of p-toluic acid with 4-methyl-3-nitrobenzoic acid.

REFERENCES in the literature to N-nitrohydrazines are rare,²⁻⁴ and generally dubious; our reasons for doubting the published formulations are given later. By far the best documented example of an N-nitrohydrazine seemed to be the compound (I; $R^1 = R^2 = H$), prepared by Picard and Boivin⁵ from NN'-dibenzoylhydrazine by treatment with nitric acid-acetic anhydride. We repeated their preparation, and can confirm the physical properties of the product, but we were ultimately forced. with regret, to conclude that they were misled by faulty analyses, and that their compound was not an N-nitrohydrazine.

¹ Part XIV, A. H. Lamberton and H. M. Yusuf, J. Chem. Soc. (C), 1969, 397.

 B. Hötte, J. prakt. Chem., [2], 1887, 35, 265.
T. Ohta, J. Pharm. Soc. Japan, 1944, 64, 49 (Chem. Abs., 1952, 46, 91).

Repeated analyses of our preparations, though individually inconsistent, undoubtedly favoured the formula $C_{14}H_{10}N_2O_6$, of molecular weight 302 (II; $R^1 = R^2 = H$) rather than C₁₄H₁₀N₄O₆, of molecular weight 330 (I; $R^1 = R^2 = H$). Determination of the molecular weight by classical methods favoured the lower value, and benzoic anhydride was the largest observable ion in the mass spectrum. When it was heated to 120°, the material was converted smoothly and quantitatively into benzoic anhydride, nitrous fumes were evolved, and this reaction possibly hampers elemental analysis (see Experimental section). Treatment with cyclohexylamine in dry ether gave only cyclohexylamine nitrite

⁴ G. Ponzio, Gazzetta, 1908, **38**(i), 509; G. Ponzio and G. Charrier, Gazzetta, 1908, **38**(i), 526. ⁵ J. P. Picard and J. L. Boivin, Canad. J. Chem., 1951, **29**,

223.

and N-cyclohexylbenzamide, without evolution of gas. Quantitative determinations of benzoic and nitrous acids (after hydrolysis in aqueous potassium hydroxide) were in agreement with the production of two molecular



equivalents of each from a compound of molecular weight 302. The material showed carbonyl absorption in the i.r. region, and gave a positive hydroxamic acid test for an ester linkage. It did not act as a nitrating agent (hence it is not a nitrate) on dissolution in sulphuric acid. N.m.r. spectroscopy suggested the presence of two distinct benzene rings, and the shape of the spectrum at τ 1.6—1.9 was identical with that from benzoic anhydride at a slightly higher field ($\tau 1.7-2.0$). For these reasons we formulate Picard's compound as aadinitrobenzyl benzoate (II; $R^1 = R^2 = H$). The i.r. spectrum is consonant with those of simple gem-dinitrocompounds,⁶ and the lack of absorption between 1600 and 1700 cm⁻¹ appears to exclude alternative $\alpha\alpha$ -formulations such as the unlikely nitroso-nitrate or the more plausible nitro-nitrite; in addition, the i.r. spectrum between 1500 and 1700 cm⁻¹ closely resembles that of dinitrodiphenylmethane.

Finally, the n.m.r. evidence was clearly decisive in the case of the homologue (II; $R^1 = R^2 = Me$), which was prepared in similar fashion and gave similar reactions; the spectrum showed two methyl singlets and signals from four different pairs of protons on *para*-substituted benzene rings. Incidentally to the preparation of (II; $R^1 = R^2 = Me$), we found that *p*-toluic acid forms a stable 1:1 molecular compound with 4-methyl-3-nitrobenzoic acid.

Additional $\alpha\alpha$ -dinitrobenzyl benzoates prepared were (II; $R^1 = R^2 = Cl$), (II; $R^1 = Me$, $R^2 = H$) and (III; $R^1 = Me$, $R^2 = H$). Structures were assigned to the mono-substituted materials on the basis of the n.m.r. evidence. In all the $\alpha\alpha$ -dinitrobenzyl benzoates prepared the signals from the aromatic hydrogens fell into two groups. The shape of the lower-field group from the unsubstituted and monosubstituted compounds was identical with that of the corresponding portion of the spectrum of benzoic anhydride, whilst in the higher-field group the shape obtained from unsubstituted material was unique.

