230. *Nitric Esters. Part I. Characterisation of the Isomeric Glycerol Dinitrates.*

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Glycerol 1,2- and 1,3-dinitrate, prepared from the corresponding dibromohydrins of glycerol, are characterised by reaction with aromatic acid chlorides. The 1,2-dinitrate is also obtained by the action of iodine–silver nitrate on allyl alcohol; derivatives of the dinitrate are prepared similarly from allyl esters and by nitration of 1-glycerides. Partial nitration of glycerol gives glycerol 1,3-dinitrate, also obtained by mild nitration of glycidol (2,3-epoxypropan-1-ol) nitrate. Denitration of glycerol trinitrate by sodium nitrite or potassium hydroxide in aqueous ethanol and by sulphuric acid confirms that the secondary nitric ester group is displaced more readily.

"Dinitroglycerine," at one time used to lower the freezing point of glycerol trinitrate, is a mixture of the 1,3- and 1,2-dinitrates of glycerol.[1] These constituents were first separated and examined by Will[2] who described three solid derivatives of glycerol 1,3-dinitrate (hydrate, m. p. 26°; benzoate, m. p. 67°; *p*-nitrobenzoate, m. p. 94°) and a *p*-nitrobenzoate of glycerol 1,2-dinitrate, m. p. 81°. The orientation of substituents assigned to the dinitrates depended upon results of nitration experiments involving the isomeric mononitrates of glycerol. That mononitrate which yielded only one dinitrate on further nitration was assigned the 2-nitrate structure and the corresponding dinitrate was assumed to be the 1,2-derivative.

It is of interest to establish reliable data for derivatives of the lower nitrates of glycerol since earlier work largely depends on the melting points of derivatives prepared by Will. For example, Berl and Delpy[3] studied the action of alcoholic potassium hydroxide on glycerol trinitrate, and identified glycerol 1,3-dinitrate as a denitration product, after isolating the *p*-nitrobenzoate described by Will. Similarly, Farmer[4] prepared the benzoate

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[1] Naoum (trans. Symmes), "Nitroglycerine and Nitroglycerine Explosives," Williams and Wilkins, Baltimore, 1928, p. 162.

[2] Will, *Ber.*, 1908, **41**, 1107.

[3] Berl and Delpy, *Ber.*, 1910, **43**, 1425.

[4] Farmer, *J.*, 1920, **117**, 814.

of glycerol 1,3-dinitrate from a product, presumably glycerol 1,3-dinitrate, obtained by partial hydrolysis of glycerol trinitrate in dilute nitric acid.

We have prepared the isomeric dinitrates by reaction between the dibromohydrins of glycerol and silver nitrate in acetonitrile. Solid derivatives were obtained by treating the nitric esters with various acid chlorides. Confirmation that no migration of substituents occurs was obtained by preparing glycerol 1,2-dinitrate and its derivatives by the action of silver nitrate and iodine on allyl alcohol and its esters, and also by nitrating 1-glycerides to form the corresponding esters of glycerol 1,2-dinitrate.

A number of nitric esters have been prepared by the metathetical reaction between silver nitrate and an alkyl halide.[5] Periodic weighing of precipitated silver bromide showed that glycerol dibromohydrins react only slowly with silver nitrate at room temperature, glycerol 1,3-dibromohydrin being the more reactive isomer. This order of reactivity was confirmed when the metatheses were performed in boiling acetonitrile.

Glycerol 1,3-dinitrate was also prepared by partial nitration of glycerol using dilute mixed acid; only small amounts of glycerol 2-nitrate and glycerol 1,2-dinitrate were formed.

A French patent [6] describes the nitration of glycidol (2,3-epoxypropan-1-ol) nitrate to yield mixed glycerol dinitrates; no attempt was made to determine which isomer predominated in the mixture. We treated glycidol nitrate in dioxan with nitric acid and obtained a product which possessed an infrared (i.r.) spectrum similar to that of glycerol 1,3-dinitrate and gave a low yield of the corresponding *p*-nitrobenzoate; determination of nitrogen content showed that the product was very impure. Formation of glycerol 1,3-dinitrate is in accord with the observation [7] that unsymmetrical epoxides react with nitric acid in dioxan to yield primary nitric esters.

