20. *Organic Nitrates. Part I. Diphenylmethyl Nitrate.**

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The decomposition of the nitrate has been investigated; its reactions with nucleophilic reagents are shown to be typical of an ester undergoing unimolecular alkyl–oxygen heterolysis. Convenient preparations of a variety of *N*-, *O*-, and *S*-diphenylmethyl derivatives are described, including *N*-diphenylmethyl-amides and -sulphonamides. In the reaction of the nitrate with piperidine either substitution or carbonyl elimination may be the predominant process, according to the conditions. Bisdiphenylmethyl ether is unexpectedly converted into benzophenone with dinitrogen tetroxide in chloroform.

RECENT work on organic nitrates has been stimulated both by their technical importance and by the widespread interest in esters of inorganic oxy-acids. Nitrates, in common with phosphates and perchlorates, have synthetic potentialities. Thus, new preparative uses have been found for sugar nitrates,[1,2] and acetone cyanohydrin nitrate has been

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* A preliminary account of some of this work has appeared in *Chem. and Ind.*, 1954, 281.

[1] (*a*) Honeyman and Ansell, *J.*, 1952, 2778; (*b*) Honeyman and Morgan, *J.*, 1955, 3660.

[2] (*a*) Segall and Purves, *Canad. J. Chem.*, 1952, **30**, 860; (*b*) Hayward and Purves, *ibid.*, 1954, **32**, 19.

established as a valuable nitrating agent for amines and active-methylene compounds.[3] Kinetic studies on the hydrolytic [4,5,6] and thermal [7,8] decomposition of alkyl mononitrates have yielded valuable information about reaction mechanisms.

There have been several investigations on the interaction of alkyl nitrates with nucleophilic reagents; with a nitrate, $R{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}NO_2$, the following overall reactions may occur:

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}NO_2 + {:}Y \longrightarrow \left\{ \begin{array}{ll} R{\cdot}CH_2{\cdot}CH_2Y + NO_3^- & \quad \ldots\ldots (1) \\ R{\cdot}CH_2{\cdot}CH_2{\cdot}O^- + YNO_2 & \quad \ldots\ldots (2) \\ R{\cdot}CH{:}CH_2 + HY + NO_3^- & \quad \ldots\ldots (3) \\ R{\cdot}CH_2{\cdot}CHO + HY + NO_2^- & \quad \ldots (4) \end{array} \right.$$

Analogy for the dual possibility of alkylation (reaction 1), involving alkyl–oxygen fission, or nitration (reaction 2), involving nitryl–oxygen fission, may be found in the reactions of carboxylic acid esters with nucleophilic reagents. In this case either alkyl–oxygen, or more commonly, acyl–oxygen fission may occur. The olefin-elimination reaction (3) corresponds to the familiar β-hydrogen-elimination reactions of alkyl halides, but there is no similar analogy to the carbonyl-elimination reaction (4), which involves α-hydrogen elimination.

A detailed study of the reactions of diphenylmethyl nitrate has now been made. This nitrate was first obtained as a pale yellow oil by the action of excess of powdered silver nitrate on ethereal diphenylmethyl chloride,[9,10] and first obtained crystalline (m. p. 36·7—37·2°) by Baker and Heggs.[4e] It has now been prepared in excellent yield by interaction of equimolecular amounts of silver nitrate and diphenylmethyl bromide in methyl cyanide. The crystalline nitrate decomposed within a few hours at room temperature, mainly into bisdiphenylmethyl ether; a little benzophenone was also formed. After three weeks at 0° over potassium hydroxide the nitrate was still 80% pure. Oily samples of the diphenylmethyl nitrate slowly decomposed into benzophenone at room temperature. This suggested that the initial products of decomposition, presumably bisdiphenylmethyl ether and oxides of nitrogen, underwent further reaction to yield benzophenone. The ether was later converted into benzophenone by dinitrogen tetroxide in chloroform. Dinitrogen tetroxide is known to form compounds with ethers [11] but this appears to be the first recorded example of ether fission by this reagent. Diphenylmethyl nitrate decomposed smoothly into benzophenone when heated; a mixture of the nitrate and powdered ammonium carbonate at 95° gave 75% of bisdiphenylmethyl ether and only a little benzophenone. The thermal decomposition of the nitrate into benzophenone may involve interaction between $H_{(\alpha)}$ and NO_2 in a transition state of a four-centre type (cf. Eaborn and Shaw [12]).

The reaction of diphenylmethyl nitrate with aniline in ether, and with warm benzylamine in the absence of solvent, gave *N*-alkyl-amines and amine nitrates. With the stronger base piperidine, concurrent substitution and carbonyl-elimination occurred, and thus 1-diphenylmethylpiperidine, benzophenone, base nitrate, and base nitrite were formed:

$$Ph_2CH{\cdot}O{\cdot}NO_2 + 2C_5H_{11}N \longrightarrow Ph_2CH{\cdot}NC_5H_{10} + C_5H_{11}N,HNO_3$$
$$Ph_2CH{\cdot}O{\cdot}NO_2 + C_5H_{11}N \longrightarrow Ph_2CO + C_5H_{11}N,HNO_2$$

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[3] Emmons and Freeman, *J. Amer. Chem. Soc.*, 1955, **77**, 4387, 4389.