We attempted, but failed, to prepare (II; $R^{\bar{1}} = R^2 =$

OMe), (II; $R^1 = OMe$, $R^2 = H$), and (III; $R^1 = R^2 = NO_2$) from the appropriate *NN'*-diacylhydrazines. In the last case the initial material was recovered; in the others p-methoxybenzoic and benzoic acids were isolated. The first two failures may have been due to inadequate experience; the $\alpha\alpha$ -dinitrobenzyl benzoates react with hot alcohol (leading easily to loss on crystallisation) and in some cases, such as (II; $R^1 = R^2 = Cl$), are so easily converted into the anhydride that in crude mixtures the presence of the lower melting $\alpha\alpha$ -dinitrobenzyl compound can scarcely be recognised.

The mechanism of the reaction remains obscure. It takes place mainly during the ageing period at $ca. 0-20^{\circ}$, since interruption of the preparation before this stage yielded mainly the initial material. It does not involve prior dehydration to the oxadiazole (IV), since addition of this compound did not increase the yield. It does not appear to involve fragmentation of the molecule, since single compounds, and not mixtures, were obtained from the mixed NN'-diacylhydrazines; also, only benzoic anhydride was isolated from a run with a mixture of NN'-diacetylhydrazine and benzoic anhydride as the initial material. We tentatively suggest attack by a nitronium ion, followed by (i) Orton-type migration of NO_2 (V) \longrightarrow (VI), (ii) migration of benzoyl from nitrogen to oxygen, with concurrent (or subsequent) excission of nitrogen (VI) \longrightarrow (VII), and (iii) addition of a second nitronium ion.



Literature Claims.—Hötte² claimed that the passage of nitrous fumes into a suspension of N'-phenyl-NNphthaloylhydrazine in acetic acid yielded an N-nitrosocompound in the absence of water, but the N-nitrocompound, $C_6H_4(CO)_2N\cdot N(NO_2)Ph$, if the acid were moist. We were unable to obtain any material other than the nitroso-compound; the m.p.s given ² are similar, and incomplete removal of water could account for the reported analyses. Hötte also reported a dinitrocompound; this was characterised more precisely by Ohta,³ who suggested the N-p-dinitro-structure C_6H_4 - $(CO)_2N\cdot N(NO_2)\cdot C_6H_4\cdot NO_2$. This substance is N'-2,4dinitrophenyl-NN-phthaloylhydrazine (m.p. 268—269°,

⁶ L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, London, 2nd edn., ch. 17; J. F. Brown, J. Amer. Chem. Soc., 1955, 77, 6341.

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as given ⁷ for preparation by another route), since in our hands hydrolysis led, after addition of acetone, to the 2,4-dinitrophenylhydrazone of the latter, and the n.m.r. spectrum confirmed the presence of the 2,4-dinitrophenyl group in the initial material. Ponzio ⁴ obtained a series of unstable compounds, formulated as ArCO·N(NO₂)·N-(NO)Ph, by the action of benzene diazonium acetate on the potassium salts of the aryldinitromethanes p-RC₆-H₄·CH(NO₂)₂ (R = H, Me, or OMe), and subsequent isomerisation of the products in dry benzene. His claim cannot be dismissed, but seems to us to be open to question.

EXPERIMENTAL

I.r. spectra were determined for potassium bromide discs with a Perkin-Elmer Infracord model 127. Identities with authentic compounds were established by mixed m.p.s and i.r. spectra. Ethereal solutions were dried with sodium sulphate before evaporation. The NN'-diacylhydrazines have all been described.⁸

αα-Dinitrobenzyl Benzoate: Preparation, Analyses, and Reactions.—Preparations carried out as described in ref. 5 under 'Nitration of NN'-dibenzoylhydrazine' were satisfactory, but minor modifications [see preparation of (II; $R^1 = R^2 = Me$)] are probably desirable. αα-Dinitrobenzyl benzoate (prisms from ethanol) had a m.p. (102°) and u.v. spectrum as reported for the erroneous formulation;⁵ v_{max} . 1765 (C=O), 1600 (aryl), and 1560 (NO₂) cm⁻¹. Analyses were inconsistent (C, 55·3—56·6; H, 3·2—3·9; N, 7·9—10·6%) until the material had been heated slowly to avoid an undue rush of nitrous fumes [Found: C, 55·6, 55·5; H, 3·6, 3·2%; *M* (cryoscopic), 298, 294, 282 (C₆H₆), and 288 (CHBr₃). C₁₄H₁₀N₂O₆ (II; R¹ = R² = H) requires C, 55·6; H, 3·3; N, 9·3%; *M*, 302. Calc. for C₁₄H₁₀N₄O₆ (I; R¹ = R² = H): C, 50·9; H, 3·0; N, 16·9%; *M*, 330].