Little use has been made of the reaction between olefins and iodine–silver nitrate [8] to prepare nitric esters. We found that allyl alcohol and allyl esters react rapidly with the reagent in boiling acetonitrile to yield glycerol 1,2-dinitrate and corresponding derivatives. Although rapid reaction also occurs with allyl 3,5-dinitrobenzoate, the initial product is an intermediate iodohydrin, probably the 3,5-dinitrobenzoate of glycerol 2-iodohydrin 1-nitrate, formed by electrophilic addition of iodonium nitrate to the double bond polarised by the 3,5-dinitrobenzoylmethyl group. It was not possible to isolate intermediate iodohydrins in experiments with allyl *m*-nitrobenzoate or allyl *p*-nitrobenzoate.

Properties of derivatives of the isomeric dinitrates (Table 2) confirm those reported by Will [2] with regard to their benzoates and the *p*-nitrobenzoate of glycerol 1,3-dinitrate. Two polymorphic forms of the last compound were obtained and the properties of the higher-melting, stable polymorph agree with those described by Will. The polymorphs gave characteristic *X*-ray powder diffraction photographs and different i.r. spectra in Nujol mulls; in acetone solution the i.r. spectra were identical. Appropriate seeding of a supercooled melt on the hot stage enabled interconversion of the polymorphs to occur. Will [2] gives the melting point of glycerol 1,2-dinitrate *p*-nitrobenzoate as 81° whereas the derivative isolated here melts at 95°. We considered whether this discrepancy may be due to polymorphism but found no indication that a lower-melting form could be obtained. In agreement with Will's observation, glycerol 1,2-dinitrate *p*-nitrobenzoate is more soluble in alcohol than is the corresponding derivative of glycerol 1,3-dinitrate.

The stable forms of the *p*-nitrobenzoates of the glycerol dinitrates have identical melting points and the compounds cannot be distinguished on this evidence alone. Similarity of melting points persists in the *m*-nitrobenzoates and 3,5-dinitrobenzoates, and for this reason i.r. analysis or *X*-ray diffraction are better methods of identification. It is of interest that the 3,5-dinitrobenzoate of glycerol 1,2-dinitrate also exhibits dimorphism.

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[5] Boschan, Merrow, and van Dolah, *Chem. Rev.*, 1955, **55**, 488.

[6] F.P. 847,260/1939.

[7] Nichols, Magnusson, and Ingham, *J. Amer. Chem. Soc.*, 1953, **75**, 4255; Ingham and Nichols, *ibid.*, 1954, **76**, 4477.

[8] Birkenbach and Goubeau, *Ber.*, 1934, **67**, 1420; Morris, *Chem. and Ind.*, 1958, 1291.

The structures of glycerol 1,2-dinitrate *p*-nitrobenzoate and of the corresponding 3,5-dinitrobenzoate were confirmed by nitrating appropriate 1-glycerides in acetic anhydride.

Denitration of glycerol trinitrate in aqueous ethanolic potassium hydroxide gave glycerol 1,2-dinitrate in addition to the 1,3-dinitrate isolated by Berl and Delpy.[3] A similar mixture was obtained by use of dilute nitric acid, although Farmer[4] reported only glycerol 1,3-dinitrate. Glycerol trinitrate reacts smoothly with sodium nitrite in aqueous ethanol,[9] giving glycerol 1,3-dinitrate in high yield. Hydrolysis of the secondary nitric ester group occurs in 70% sulphuric acid, glycerol 1,3-dinitrate and 1-nitrate being the chief products.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus. I.r. spectra of glycerol dinitrates and derivatives, measured with samples as liquid films or as Nujol mulls, using a Perkin-Elmer 237 grating spectrophotometer, have been submitted to the D.M.S. Index (Butterworths, London).