[4] Baker and his co-workers, *J.*, 1952, (*a*) 1193, (*b*) 1208; (*c*) *J.*, 1954, 3225; *J.*, 1955, (*d* 608, (*e*) 616.

[5] Cristol, Franzus, and Shadan, *J. Amer. Chem. Soc.*, 1955, **77**, 2512.

[6] See also Anbar, Dostrovsky, Samuel, and Yoffe, *J.*, 1954, 3603.

[7] Levy, *J. Amer. Chem. Soc.*, 1954, **76**, 3254, 3790.

[8] Pollard, Marshall, and Pedler, *Trans. Faraday Soc.*, 1956, **52**, 59.

[9] Cheeseman, *Chem. and Ind.*, 1954, 281.

[10] Merrow and Boschan, *J. Amer. Chem. Soc.*, 1954, **76**, 4622.

[11] Gray and Yoffe, *Quart. Rev.*, 1955, **9**, 362.

[12] Eaborn and Shaw, *J.*, 1955, 1420.

Diphenylmethanol was also produced, probably by interaction of the nitrate with water:

$$Ph_2CH{\cdot}O{\cdot}NO_2 + H_2O \longrightarrow Ph_2CH{\cdot}OH + HNO_3$$

The further possibility of nucleophilic attack on nitrogen cannot be excluded:

$$Ph_2CH{\cdot}O{\cdot}NO_2 + C_5H_{11}N \longrightarrow Ph_2CH{\cdot}OH + C_5H_{10}N{\cdot}NO_2$$

No nitropiperidine was isolated, but small quantities of this liquid may have been present in the products. The proportion of substitution and carbonyl elimination in the total reaction was determined both from the yields of 1-diphenylmethylpiperidine and benzophenone, and by the estimation of water-soluble nitrate and nitrite. The yields obtained in five experiments are summarised in the accompanying Table; in each case the nitrate was caused to react with 2 mols. of piperidine. No solvent was used in experiments (i) and (ii); in (iii) and (iv) the reactants were dissolved in methyl cyanide. In experiments (ii) and (iv) the reaction was moderated by ice-water, and ice–salt cooling, respectively. These results indicated that carbonyl elimination was favoured at low temperatures, and substitution by the use of ionising solvent. The considerably higher yield of nitrate than of alkylated base was evidence that the organic nitrate simultaneously reacted with adventitious water. A maximal yield of 1-diphenylmethylpiperidine was obtained in experiment (v) which was carried out after carefully drying both reactants and methyl cyanide, and with water-cooling. When diphenylmethyl nitrate was treated with morpholine under the conditions which gave maximum carbonyl elimination with piperidine, [experiment (ii) above] substitution was the predominant reaction. As these two bases have similar steric requirements, this showed that the weaker base was less efficient in removing α-hydrogen. It is of interest that in the weakly alkaline hydrolysis of diphenylmethyl nitrate in 90% aqueous ethanol at 20°, carbonyl elimination constituted only 1% of the total reaction.[4e] Reaction of the nitrate with pyridine gave a pyridinium salt (see Lane [13]) and with thiourea a thiuronium salt, readily hydrolysed to diphenylmethanol in boiling water. Diphenylmethyl nitrate was converted into bisdiphenylmethylamine by gaseous ammonia at 95°. Although bisdiphenylmethyl ether had previously been isolated from the reaction of the nitrate with hydrazine,[10] *N*-alkylation occurred under reflux. Treatment of the nitrate with phenylhydrazine in pyridine gave *N*-diphenylmethyl-*N'*-phenylhydrazine in poor yield.

	1-Diphenylmethylpiperidine	Nitrate	Benzophenone *	Nitrite
(i)	17·5	69	—	12
(ii)	5	22	66	75
(iii)	36	80	—	7
(iv)	11	46	42	32
(v)	42	77	—	19

* Isolated as its oxime.

The *N*-diphenylmethyl derivatives of formamide, acetamide, and benzamide were prepared by heating the nitrate with excess of amide. *N*-Diphenylmethylurethane and *NN'*-bisdiphenylmethylurea were similarly obtained, but the reaction failed with malonamide and phthalimide. Methanesulphonamide, benzenesulphonamide, and toluene-*p*-sulphonamide were converted into *N*-diphenylmethylsulphonamides when heated with the nitrate. High yields of substituted amides and sulphonamides were obtained; diphenylmethyl nitrate is, therefore, a convenient and useful alkylating reagent for these compounds.