Addition of cyclohexylamine (0.8 ml) in ether (50 ml) to $\alpha\alpha$ -dinitrobenzyl benzoate (200 mg) in ether (20 ml) gave rapidly crystals of pure cyclohexylamine nitrite, m.p. 123° (Found: C, 49.5; H, 9.6; N, 19.1. Calc. for C₆H₁₄N₂O₂: C, 49.3; H, 9.6; N, 19.2%), identical with authentic material and in yields of 90—95% on the basis of the equation PhC(NO₂)₂·O₂CPh + 4C₆H₁₁NH₂ = 2C₆H₁₁·NH₃- $\overline{NO_2}$ + 2PhCO·NH·C₆H₁₁. Evaporation of the mother liquor yielded *N*-cyclohexylbenzamide, identified by com-

liquor yielded N-cyclohexylbenzamide, identified by comparison with authentic material.

Methods for the quantitative hydrolysis of $\alpha\alpha$ -dinitrobenzyl benzoate were developed with suitable mixtures of benzoic acid and sodium nitrite. Acidimetry after hydrolysis in ethanol was impossible, probably owing to esterification of the nitrous acid at or near the end-point on back titration, but the amount of ethanol (2 drops) introduced with the indicator was found to be harmless. A weighed quantity (ca. 35 mg) of the dinitrobenzyl benzoate was heated under reflux for 1.5 h with a weighed volume (from a 5 ml pipette) of 0.16N-aqueous potassium hydroxide, with exclusion of carbon dioxide. After washing of the condenser with water (10—15 ml), the hydrolysate was back titrated (phenolphthalein) under a stream of carbon dioxide-free air with 0.05N-sulphuric acid; the potassium hydroxide solution was standardised in terms of ml of 0.05N-sulphuric acid per g of

⁷ J. Cerezo and E. Olay, Anales real. soc. españ. Fis. Quim., 1934, **32**, 1090 (Chem. Abs., 1935, **29**, 2932). solution. Results were calculated for $\alpha\alpha$ -dinitrobenzyl benzoate on the basis of the equation PhC(NO₂)₂·O₂CPh + 4KOH = 2PhCO₂K + 2KNO₂ + 2H₂O; controls (benzoic acid-sodium nitrite mixtures) were put through the entire process [Found: *M*, 302, 297, and 302; controls, 121 and 121. C₁₄H₁₀N₂O₆ requires *M*, 302. Calc. for controls (PhCO₆H): *M*, 122].

Determination of the nitrite produced, again developed on suitable mixtures, was confirmatory though inherently less accurate. The hydrolysate (see before) from $\alpha\alpha$ -dinitrobenzyl benzoate (ca. 30 mg) was cooled and washed into a ca. 15% excess of standard acidified 0.04N-potassium permanganate (previously measured from a burette, with 5 ml of 2N-sulphuric acid added). After 1 min at 20—25°, the mixture was washed into acidified hydrogen peroxide (a weighed volume of 0.0226N, from a 5 ml pipette, with 5 ml of 2N-sulphuric acid added). The peroxide solution had been standarised in terms of ml of permanganate per g; the determination was completed by back titration with the permanganate until the colour of 1 drop persisted for over 10 s [Found: M, 306 and 312; controls 69, 68. Calc. for controls (NaNO₂): M, 69].

4-Methyl-aa-dinitrobenzyl 4-Methylbenzoate (II; $R^1 =$ $R^2 = Me$).—Fuming nitric acid (9 ml) was added dropwise, at -30° , to a stirred suspension of NN'-p-toluoylhydrazine (5 g) in acetic anhydride (50 ml). The mixture was allowed to warm slowly (0° after $\frac{1}{2}$ h, 20° after $1\frac{1}{2}$ h; occasional cooling was required), then poured into ice-water (500 ml) and set aside overnight. The resultant precipitate was collected, dissolved in ether (40 ml), and washed (NaHCO3); evaporation of the ether yielded crude neutral material which was dried in vacuo, but remained somewhat 'sticky' and yellow in colour (3-4 g of m.p. ca. 90°). Crystallisation from ethanol (charcoal) yielded 4-methyl- $\alpha \alpha$ -dinitrobenzyl 4-methylbenzoate (0.5-1.0 g) as needles, m.p. 115°, v_{max} 1750 (C=O), 1600 (aryl), and 1560 (NO₂) cm⁻¹ (Found: C, 58.0; H, 4.3; N, 8.2. C₁₆H₁₄N₂O₆ requires C, 58.2; H, 4.3; N, 8.5%). The compound reacts with hot ethanol, and contact should not be prolonged; light petroleum seemed to give less satisfactory purification.