Glycerol 1,3-*Dinitrate*.—Redistilled glycerol 1,3-dibromohydrin (50 g.) was added to dry silver nitrate (120 g.) in acetonitrile (100 ml., distilled from phosphoric anhydride), and the mixture, after standing at room temperature overnight, was heated under reflux in the absence of light for 2 hr. Silver bromide (85·8 g., 99·5%) was filtered off from the cooled reaction mixture, and the filtrate and acetonitrile washings were added to a solution of sodium bromide (36 g.) in water to precipitate excess of silver as the bromide. The filtrate was continuously extracted with ether, and the dried ($MgSO_4$) extract was evaporated under diminished pressure to yield glycerol 1,3-dinitrate as a pale yellow liquid (39 g., 93·4%) which was obtained colourless after careful distillation behind a protective screen (CAUTION), b. p. 115—116°/0·6 mm. The product was converted into a crystalline hydrate, prisms, m. p. 25° (from ether) (lit.,[2] 26°), by adding 3% w/w of water and cooling in solid carbon dioxide for several days. The hydrate lost 0·31 mole of water per mole of dinitrate *in vacuo* over phosphoric anhydride, confirming Will's molecular formula, $(C_3H_6N_2O_7)_3,H_2O$, and yielding glycerol 1,3-dinitrate as a colourless liquid, n_D^{20} 1·4715 (lit.,[10] 1·4683, an unexpectedly low value in view of corresponding data for glycerol mononitrates[11]), d_4^{20} 1·523 g./c.c. (Found: C, 19·9; H, 3·5; N, 15·3. Calc. for $C_3H_6N_2O_7$: C, 19·8; H, 3·3; N, 15·4%).

Glycerol 1,2-*Dinitrate*.—When the above experiment was repeated using glycerol 1,2-dibromohydrin, the crude product contained unreacted halogen. The material was heated under reflux in acetonitrile (100 ml.) with more silver nitrate (20 g.) for 5 hr., and the product was isolated, in the usual manner, as a pale yellow liquid (32·6 g.) which was distilled under dimished pressure (CAUTION), to yield glycerol 1,2-dinitrate containing a small amount of water-insoluble oil. The crude dinitrate was examined by paper chromatography using Whatman No. 3MM paper and solvents consisting of the upper layers from mixtures of hexane, water, and methanol (20 : 3 : 7, 20 : 1 : 9 v/v). The yellow colour produced by ultraviolet irradiation after spraying with 1% ethanolic diphenylamine was used to locate nitric esters.[12] Glycerol 1,2-dinitrate was not eluted by the above solvent mixtures but impurities with R_F values from 0·25 to 0·44 were present. The impurities, isolated by column chromatography of crude glycerol 1,2-dinitrate on cellulose powder using hexane saturated with methanol as mobile phase, were shown by i.r. analysis to be glycerol trinitrate and a carbonyl-containing compound. On paper the R_F values were: glycerol trinitrate, 0·40 (20 : 3 : 7 solvent mixture), 0·26 (20 : 1 : 9); carbonyl compound, 0·40—0·44 (20 : 3 : 7) and 0·30 (20 : 1 : 9). These impurities were removed by dissolving the crude dinitrate (28·4 g.) in water (700 ml.), separating insoluble material (3·1 g.), and extracting the aqueous layer with ether (4 × 250 ml.). The extract was washed with 5% aqueous sodium hydrogen sulphite, water, 5% aqueous sodium carbonate, and water, dried ($MgSO_4$), and evaporated, to give glycerol 1,2-dinitrate (21·4 g., 51·1%) as a colourless liquid, b. p. 106°/0·5 mm., n_D^{20} 1·4714 (lit.,[10] 1·4682), d_4^{20} 1·523 g./c.c. (Found: C, 19·9; H, 3·4; N, 15·2%).

Solubility of Glycerol Dinitrates in Water.—Solubilities of the dinitrates in water at 20° were measured by preparing saturated solutions at 25°, cooling to 20° in a thermostat bath, and

[9] Honeyman and Morgan, *Adv. Carbohydrate Chem.*, 1957, **12**, 128.