Baker and Heggs's kinetic study [4e] of solvolytic and alkaline hydrolytic decomposition of diphenylmethyl nitrate in aqueous-ethanolic solvents showed that substitution by solvent molecules or hydroxide ions followed a unimolecular mechanism. It was therefore of interest to demonstrate that the nitrate had the typical reactivity of an ester undergoing

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[13] Lane, *J.*, 1953, 1172.

unimolecular alkyl–oxygen heterolysis.[14] Esters of this type will, for example, alkylate alcohols to give ethers, and thiols to give sulphides. When diphenylmethyl nitrate was treated with ethanol at 20° diphenylmethyl ethyl ether was formed (Merrow and Boschan[10] had previously isolated bisdiphenylmethyl ether from this reaction but give no experimental details). Interaction of the nitrate and thiophenol in methyl cyanide furnished diphenylmethyl phenyl sulphide. Other reactions diagnostic of the formation of carbonium ions include the ring substitution of suitably activated aromatic compounds and the formation of hydrocarbons with Grignard reagents and sulphones with sodium toluene-*p*-sulphinate. The reaction of diphenylmethyl nitrate with 1 : 3 : 5-trimethoxybenzene, phenylmagnesium bromide, and sodium toluene-*p*-sulphinate gave 2-diphenylmethyl-1 : 3 : 5-trimethoxybenzene, triphenylmethane, and diphenylmethyl *p*-tolyl sulphone, respectively. These results are, therefore, consistent with a unimolecular mechanism for the reaction of the nitrate with nucleophilic reagents.

EXPERIMENTAL

Nitrate was estimated gravimetrically as nitron nitrate,[15] and nitrite colorimetrically by the method which involves diazotisation of sulphanilamide and coupling with *N*-1-naphthylethylenediamine.[16] Colour measurements were made with a Hilger absorptiometer and an OGI green light filter.

pH measurements were made with a Cambridge pH meter and glass and calomel electrodes. The pK_a values of morpholine and the *N*-diphenylmethyl derivatives of morpholine and piperidine were determined in 50% ethanol at 25°, and found to be 8·15 ± 0·01 (M/100), 4·84 ± 0·05 (M/100), and 7·17 ± 0·03 (M/200), respectively (the limits define the spread in the calculated pK_a values on a single titration). The pK_a of morpholine was obtained by back-titration of the nitrate with carbonate-free sodium hydroxide. As expected, 4-diphenylmethylmorpholine is a much weaker base than morpholine itself or the corresponding piperidine derivative.

Diphenylmethyl Nitrate.—(*a*) Diphenylmethyl bromide[17] (40 g., 0·16 mole) in methyl cyanide (40 c.c.) was added dropwise to a stirred solution of silver nitrate (27·2 g., 0·16 mole) in methyl cyanide (100 c.c.) at 5°; there was an immediate precipitation of silver bromide. The mixture was stirred for a further 30 min., then filtered. The filtrate was evaporated in a vacuum and the residue dissolved in light petroleum (b. p. 40—60°; 40 c.c.). Small amounts of insoluble matter were removed, and the filtrate at 0° deposited colourless needles of diphenylmethyl nitrate (31·8 g., 87%), m. p. 35—38°. Complete solvolysis showed 97% purity. The nitrate was stored at 0° in a desiccator (KOH). Complete solvolysis after 1, 2, and 3 weeks showed 94, 88·5, and 80% purity, respectively. Baker and Heggs[4e] give m. p. 36·7—37·2°.

(*b*) Powdered silver nitrate (17 g., 0·1 mole) was added to a solution of diphenylmethyl chloride[18] (20·2 g., 0·1 mole) in dry ether (50 c.c.), and the mixture heated under reflux for 1 hr. (bath-temp. 55°). Silver nitrate (17 g.) was then added and heating continued for 1 hr. Silver salts were removed and the filtrate evaporated in a vacuum. Crystallisation of the residue from light petroleum (b. p. 40—60°) gave diphenylmethyl nitrate in 57—80% yield.

Decomposition of Diphenylmethyl Nitrate.—(a) *At room temperature.* Crystalline diphenylmethyl nitrate (0·95 g.) was left in a porcelain dish at room temperature for 3 days. 96% Ethanol (5 c.c.) was then added and, after cooling to 0°, the crystalline precipitate of bisdiphenylmethyl ether (0·64 g.), m. p. 108—110° (undepressed on admixture with an authentic sample[19]), filtered off. The filtrate contained benzophenone, which was isolated as its 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 238—239°). An oily sample of diphenylmethyl nitrate decomposed to a green oil which gradually became yellow and deposited crystals of benzophenone.

(b) *On heating.* Diphenylmethyl nitrate (0·025 mole) was heated at 140—150° until brown fumes were no longer evolved. The cooled residue solidified when seeded with benzophenone; it was converted in 90% yield into benzophenone oxime, m. p. and mixed m. p. 142—143°.

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[14] Davies and Kenyon, *Quart. Rev.*, 1955, **9**, 203.
[15] " Organic Reagents for Metals," Hopkin and Williams Ltd., 5th Edn., 1955, Vol. I, p. 119.
[16] Barnes and Folkard, *Analyst*, 1951, **76**, 55.
[17] Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2959.
[18] Ward, *J.*, 1927, 2288.
[19] Burton and Cheeseman, *J.*, 1953, 968.