Acidification of the sodium hydrogen carbonate wash gave a mixture of acids (0.75 g of m.p. 180°) which yielded on crystallisation from benzene (charcoal) the 1:1 molecular adduct of 4-methyl- and 4-methyl-3-nitro-benzoic acids as stout, faintly yellow needles, m.p. 182° (Found: C, 60.5; H, 4.7; N, 4.8%; equiv. wt., 159. C₁₆H₁₅NO₆ requires C, 60.6; H, 4.8; N, 4.4%; equiv. wt., 159). M.p.s (to the disappearance of the last trace of solid) of the authentic acids, and synthetic mixtures thereof, are given in terms of the molar percentage of 4-methyl-3-nitrobenzoic acid: 0%, 178°; 18%, 167°; 36%, 180°; 49%, 182°; 65%, 177°; 81%, 174°; and 100%, 188°.

Like the unsubstituted dinitrobenzyl benzoate, compound (II; $R^1 = R^2 = Me$) gave Liebermann and diphenylamine tests for nitrous acid on dissolution in sulphuric acid, and evolved nitrous fumes when heated to above the m.p.; treatment with cyclohexylamine in ether gave cyclohexylamine nitrite (87% from a 50 mg scale experiment) and N-cyclohexyl-p-toluamide, both identified by comparison with authentic materials.

Additional aa-Dinitrobenzyl Benzoates.-These were pre-

⁸ Beilstein, 4th edn., vol. 9 and supplements; A. P. Grekov, L. N. Kulakova and O. P. Shvaika, *J. Gen. Chem.* (U.S.S.R.), 1959, 29, 3020; A. P. Grekov and O. P. Shvaika, *ibid.*, 1960, 30, 3763.

pared in similar fashion. When the crude initial precipitate was insufficiently solid for collection, it was extracted directly into ether, and in some cases it seemed advantageous to press the crude neutral product (from evaporation of its ethereal solution) on porous plate before it was crystallised. In the preparation of (II; $\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{C}$), material (found to be a mixture of *p*-chlorobenzoic acid and anhydride) insoluble in the acetic anhydride at room temperature was collected before addition of the filtrate to water; even so, crude neutral compound (II; $\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{C}$) contained a considerable proportion of *p*-chlorobenzoic anhydride (v_{max} . 1790 and 1720 cm⁻¹, the second of which was separately observable in mixtures with the corresponding $\alpha\alpha$ -dinitrobenzyl benzoate), and had m.p. 180—200°, with only softening around 125°.

All were finally crystallised from ethanol, and yields are of purified material from 5 g of the diacylhydrazine: 4chloro- $\alpha\alpha$ -dinitrobenzyl 4-chlorobenzoate (still slightly contaminated with anhydride), prisms (1.0 g), m.p. 129° (decomp.) on rapid heating (6°/min), with resolidification and remelting at 190° (pure anhydride has m.p. 192—193°), ν_{max} 1770 (C=O), 1600 (aryl), and 1589 (NO₂) cm⁻¹ (Found: C, 47.0; H, 2.2; Cl, 19.3; N, 8.1. C₁₄H₈Cl₂N₂O₆ requires C, 45.3; H, 2.2; Cl, 19.1; N, 7.6%); 4-methyl- $\alpha\alpha$ -dinitrobenzyl benzoate, prisms (0.6 g), m.p. 117° [depression with (II; R¹ = R² = Me]], ν_{max} 1760 (C=O), 1600 (aryl), and 1560 (NO₂) cm⁻¹ (Found: C, 56.9; H, 4.1; N, 8.7. C₁₅H₁₂N₂O₆ requires C, 56.9; H, 3.8; N, 8.9%); and 3-methyl- $\alpha\alpha$ dinitrobenzyl benzoate, needles (0.2 g), m.p. 102° [(depression with (II, R¹ = R² = H)], ν_{max} 1770 (C=O), 1600 (aryl), 1570 (NO₂) cm⁻¹ (Found: C, 57.1; H, 4.0; N, 8.8. C₁₅H₁₂N₂O₆ requires C, 56.9; H, 3.8; N, 8.9%).