[10] Urbanski and Witanowski, *Trans. Faraday Soc.*, 1963, **59**, 1047.

[11] Part II, following Paper.

[12] Coldwell, *Analyst*, 1959, **84**, 665; Jackson and Hayward, *J. Chromatog.*, 1961, **5**, 166.

separating aliquots which were weighed and evaporated to dryness to determine nitric ester content. Mean values from three determinations, using dinitrates which were colourless and free from halogen and from impurities detectable by paper chromatography and i.r. analysis, were: glycerol 1,2-dinitrate, 6·57 g./100 g.; glycerol 1,3-dinitrate, 7·84 g./100 g. water.

Relative Rates of Reaction of Glycerol Dibromohydrins with Silver Nitrate.—Portions (1·06 g. 0·00486 mole) of the glycerol dibromohydrins were placed in a series of 25-ml. stoppered flasks and treated with 4·77M-silver nitrate (in acetonitrile) (3 ml., 0·0143 mole). The flasks were kept in the dark and the rate of reaction was observed by weighing silver bromide at suitable intervals after removing supernatant solution and washing the residue with a small amount of acetonitrile.

TABLE 1.

Relative rates of reaction of glycerol dibromohydrins with silver nitrate in acetonitrile.

Reaction period (days)		1	2	3	7	11	15	23	32
Extent of reaction (%)	Glycerol 1,2-dibromohydrin	40·9	52·8	61·3	77·4	79·0	86·9	92·9	99·2
	Glycerol 1,3-dibromohydrin	56·0	68·7	77·0	93·6	98·2	99·4	—	—

Partial Nitration of Glycerol.—Glycerol (50 g., 0·54 mole) was added dropwise during 15 min. to a cooled (20°), stirred mixture of sulphuric acid (163 g., 1·66 moles), nitric acid (55 g., 0·87 mole), and water (22 g., 1·20 moles). After a further 10 min. the mixture was poured into water (1·5 l.), giving glycerol trinitrate as a colourless oil, and an aqueous solution (A) containing the lower nitrates of glycerol.

Ether extraction of aqueous solution A; isolation of glycerol 1,3-*dinitrate.* A mixture of dinitrates, containing some trinitrate, was obtained by extracting solution A with ether (4 × 100 ml.) and washing the extract with 4% aqueous sodium carbonate (50 ml.) and water (50 ml.). The oil from four experiments was treated with water (1 l.) to give aqueous solution B and a further quantity of glycerol trinitrate as a water-insoluble oil. Total yield of trinitrate from four nitrations was 53·8 g. (10·9%). An ether extract C (1 × 300 ml.) of aqueous solution B was treated with calcium chloride to remove glycerol 1-nitrate,[11] filtered, and evaporated, to yield the dinitrates as an oil (73·4 g., 18·6%). Water (2·45 g.) was added to the oil, and the cooled (0°) mixture was seeded to obtain the hydrate of glycerol 1,3-dinitrate as a solid (46·6 g., 11·4%), which formed prisms, m. p. 25° (from ether, 15 ml.). The hydrate underwent dehydration to yield pure 1,3-dinitrate, identical with that prepared from glycerol 1,3-dibromohydrin. A portion (5 g.) of the oil (28·3 g.), obtained after separating the crystalline hydrate, reacted with *p*-nitrobenzoyl chloride in benzene–pyridine to give the mixed glycerol dinitrate *p*-nitrobenzoates; chromatography on alumina, using benzene as eluant, showed that the original mixture contained glycerol 1,3- and 1,2-dinitrate in the ratio 80 : 20, corresponding to yields of 5·7 and 1·4%, respectively, based on glycerol. Total yield of glycerol 1,3-dinitrate was 17·1%.