(c) *On heating in the presence of ammonium carbonate.* A mixture of diphenylmethyl nitrate (0·05 mole) and powdered ammonium carbonate (25 g.) was heated at 95° until no more ammonia was evolved (about 30 min.). The addition of water precipitated an oil which gradually solidified. Crystallisation of the crude solid from ethanol gave bisdiphenylmethyl ether (6·6 g., 75%), m. p. (mainly) 107—109°. Excess of 2 : 4-dinitrophenylhydrazine sulphate was added to the mother-liquor, and the precipitate of benzophenone 2 : 4-dinitrophenylhydrazone (0·32 g.), m. p. and mixed m. p. 237—238°, collected. The initial aqueous filtrate was evaporated to small bulk and on cooling deposited unidentified colourless needles (0·18 g.), m. p. 200—201° (decomp.).

Reaction of Bisdiphenylmethyl Ether with Dinitrogen Tetroxide.—Dinitrogen tetroxide (1·8 g.) in chloroform (5 c.c.) was added at 0° to the ether (1·8 g.) in chloroform (10 c.c.). The mixture was set aside at room temperature for 24 hr., then shaken with excess of sodium hydrogen carbonate solution. The organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated, yielding a residue which partly crystallised when seeded with benzophenone. Treatment with alkali and excess of hydroxylamine gave benzophenone oxime (1·1 g.), m. p. (mainly) 141—142°. Unchanged ether was isolated from the alkali-insoluble material. The oxime was hydrolysed to benzophenone, m. p. 43—46°, which was further identified as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 238—239°.

Reaction of Diphenylmethyl Nitrate with Amines.—(a) *With aniline.* A mixture of the nitrate (0·02 mole) and aniline (0·04 mole) in ether (10 c.c.) was kept at room temperature overnight, then cooled to 0°. The crystalline precipitate of aniline nitrate (2·7 g.), m. p. 197—199° (decomp.) (Found : C, 46·5; H, 5·5; N, 17·7. Calc. for $C_6H_8O_3N_2$: C, 46·2; H, 5·2; N, 17·95%), was filtered off and the filtrate shaken with excess of 2N-nitric acid. Colourless crystals of *N*-diphenylmethylaniline nitrate (4·5 g.), m. p. *ca.* 150—152° (decomp.), separated. Successive crystallisations from ethanol (15 parts) gave prisms, m. p. 156° (decomp.) (undepressed on admixture with an authentic sample [20]). The nitrate yielded *N*-diphenylmethylaniline as a viscous pale yellow oil, b. p. 202—206°/1·5 mm. The amine was further characterised as its hydrochloride, which crystallised from ethanol (50 parts) as colourless needles, m. p. 193—194° (decomp.) (undepressed on admixture with an authentic sample [20]). *N*-Diphenylmethylaniline is stated to have b. p.s ranging from 232—234°/20 mm. to 165°/5 mm.

(b) *With benzylamine.* A mixture of the nitrate (0·02 mole) and benzylamine (0·04 mole) was heated cautiously to 95°, and kept at 95° for 30 min. On cooling, crystals of benzylamine nitrate (2·2 g.), m. p. (mainly) 134—137°, separated : these were filtered off and washed with ether. Crystallisation from ethanol–benzene (1 : 4; 10 parts) gave the nitrate as colourless needles, m. p. 136—137° (Found : C, 49·7; H, 5·9; N, 16·6. Calc. for $C_7H_{10}O_3N_2$: C, 49·4; H, 5·9; N, 16·5%). The ethereal filtrate was washed successively with water, 2N-sodium hydroxide, and water and then dried (Na_2SO_4). After evaporation, treatment of a portion of the residue with 2N-nitric acid gave *N*-diphenylmethylbenzylamine nitrate which crystallised from ethanol (10 parts) as colourless needles, m. p. 197° (decomp.) (Found : C, 71·0; H, 5·9; N, 8·1. Calc. for $C_{20}H_{20}O_3N_2$: C, 71·4; H, 6·0; N, 8·3%). Grammaticakis [21] gives m. p. 206°. The *picrate*, prepared in ethanol, had m. p. 181—182° (decomp.) (Found : C, 62·4; H, 4·2; N, 11·3. $C_{26}H_{22}O_7N_4$ requires C, 62·2; H, 4·4; N, 11·15%).

(c) *With piperidine.* (i) Much heat was evolved when diphenylmethyl nitrate (0·0281 mole) and 98% piperidine (5·1 g.) were mixed. After 18 hr., water and ether were added, and the organic layer was separated and washed with water until the washings no longer gave a positive nitrite reaction. The dried (Na_2SO_4) ethereal layer was evaporated in a vacuum and the residue distilled at 0·6 mm. through a short Vigreux column. The distillate (4·95 g.) had b. p. 120—148°. Fractions of b. p. 125—148° were combined and dissolved in methanol (5 c.c.). On cooling to 0°, crystals of 1-diphenylmethylpiperidine (1·32 g.; m. p. 69—73°) separated. The m. p. was raised to 79—80° by further crystallisation from methanol (Found : C, 86·0; H, 8·3; N, 5·7. Calc. for $C_{18}H_{21}N$: C, 86·0; H, 8·4; N, 5·6%). The fraction (0·3 g.), b. p. 120—125°, partly crystallised on being seeded with benzophenone; it gave benzophenone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 239—240°. The combined aqueous washings contained 0·0194 mole of nitrate and 0·0034 mole of nitrite. Christiaen [22] records the m. p. of 1-diphenylmethylpiperidine as 75°.