Quantitative Pyrolysis of the $\alpha\alpha$ -Dinitrobenzyl Benzoates.— Small (ca. 40 mg) quantities were heated in a paraffin-bath, and the residues were weighed; yields are in terms of possible pure anhydride. Heating $(120^{\circ} \pm 2^{\circ} \text{ for } 20-25 \text{ min})$ of (II; $\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{H})$ gave benzoic anhydride (100%), m.p. 39° (on seeding; pure, m.p. 41°), heating of (II, $\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{M}e)$ gave p-toluic anhydride (102%), m.p. 86° (pure, m.p. 93°), heating of (II; $\mathbb{R}^1 = \mathbb{M}e$, $\mathbb{R}^2 = \mathbb{H})$ gave a liquid which was presumed to be mixed anhydride (101%), and heating of (III; $\mathbb{R}^1 = \mathbb{M}e$, $\mathbb{R}^2 = \mathbb{H})$ gave a liquid which was presumed to be mixed anhydride (102%). For (II; $\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{C}l)$ see previous comments on m.p.

N.m.r. Spectra.—All measurements were made with a Varian A60 spectrometer, for solution in deuteriochloroform unless otherwise specified, with tetramethylsilane as internal standard, and at concentrations and temperatures of *ca.* 5-10% and 35° respectively.

In all the compounds which could contain an unsubstituted benzoyl group, the 2-H low-field portion of the spectrum at 100 Hz sweep width was a complex multiplet of identical shape. This, from the hydrogens ortho to the carbonyl, appeared at 500 Hz sweep width essentially as four peaks, as if resulting simply from $J_{ortho,meta}$ 8 Hz and $J_{ortho,para}$ 2 Hz (cf. benzyl benzoate ^{9a}). The symmetrical spectra from the hydrogens in para-disubstituted benzene rings are reported as doublets whenever assignations could be made, though 100 Hz sweep width resolution showed signs of the finer structure (cf. p-bromophenetole ^{9b}).

Benzoic anhydride: 7 1.74-1.96 (4H, m, ortho-H) and 2.27-2.68 (6H, m, meta- and para-H); p-toluic anhydride: τ 1.94 (4H, d, ortho-H), 2.68 (4H, d, $J_{2,3}$ 8 Hz, meta-H), and 7.55 (6H, s, Me); p-chlorobenzoic anhydride: τ 1.83 (4H, d, ortho-H) and 2.38 (4H, d, $J_{2,3}$ 9 Hz, meta-H); aa-dinitrobenzyl benzoate (II; $R^1 = R^2 = H$): $\tau 1.64$ -1.85 (2H, m, benzoate ortho-H) and 2.00-2.60 (8H, m, Ar); compound (II; $R^1 = R^2 = Me$): τ 1.89 (2H, d, benzoate ortho-H), 2.64 [2H, d, J_{2.3} (benzoate) 8 Hz, benzoate meta-H], 2.27 (2H, d, benzyl ortho-H), 2.68 [2H, d, J_{2.3} (benzyl) 9 Hz, benzyl meta-H], 7.52 (3H, s, Me), and 7.59 (3H, s, Me); assignments of the signals at $\tau 2.64$ and 2.68 are based on J values (8.3 and 8.7 Hz) measured at 100 Hz sweep width; compound (II; $R^1 = R^2 = Cl$): $\tau 1.88$ (2H, d, benzoate ortho-H), 2.45 [2H, d, $J_{2,3}$ (benzoate) 9 Hz, benzoate meta-H], 2.25 (2H, d, benzyl ortho-H), and 2.51 [2H, d, $J_{2.3}$ (benzyl) 9 Hz, benzyl meta-H]; assignments of the signals at $\tau 2.45$ and 2.51 are based on J values (8.7 and 9.1) measured at 100 Hz sweep width; compound (II; $R^1 =$ Me, $R^2 = H$: τ 1.65—1.89 (2H, m, benzoate ortho-H), 2.14-2.80 (7H, m, Ar), and 7.58 (3H, s, Me); compound (III; $R^1 = Me$, $R^2 = H$): $\tau 1.65 - 1.77$ (2H, m, benzoate ortho-H), 2.17-2.64 (7H, m, Ar), and 7.57 (3H, s, Me); and N'-2,4-dinitrophenyl-NN-phthaloylhydrazine (Ohta's compound) (in dimethyl sulphoxide): $\tau - 0.47$ br (s, NH), 1.00 (1H, d, phenyl 3-H), 1.67 (1H, q, phenyl 5-H), 1.93 (4H, s, phthaloyl), and 2.37 (1H, d, phenyl 6-H) $(J_{5,6} 9 \text{ Hz}, J_{3,5})$ 2.5 Hz) (cf. acetone 2,4-dinitrophenylhydrazone in deuteriochloroform 9c).

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⁹ Varian High Resolution N.m.r. Catalog, National Press; (a), 1963, spectrum no. 627; (b), 1962, spectrum no. 196; (c), 1962, spectrum no. 233.