Continuous ether extraction of aqueous solutions A and B ; isolation of glycerol 2-*nitrate.* Aqueous solution A, from four nitrations, was neutralised with sodium carbonate, evaporated to half volume, filtered, and combined with solution B; extraction continuously with ether yielded an oil (90 g.) which was dissolved in water (solution D) and washed with ether (3 × 50 ml.) to remove glycerol dinitrates; this ether extract was added to extract C. The ether solution obtained by continuous extraction of solution D was stirred with granular calcium chloride for 24 hr., to give an insoluble calcium chloride complex of glycerol 1-nitrate which was collected by filtration. Evaporation of the filtrate yielded an oil (5·9 g.) consisting of glycerol 2-nitrate contaminated with 1-nitrate. Most of the latter was removed by redissolving the oil in ether (100 ml.) and treating the solution with another portion of calcium chloride in the presence of water (2 ml.). Final traces of 1-nitrate were destroyed by adding an aqueous solution (25 ml.) of periodic acid (3 g.) to the mononitrate (3·7 g.) in water (25 ml.). After 5 hr. the solution was neutralised with aqueous sodium hydroxide and extracted continuously with ether, to give glycerol 2-nitrate as an oil which crystallised from ether as needles, m. p. 54° (lit.,[2] 54°) (3·0 g., 1%) (Found: C, 26·0; H, 5·5; N, 10·4. Calc. for $C_3H_7NO_5$: C, 26·3; H, 5·1; N, 10·2%).

Isolation of glycerol 1-*nitrate.* Water (500 ml.) was added to the calcium chloride residues, then, after precipitation of calcium carbonate with sodium carbonate, the filtered solution was continuously extracted with ether, to give glycerol 1-nitrate, prisms (from ether), m. p. 55°

(lit.,[2] 58—59°) (43·2 g., 14·5%) (Found: C, 26·6; H, 5·5; N, 10·2; vincinal OH, 24·5. Calc. for $C_3H_7NO_5$: vincinal OH, 24·8%).

Nitration of Glycidol Nitrate in Dioxan.—Nitric acid (*d* 1·5) (5 ml.) and a solution of glycidol nitrate (12 g.) in anhydrous dioxan (40 ml.) were added dropwise to stirred, cooled (0°) dioxan (10 ml.) [7] during 75 min., and the mixture was heated at 40° for 1 hr., cooled, neutralised with sodium hydrogen carbonate, and filtered. Evaporation of dioxan under diminished pressure gave a colourless liquid (14·5 g.) which was dissolved in ether and washed with aqueous sodium hydrogen sulphite, sodium carbonate, and water. The i.r. spectrum of this product resembled that of glycerol 1,3-dinitrate but nitrogen content (13·0%) was low. Presence of 1,3-dinitrate was confirmed by treating the product (2 g.) with *p*-nitrobenzoyl chloride (3·1 g.) in benzene–pyridine, to give the *p*-nitrobenzoate of glycerol 1,3-dinitrate (0·75 g., 21%), identified by i.r. and *X*-ray analysis.

Derivatives of Glycerol Dinitrates.—These were prepared by treating each dinitrate with the acid chloride in benzene–pyridine; the *compounds* are described in Table 2.

TABLE 2.

Derivatives of glycerol dinitrates.

No.	Derivative	Form	Solvent	M. p.
		Glycerol 1,2-*dinitrate*		
1	Benzoate	Oil	—	—
2	*m*-Nitrobenzoate	Needles	MeOH	78°
3	*p*-Nitrobenzoate	Plates	MeOH–H_2O	95 (lit.,[2] 81)
4	3,5-Dinitrobenzoate	Thick needles	MeOH	78
5		Fine needles	Et_2O	88
6	*p*-Methoxybenzoate *	Tablets	Bz–Pet (b. p. 40—60°)	77
		Glycerol 1,3-*dinitrate*		
7	Benzoate	Thick needles	MeOH	66 (lit.,[2] 67)
8	*m*-Nitrobenzoate	Needles	Et_2O	71—72
9	*p*-Nitrobenzoate	Plates	EtOH	81—82
10		Prisms	EtOH	95 (lit.,[2] 94)
11	3,5-Dinitrobenzoate	Short rods	Et_2O	87