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[20] Gilman, Kirby, and Kinney, *J. Amer. Chem. Soc.*, 1929, **51**, 2252.
[21] Grammaticakis, *Compt. rend.*, 1938, **207**, 1224.
[22] Christiaen, *Bull. Soc. chim. belges*, 1924, **33**, 481.

(ii) A mixture of diphenylmethyl nitrate (0·0291 mole) and 98% piperidine (5·1 g.), cooled in ice-water for several hours and then left at room temperature overnight, similarly gave 1-diphenylmethylpiperidine (0·4 g.; m. p. 66—76°) and a fraction (4·4 g.), b. p. 148—158°/2·5 mm. This gave benzophenone oxime (3·9 g.; m. p. 142—143°) and crude diphenylmethanol (0·45 g.), m. p. 58—70°, on treatment with alkali and excess of hydroxylamine. The aqueous washings contained 0·0064 mole of nitrate and 0·0218 mole of nitrite.

(iii) When diphenylmethyl nitrate (0·029 mole) was added at room temperature to a solution of 98% piperidine (5·1 g.) in methyl cyanide (15 c.c.) the temperature rose initially to the b. p. of the solvent. After 18 hr., water and ether were added and 1-diphenylmethylpiperidine (2·7 g.; m. p. 73—74°) and a fraction, b. p. 151—155°/1·7 mm., isolated as described above. The latter was converted into benzophenone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 239—240°. The aqueous extracts contained 0·0233 mole of nitrate and 0·0019 mole of nitrite.

(iv) A solution of diphenylmethyl nitrate (0·0293 mole) and 98% piperidine (5·1 g.) in methyl cyanide (15 c.c.), cooled in ice-salt overnight and then allowed to warm to room temperature, similarly gave 1-diphenylmethylpiperidine (0·85 g.; m. p. 68—73°) and a fraction, b. p. 110—115°/0·4 mm., giving benzophenone oxime (2·45 g.), m. p. (mainly) 141—142°, and crude diphenylmethanol (0·85 g.), m. p. 62—72°, on treatment with alkali and excess of hydroxylamine. The aqueous extracts contained 0·0134 mole of nitrate and 0·0092 mole of nitrite.

(v) Piperidine (5·1 g.; Na-dried) was weighed into dry methyl cyanide (10 c.c.), and the solution added to a water-cooled solution of diphenylmethyl nitrate (0·0293 mole) in dry methyl cyanide (15 c.c.). After 3 days, water and ether were added and 1-diphenylmethylpiperidine (3·2 g.; m. p. 68—73°) and a fraction (1·1 g.), b. p. (mainly) 129—133°/1·1 mm., isolated as described above. This was converted into benzophenone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 239—240°. The aqueous extracts contained 0·0226 mole of nitrate and 0·0056 mole of nitrite.

(d) *With morpholine.* (i) Diphenylmethyl nitrate (0·0285 mole) was added to a solution of morpholine (5·2 g.) in methyl cyanide (10 c.c.). Colourless crystals of morpholine nitrate soon separated; after 18 hr. water and benzene were added. The organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from methanol (3 c.c.) gave colourless crystals of 4-diphenylmethylmorpholine (5·9 g., 81%), m. p. (mainly) 68—75°. The m. p. was raised to 75—76° by crystallisation from light petroleum (b. p. 40—60°; 2 parts; 93% recovery) (Found : C, 80·2; H, 7·5; N, 5·7. Calc. for $C_{17}H_{19}ON$: C, 80·6; H, 7·6; N, 5·5%). Cromwell[33] gives m. p. 76—78°. Evaporation of the aqueous layer gave a crystalline residue which yielded colourless plates of ***morpholine nitrate***, m. p. 139—141°, on recrystallisation from ethanol (8 parts) (Found : C, 32·3; H, 6·7; N, 19·0; NO_3, 41·4. $C_4H_{10}O_4N_2$ requires C, 32·0; H, 6·7; N, 18·7; NO_3, 41·3%).

(ii) A mixture of diphenylmethyl nitrate (0·0291 mole) and morpholine (5·2 g.), was cooled in ice-water for several hours and then allowed to warm to room temperature. After 18 hr., water and ether were added, the organic layer separated, and then washed exhaustively with water until the washings no longer contained nitrite. The dried (Na_2SO_4) ethereal layer was evaporated in a vacuum. Distillation of the residue through a short Vigreux column gave 5·7 g., b. p. 156—184°/2 mm. Crystallisation of the combined fractions of b. p. 166—184° from methanol gave 4-diphenylmethylmorpholine, m. p. 75—76°. The fraction of b. p. 156—166° partly crystallised when seeded with benzophenone and was converted into benzophenone 2 : 4-dinitrophenylhydrazone. The combined aqueous washings contained 0·0218 mole of nitrate and 0·0062 mole of nitrite.

