

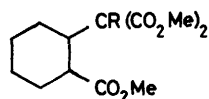
Preparation of Some Nitro-triesters, and a Synthesis of $\gamma\gamma$ -Bis(methoxycarbonyl)- γ -lactones

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The condensation of dimethyl nitromalonate with methyl acrylate led to either dimethyl α -methoxycarbonyl- α -nitroglutarate or dimethyl 1-methoxycarbonyl- γ -nitropimelate, depending on the nature of the basic catalyst and the conditions. Michael addition of dimethyl nitromalonate to more highly substituted $\alpha\beta$ -olefinic esters could not be achieved.

Treatment of three $\gamma\gamma$ -bis(methoxycarbonyl)-esters with cold fuming nitric acid gave $\gamma\gamma$ -bis(methoxycarbonyl)- γ -butyrolactones accompanied in two cases by smaller amounts of the γ -nitro-triesters; a $\delta\delta$ -bis(methoxycarbonyl)-ester gave the δ -hydroxy- and the δ -nitro-triester.

We report the results of an investigation into the synthesis of nitro-triesters of types (1a) and (2a).



(1)



(2) $\alpha, \text{R} = \text{NO}_2$

The Michael addition of a nitromalonic ester to an $\alpha\beta$ -olefinic ester has not been reported hitherto, although the reaction¹ of dimethyl nitromalonate with a mixture of methyl acetoacetate and formaldehyde to give (2; $\text{R} = \text{NO}_2$, $\text{R}^1 = \text{MeCO}$, $\text{R}^2 = \text{H}$) must involve a step of this sort. Reaction of dimethyl nitromalonate² with an equimolar amount of methyl acrylate, using Triton B catalyst, gave dimethyl α -methoxycarbonyl- α -nitroglutarate (2; $\text{R} = \text{NO}_2$, $\text{R}^1 = \text{R}^2 = \text{H}$) in 31% yield.

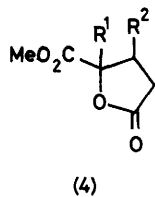
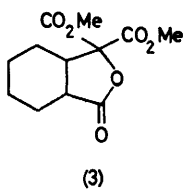
¹ H. Hellmann and D. Dieterich, *Annalen*, 1960, **632**, 73; 1962, **656**, 63.

When two molar proportions of methyl acrylate were used compound (2; $\text{R} = \text{NO}_2$, $\text{R}^1 = \text{R}^2 = \text{H}$) was accompanied by a second product. This was separated by preparative g.l.c. and identified as dimethyl γ -methoxycarbonyl- γ -nitropimelate by comparison with a sample prepared by condensation of methyl nitroacetate with methyl acrylate in the presence of Triton B. When tetramethylguanidine was used as catalyst for the condensation of dimethyl nitromalonate with methyl acrylate (in a 1 : 2 molar ratio) the only product was dimethyl γ -methoxycarbonyl- γ -nitropimelate. Presumably the nitropimelate is formed by the demethoxycarbonylation of the first-formed adduct (2; $\text{R} = \text{NO}_2$, $\text{R}^1 = \text{R}^2 = \text{H}$) by a retro-Claisen reaction involving nucleophilic attack at one of the malonate ester carbonyl groups by the catalyst, followed by Michael addition of the resultant nitrodiester to a second molecule of methyl acrylate. We have been unable to find conditions under which dimethyl nitromalonate will undergo Michael addition to either

² D. I. Weisblat and D. A. Lytte, *J. Amer. Chem. Soc.*, 1949, **71**, 3079.

methyl crotonate or methyl cyclohex-1-enecarboxylate, although a wide variety of catalysts (Triton B, piperidine, triethylamine, sodium methoxide, tetramethylguanidine, and potassium fluoride) was explored. The effect of increasing substitution in inhibiting the Michael acceptor activity of $\alpha\beta$ -olefinic carbonyl compounds towards nitroalkanes had been noted previously.³

As ethyl cyclohex-1-enecarboxylate had been shown⁴ to undergo the Michael reaction with diethyl malonate, we carried out the corresponding condensation in the methyl ester series to prepare the triester (1; R = N) * and investigated the nitration of this as a route to the desired nitro-triester (1a). An attempt to convert (1) into (1a) by the acetone cyanohydrin nitrate method⁵ was unsuccessful. The reaction also failed with dimethyl α -methoxycarbonyl- β -methylglutarate (2; R = R¹ = H; R² = Me) but we did isolate dimethyl α -methoxycarbonyl- α -nitroglutarate (2; R = NO₂, R¹ = R² = H), identical with the material prepared *via* the Michael reaction, in very low yield, when the reaction was applied to dimethyl α -methoxycarbonylglutarate (2; R = R¹ = R² = H). In a second approach we investigated the reactions of the triesters (1) and (2) with fuming nitric acid; the method⁶ has been applied successfully to the nitration of simple dialkyl malonates. Treatment of the triester (1) with fuming nitric acid gave one major, nitrogen-free product, identified by microanalytical data and spectroscopic properties, particularly an absorption at 1 815 cm⁻¹, as the lactone (3); none of the desired



nitro-triester (1a) was formed. Treatment of the triester (2; R = R¹ = R² = H) with fuming nitric acid gave two products, which were separated by preparative g.l.c. The minor product was identified as the nitro-ester (2; R = NO₂, R¹ = R² = H) by direct comparison with the material prepared by the two methods already described. The major product, which had an absorption at 1 815 cm⁻¹, was identified as the lactone (4; R¹ = CO₂Me, R² = H). Similarly the triester (2; R = R¹ = H, R² = Me) gave a mixture of the desired nitrotriester (2; R = NO₂, R¹ = H, R² = Me) and the lactone (4; R¹ = CO₂Me, R² = Me) which had an absorption at 1 810 cm⁻¹. The introduction of a methoxycarbonyl group into the γ -

* The stereochemistry of these compounds, which contain two chiral centres and so may be present as mixtures of two racemic modifications, has not been investigated; they run as a single material on g.l.c.