	Found (%)				Required (%)		
No.	C	H	N	Formula	C	H	N
1	41·8	3·7	9·8	$C_{10}H_{10}N_2O_8$	42·0	3·5	9·8
2	36·7	2·6	12·6	$C_{10}H_9N_3O_{10}$	36·3	2·7	12·7
3	36·3	2·7	12·7	,,	,,	,,	,,
4	32·2	2·3	14·2	$C_{10}H_8N_4O_{12}$	31·9	2·1	14·9
5	32·0	2·3	14·9	,,	,,	,,	,,
6	41·7	3·9	8·7	$C_{11}H_{12}N_2O_9$	41·8	3·8	8·9
7	41·9	3·6	9·8	$C_{10}H_{10}N_2O_8$	42·0	3·5	9·8
8	36·8	3·0	12·6	$C_{10}H_9N_3O_{10}$	36·3	2·7	12·7
9	36·8	3·0	12·8	,,	,,	,,	,,
10	36·3	3·0	12·9	,,	,,	,,	,,
11	32·2	2·2	14·7	$C_{10}H_8N_4O_{12}$	31·9	2·1	14·9

* Separated from anisic anhydride by chromatography on alumina, using benzene as eluant.

Action of Iodine–Silver Nitrate on Allyl Esters and Allyl Alcohol.—Allyl *p*-nitrobenzoate,[13,14] allyl 3,5-dinitrobenzoate,[14] and *allyl* m-*nitrobenzoate*, b. p. 131—132°/0·5 mm., m. p. 21° (Found: C, 58·3; H, 4·7; N, 6·5. $C_{10}H_9NO_4$ requires C, 58·0; H, 4·4; N, 6·8%), were prepared in the usual manner.

General procedure. A solution of the ester (0·03 mole) and silver nitrate (0·09 mole) in acetonitrile (100 ml.) was heated under reflux and treated with iodine (0·035 mole), added by percolation during 1—2 hr. After being heated for a further 3 hr. the mixture was cooled and filtered into water, to yield the product as an oil which was isolated by extraction, crystallised from the appropriate solvent, and identified by i.r. analysis and *X*-ray powder diffraction.

By this procedure, allyl *m*-nitrobenzoate and allyl *p*-nitrobenzoate were converted into the *m*-nitrobenzoate (26%) and *p*-nitrobenzoate (47%) of glycerol 1,2-dinitrate.

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[13] Meisenheimer, *Ber.*, 1919, **52**, 1675; Adams, Rideal, Burnett, Jenkins, and Dreger, *J. Amer. Chem. Soc.*, 1926, **48**, 1768.

[14] Fairbourne and Foster, *J.*, 1926, 3147.

When a reduced amount of silver nitrate (0·06 mole) and a shorter reaction period (addition of iodine during 30 min. and no further heating) were used, allyl 3,5-dinitrobenzoate yielded a product which is probably the *3,5-dinitrobenzoate of glycerol 2-iodohydrin 1-nitrate*, needles (from absolute methanol), m. p. 89° (34%) (Found: C, 27·3; H, 1·9; I, 28·5; N, 9·2%; *M*, 429. $C_{10}H_8IN_3O_9$ requires C, 27·2; H, 1·8; I, 28·8; N, 9·5%; *M*, 441). The iodohydrin (0·0045 mole) was converted into the 3,5-dinitrobenzoate of glycerol 1,2-dinitrate (91·5%) by heating with silver nitrate (0·0096 mole) in boiling acetonitrile (50 ml.) for 70 hr. The dinitrate (70%) was also obtained when allyl 3,5-dinitrobenzoate (0·02 mole) was treated with iodine (0·024 mole) and silver nitrate (0·06 mole) in boiling acetonitrile for 70 hr.

With allyl alcohol, reaction was excessively vigorous and oxidative decomposition occurred. Better control was achieved by using a reduced proportion of silver nitrate (2 moles per mole of alcohol) and by adding iodine slowly in small portions. After being treated with aqueous sodium bromide to precipitate silver bromide, the filtrate from the reaction mixture was continuously extracted with ether, and the extract was washed with aqueous sodium thiosulphate to remove elemental iodine, and evaporated, to yield glycerol 1,2-dinitrate as a yellow liquid (69%).