(e) *With pyridine.* A mixture of diphenylmethyl nitrate (0·01 mole) and pyridine (0·01 mole) was heated carefully to 95° and kept at 95° for 5 min. When cold, ether was added and the crystalline precipitate (3·1 g.), m. p. 174° (decomp.), filtered off. Crystallisation from ethanol gave ***diphenylmethylpyridinium nitrate***, m. p. 177—178° (decomp.) (Found: C, 70·0; H, 5·2; N, 9·0. $C_{18}H_{16}O_3N_2$ requires C, 70·1; H, 5·2; N, 9·1%).

Reaction of Diphenylmethyl Nitrate with Ammonia.—When dry ammonia was bubbled for 2 hr. through a melt of the nitrate (0·05 mole) at 95°, the mixture partly solidified. 2N-Hydrochloric acid and chloroform were added, and the organic layer was separated, washed free from acid, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from light petroleum (b. p. 60—80°; 10 c.c.) gave colourless needles of bisdiphenylmethylamine (2·3 g., 27%), m. p. (mainly) 140—141°. The m. p. was raised to 141—142° by successive crystallisations from

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[33] Cromwell, *J. Amer. Chem. Soc.*, 1947, **69**, 1857.

light petroleum (b. p. 60—80°; 30 parts) and ethanol (20 parts) (Found: C, 89·35; H, 6·5; N, 3·8. Calc. for $C_{26}H_{23}N$: C, 89·4; H, 6·6; N, 4·0%). De Leeuw [24] gives m. p. 143°.

Reaction of Diphenylmethyl Nitrate with Hydrazine.—A mixture of the nitrate (0·03 mole) and 98% hydrazine (20 c.c.) was heated under reflux for 6 hr. Water was added. The precipitated oil solidified on trituration with ether. Crystallisation from ethanol (75 c.c.) gave colourless needles of slightly impure *NN'*-bisdiphenylmethylhydrazine (1·15 g.), m. p. *ca.* 124° (decomp.) (Found: C, 85·8; H, 6·0; N, 8·2. Calc. for $C_{26}H_{24}N_2$: C, 85·6; H, 6·6; N, 7·7%). This material was converted into 1:1:2:2-tetraphenylethane, m. p. 210—212°, undepressed on admixture with an authentic sample [17].

Reaction of Diphenylmethyl Nitrate with Phenylhydrazine.—Redistilled phenylhydrazine (0·02 mole) was added to the nitrate (0·02 mole) in dry pyridine (10 c.c.), and the mixture set aside at room temperature overnight. Water was added and the product isolated in benzene. After removal of solvent in a vacuum, the residue was dissolved in methanol (2 c.c.). On cooling, crystals of *N*-diphenylmethyl-*N'*-phenylhydrazine (0·7 g.), m. p. (mainly) 71—73°, separated. The m. p. was raised to 75—76° by crystallisation from ethanol (4 parts; 70% recovery) and undepressed on admixture with an authentic sample.[25]

Reaction of Diphenylmethyl Nitrate with Amides.—The following *N*-diphenylmethylamides were prepared by heating a mixture of the nitrate (0·01 mole) and the appropriate amide (0·04 mole). The temperature was raised carefully to 140° and kept at 140° for 1½ hr. After cooling, the mixture was extracted with water, and the product filtered off.

(a) N-*Diphenylmethylformamide.* Two layers separated on heating and brown fumes were evolved. Addition of water precipitated an oil which was extracted with chloroform. Crystallisation of the dried and evaporated extract from benzene–light petroleum (b. p. 40—60°) (1 : 1) gave colourless crystals (32%) of the amide, m. p. 132—134°, undepressed on admixture with an authentic sample.[26]

(b) N-*Diphenylmethylacetamide.* The nitrate was caused to react with acetamide at 80—120° for 1 hr. The product had m. p. 146—148° (yield, 98%). Crystallisation from benzene (5 parts; 92% recovery) gave the amide as colourless needles, m. p. 148° (Found: C, 80·6; H, 6·75; N, 5·7. Calc. for $C_{15}H_{15}ON$: C, 80·0; H, 6·7; N, 6·2%). Wheeler [27] gives m. p. 146—147°. The amide was also obtained by heating a mixture of diphenylmethanol (0·02 mole), acetamide (0·10 mole), and concentrated sulphuric acid (3 drops). The temperature was raised carefully to 210° and kept at 210—225° for 1½ hr. After cooling, the mixture was extracted with water, and the product filtered off. Crystallisation from benzene gave the amide (4·1 g., 91%), m. p. 145—147°.

(c) N-*Diphenylmethylbenzamide.* Crystallisation from 96% ethanol (20 parts) gave the amide as colourless needles (84%), m. p. 174—176° (Found: C, 83·6; H, 5·7; N, 5·2. Calc. for $C_{20}H_{17}ON$: C, 83·6; H, 6·0; N, 4·9%). Busch and Leefhelm [28] give m. p. 172°.

(d) N-*Diphenylmethylurethane.* Crystallisation from ethanol (2 parts) gave the amide as colourless needles (85%), m. p. 128—129° (Found: C, 75·8; H, 6·6. Calc. for $C_{16}H_{17}O_2N$: C, 75·3; H, 6·7%). Jones and Hurd [29] give m. p. 124°.

(e) NN'-*Bisdiphenylmethylurea.* Crystallisation from ethanol (100 parts) gave colourless needles (79%) of the *NN'*-diaralkylurea, m. p. 269—271°. The m. p. was raised to 271—272° by further crystallisation from ethanol (Found: C, 82·8; H, 6·0; N, 7·1. Calc. for $C_{27}H_{24}ON_2$: C, 82·6; H, 6·2; N, 7·1%). Jones and Hurd [29] give m. p. 269·5—270°.

Reaction of Diphenylmethyl Nitrate with Sulphonamides.—The following *N*-diphenylmethylsulphonamides were prepared by heating a mixture of the nitrate (0·01 mole) and the appropriate sulphonamide (0·02 mole). The temperature was raised carefully to 100° and kept at 100° for 5 min. Water was added to the cooled mixture and the precipitate filtered off.

(a) N-*Diphenylmethylmethanesulphonamide.* Crystallisation from ethanol (3 parts) gave colourless crystals of the *sulphonamide*, m. p. 144—147° (82%). The m. p. was raised to 151—152° by successive crystallisations from benzene (5 parts) and ethanol (8 parts) (Found: C, 64·5; H, 5·4; N, 5·05; S, 11·8. $C_{14}H_{15}O_2NS$ requires C, 64·3; H, 5·8; N, 5·4; S. 12·3%).

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[24] De Leeuw, *Rec. Trav. chim.*, 1911, **30**, 239.

[25] Wieland, Heymann, Tsatsas, Juchum, Varroglis, Labriola, Dobblestein, and Boyd-Barrett, *Annalen*, 1934, **514**, 145.

[26] Leuckart and Bach, *Ber.*, 1886, **19**, 2128.

[27] Wheeler, *Amer. Chem. J.*, 1901, **26**, 345.

[28] Busch and Leefhelm, *J. prakt. Chem.*, 1908, **77**, 1.

[29] Jones and Hurd, *J. Amer. Chem. Soc.*, 1921, **43**, 2422.

(b) N-*Diphenylmethylbenzenesulphonamide*. The nitrate and benzenesulphonamide were caused to react at 120—130° for 5 min. Crystallisation from 96% ethanol (8 parts) gave the sulphonamide as colourless needles, m. p. (mainly) 178—181° (63%). The m. p. was raised to 183—184° by further crystallisation from 96% ethanol (18 parts; 85% recovery) (Found: C, 70·25; H, 5·4; S, 9·9. Calc. for $C_{19}H_{17}O_2NS$: C, 70·6; H, 5·3; S, 9·9%). Busch and Leefhelm [28] give m. p. 182°.

(c) N-*Diphenylmethyltoluene*-p-*sulphonamide*. The nitrate was caused to react with 1 mol. of toluene-*p*-sulphonamide. 96% Ethanol was added to the cooled mixture and the crude sulphonamide, m. p. (mainly) 154—156°, filtered off. Crystallisation from 96% ethanol (25 parts; 65% recovery) gave colourless needles of N-*diphenylmethyltoluene*-p-*sulphonamide*, m. p. 155—156° (Found: C, 71·5; H, 5·8; N, 3·9; S, 9·3. $C_{20}H_{19}O_2NS$ requires C, 71·2; H, 5·7; N, 4·15; S, 9·5%).

Reaction of Diphenylmethyl Nitrate with Thiourea.—A mixture of the nitrate (0·01 mole) and thiourea (0·02 mole) was heated cautiously until reaction occurred, the temperature of the mixture being kept below 100°. The mixture was then kept at 70° for 30 min. After cooling, water was added and the precipitate (3·15 g.) filtered off, dried, and dissolved in ethanol (15 c.c.) and benzene (30 c.c.). Insoluble matter was removed. Dilution of the filtrate with benzene (120 c.c.) gave colourless needles of S-*diphenylmethylthiuronium nitrate* (1·45 g.), m. p. 154° (decomp.) (Found: C, 54·9; H, 5·2; N, 13·4; S, 10·4. $C_{14}H_{15}O_3N_3S$ requires C, 55·1; H, 4·95; N, 13·8; S, 10·5%).

Reaction of Diphenylmethyl Nitrate with Ethanol.—When a mixture of the nitrate (0·03 mole) and ethanol (10 c.c.) was left at room temperature, the undissolved solid gradually went into solution. After 18 hr., water and ether were added, and the organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated. Distillation of the residue gave diphenylmethyl ethyl ether (5·6 g., 88%), b. p. 128—132°/1·2—1·4 mm., n_D^{19} 1·555. The ether was converted into diphenylmethyl bromide, m. p. 39—41°, by boiling hydrobromic–acetic acid (50% w/w). In one experiment, crystallisation of the residue in the distillation flask gave a small quantity of bisdiphenylmethyl ether. This compound is a likely impurity in the nitrate and may therefore not have been a product of reaction.