Nitration of 1-*Glycerides*.—Glycerol 1-*p*-nitrobenzoate, m. p. 106—107° (107° [15]), and glycerol 1-(3,5-dinitrobenzoate), m. p. 119—120° (118° [16]) were prepared from corresponding esters of isopropylideneglycerol. Each 1-glyceride was added to nitric acid in acetic anhydride,[17] to yield glycerol 1,2-dinitrate *p*-nitrobenzoate, and the 3,5-dinitrobenzoate of glycerol 1,2-dinitrate. I.r. analysis and *X*-ray powder diffraction confirmed the identities of the products.

Denitration of Glycerol Trinitrate.—*In alkali*. Glycerol trinitrate (15 g.) in ethanol (200 ml.) was added slowly to a stirred, cooled (15°) solution of potassium hydroxide (7·4 g.) in 10% (v/v) aqueous ethanol (200 ml.). After 30 min. the decanted solution and ethanol washings were neutralised (dilute sulphuric acid), diluted with water (300 ml.), and concentrated under diminished pressure to remove ethanol. Unchanged trinitrate (6·89 g., 46%) was separated, then the aqueous solution was extracted with ether to give an oil (1·76 g.) which was treated with water (50 ml.) to yield a further quantity of glycercol trinitrate (1·11 g., 7%) as an insoluble residue. Ether extraction of the aqueous solution gave the mixed glycerol dinitrates (0·75 g., 6%); i.r. analysis of the *p*-nitrobenzoylated product showed that the mixture contained glycerol 1,2- and 1,3-dinitrate in the ratio 40 : 60.

In acid. A mixture of glycerol trinitrate (5·85 g.) and 0·2N-nitric acid (400 ml.) was stirred and heated at 70° for 7 hr., cooled, and neutralised with solid sodium carbonate. After separating unchanged trinitrate (3·75 g.), the aqueous solution was extracted with ether to give an oil (0·89 g.) which, in water (20 ml.), yielded glycerol trinitrate (0·59 g.) as an insoluble residue (total recovery of trinitrate, 74%). Mixed glycerol dinitrates (0·3 g., 6·4%) were obtained by extracting the aqueous solution with ether; the ratio of glycerol 1,2-dinitrate to the 1,3-dinitrate was 60 : 40 (measured by i.r. and *X*-ray analysis after *p*-nitrobenzoylation). Continuous ether extraction of the aqueous residues gave a small amount (0·04 g., 1·1%) of glycerol 1-nitrate as an oil, identified by i.r. analysis.

Glycerol trinitrate (4·95 g.) was stirred with 70% (w/w) sulphuric acid at room temperature for 1 hr., and the mixture was diluted with water (250 ml.), neutralised, and extracted with ether, to yield glycerol 1,3-dinitrate (0·52 g., 13%); continuous ether extraction gave glycerol 1-nitrate (0·93 g., 31%). Both products were characterised as *p*-nitrobenzoates.

By reaction with sodium nitrite. A solution of glycerol trinitrate (4·06 g.) in ethanol (30 ml.) was heated under reflux with sodium nitrite (3·71 g.) in water (7·5 ml.) for 24 hr. After adding water (50 ml.), ethanol was removed under diminished pressure, and the aqueous solution was extracted with ether to yield glycerol 1,3-dinitrate as an oil (1·72 g., 53%), characterised by *p*-nitrobenzoylation. Glycerol 1-nitrate (0·21 g., 9%), identified by i.r. analysis, was obtained by continuous ether extraction of the aqueous solution.

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[15] Fischer, Bärwind, and Bärwind, *Ber.*, 1920, **53**, 1596.
[16] Fairbourne and Foster, *J.*, 1925, **127**, 2763.
[17] Honeyman and Morgan, *Chem. and Ind.*, 1953, 1035.