Reaction of Diphenylmethyl Nitrate with Thiophenol.—A mixture of the nitrate (4·1 g.) and thiophenol (4·1 g.) in methyl cyanide (10 c.c.) was set aside at room temperature for 2 days, then poured into water and ether. The organic layer was separated, washed with water, and dried azeotropically by evaporation with benzene. 96% Ethanol (10 c.c.) was added to the residue and, after cooling to 0°, the crystalline precipitate (5·1 g.), m. p. (mainly) 65—70°, filtered off. Crystallisation from light petroleum (b. p. 40—60°; 10 parts) gave diphenylmethyl phenyl sulphide (3·85 g., 78%), m. p. 78—79°, undepressed on admixture with an authentic sample [30] (Found: C, 82·75; H, 5·9; S, 11·35. Calc. for $C_{19}H_{16}S$: C, 82·6; H, 5·8; S, 11·6%). The sulphide was converted into diphenylmethyl phenyl sulphone, m. p. 187—188°, by oxidation with hydrogen peroxide in glacial acetic acid. Knoll [31] gives m. p. 188°.

Reaction of Diphenylmethyl Nitrate with 1 : 3 : 5-*Trimethoxybenzene.*—A mixture of the nitrate (0·01 mole) and 1 : 3 : 5-trimethoxybenzene [32] (0·02 mole) in methyl cyanide (5 c.c.) rapidly became blue. After 18 hr., the crystalline precipitate (1·0 g.) was filtered off and washed with methyl cyanide. This was converted into 2 : 6-dimethoxybenzoquinone, m. p. and mixed m. p. 251—252°, by boiling aqueous ethanol. Addition of water to the initial mother-liquor precipitated a crude solid (1·75 g.) which was dissolved in benzene (10 c.c.). The solution was filtered through a column of aluminium oxide (100 g.; Spence, type H, mesh 100—200), and the chromatogram developed with benzene. The eluate afforded fraction (i) (0·82 g.), m. p. (mainly) 118—120°, and (ii) (0·60 g.), m. p. 118—120°; the latter, on crystallisation from light petroleum (b. p. 60—80°; 25 c.c.), gave colourless needles of 2-*diphenylmethyl*-1 : 3 : 5-*trimethoxybenzene* (0·35 g.), m. p. 121—122° (Found: C, 78·7; H, 6·4. $C_{22}H_{22}O_3$ requires C, 79·0; H, 6·6%).

Reaction of Diphenylmethyl Nitrate with Phenylmagnesium Bromide.—A solution of diphenylmethyl nitrate (from diphenylmethyl chloride, 10·1 g.) in ether (50 c.c.) was added dropwise to one of phenylmagnesium bromide (prepared from magnesium, 1·25 g.) in ether (50 c.c.) at such a rate that steady refluxing was maintained. The mixture, from which solid had separated,

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[30] Finzi and Bellavita, *Gazzetta*, 1932, **62**, 699.

[31] Knoll, *J. prakt. Chem.*, 1926, **113**, 40.

[32] Mannich, *Arch. Pharm.*, 1904, **242**, 506.

was heated under reflux for 1 hr., cooled, and decomposed with 2N-sulphuric acid. The ethereal layer was separated, washed free from acid, dried (Na_2SO_4), and evaporated. Distillation of the residue gave one main fraction (6·0 g.), b. p. 180—184°/2 mm. This readily crystallised, and on recrystallisation from ethanol furnished colourless needles of triphenylmethane, m. p. 92—94°, undepressed on admixture with an authentic sample.[33]

Reaction of Diphenylmethyl Nitrate with Sodium Toluene-p-*sulphinate*.—The nitrate (6·1 g.) was added to solution of sodium toluene-*p*-sulphinate (5·3 g.) in formic acid (5 c.c.); there was an immediate precipitation of solid. This was collected after 2 hr. and extracted with hot water. Successive crystallisations from 96% ethanol and benzene gave colourless needles of diphenylmethyl *p*-tolyl sulphone (3·5 g., 41%), m. p. (mainly) 192—193°, raised to 193—194° by further crystallisation from ethanol (75 parts) (Found: C, 74·65; H, 5·7. Calc. for $C_{20}H_{18}O_2S$: C, 74·5; H, 5·6%). Klenk, Suter, and Archer [34] give m. p. 186—187°.

This research was carried out during the tenure of an Imperial Chemical Industries Fellowship awarded by the University of London. The author is indebted to Professor H. Burton for his encouragement and helpful suggestions and to Dr. P. F. G. Praill for a sample of 2 : 6-dimethoxybenzoquinone.

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[*Received, July 27th,* 1956.]

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[33] Burton and Cheeseman, *J.*, 1953, 832.
[34] Klenk, Suter, and Archer, *J. Amer. Chem. Soc.*, 1948, **70**, 3846.