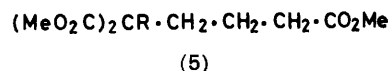
³ S. Kambe and H. Yasuda, *Bull. Chem. Soc. Japan*, 1966, **39**, 2549.

⁴ L. Helfer, *Helv. Chim. Acta*, 1926, **9**, 814.

⁵ W. D. Emmons and J. P. Freeman, *J. Amer. Chem. Soc.*, 1955, **77**, 4385, 4391.

butyrolactone structure (4; R¹ = R² = H) shifts⁷ the lactone carbonyl absorption to 1 800 cm⁻¹; and in the lactones (3) and (4; R¹ = CO₂Me, R² = H or Me) the effect of a second methoxycarbonyl group is to shift the absorption to even shorter wavelengths.

To see if this novel method for the synthesis of $\gamma\gamma$ -bis(methoxycarbonyl)-lactones was also applicable to the preparation of δ -lactones, we treated dimethyl α -methoxycarbonyladipate (5; R = H) with fuming nitric acid. Two products were obtained, neither of which was a δ -lactone. Microanalytical and spectroscopic data



showed that the major product was dimethyl α -hydroxy- α -methoxycarbonyladipate (5; R = OH) and the minor product dimethyl α -methoxycarbonyl- α -nitroadi-pate (5; R = NO₂).

The production of γ -lactones by the oxidation of certain alkanolic acids having a tertiary γ -hydrogen atom with fuming nitric acid was observed many years ago by Brecht,⁸ who also observed the introduction of hydroxy- and nitro-groups when there was a tertiary hydrogen atom at the β -position. Current views⁶ on the mechanism of aliphatic nitration by fuming nitric acid lead us to suggest that all the observed products arise as a result of initial abstraction of the tertiary hydrogen atoms in the substrates which we have examined by an NO₃[•] radical, to give organic radicals in which the unpaired electron is delocalised over the two adjacent ester carbonyl groups. The γ -lactones are then formed by cyclisation of this type of radical onto the non-adjacent ester carbonyl group, followed by further oxidation and loss of the methyl group attached to oxygen by nucleophilic attack. We further suggest that the production of (5; R = OH or NO₂) involves radical coupling, of known types,⁶ to give the nitro-ester (5; R = NO₂) directly, or some precursor [*e.g.* (5; R = ONO₂)] which would be hydrolysed to the hydroxy-ester (5; R = OH) during work-up. Distillation of methyl 4-hydroxybutanoate gives⁹ a 3 : 1 mixture of that ester and γ -butyrolactone, but we discount the possibility that the γ -lactones (3) and (4) arise by internal transesterification of the corresponding γ -hydroxy-esters, as the lactones (3) and (4) are formed prior to any distillation step in our experiments. Methyl 5-hydroxypentanoate can be distilled unchanged,⁹ as can our analogous product (5; R = OH).

EXPERIMENTAL

¹H N.m.r. spectra were recorded with a Perkin-Elmer R12 or Varian HA 100 instrument for solutions in CCl₄.

⁶ O. von Schickh, H. G. Padeken, and A. Segnitz, in 'Methoden der Organischen Chemie (Houben-Weyl)', Thieme Verlag, Stuttgart, vol. 10, part 1, 1971, Section A1.

⁷ H. Machleidt, *Annalen*, 1964, **676**, 66.

⁸ J. Brecht and J. B. C. Kershaw, *Ber.*, 1899, **32**, 3661; J. Brecht, *Ber.*, 1881, **14**, 1780; 1882, **15**, 2318.

⁹ H. Machleidt, E. Cohnen, and R. Tschesche, *Annalen*, 1962, **655**, 70.

unless otherwise stated (Me_4Si as internal standard). In all cases the integration agreed with the proton assignments. I.r. spectra were measured with a Perkin-Elmer 157G or 457 instrument. Low resolution mass spectra were obtained with an A.E.I. MS-12 instrument and high resolution mass spectra with an A.E.I. MS-9 instrument. Analytical g.l.c. was carried out with a Perkin-Elmer F11 chromatograph containing glass columns (3 mm inside diameter) of 2.5% OV 17 on 80–100 Chromosorb G. Preparative g.l.c. was carried out with a Pye 105 chromatograph containing glass columns (8 mm inside diameter) of 1% OV 17 on 60–80 Chromosorb G except where otherwise stated. Both instruments used flame ionisation detectors, with nitrogen as carrier gas. Solutions in organic solvents were dried over magnesium sulphate.

Starting Materials.—Methyl nitroacetate,¹⁰ b.p. 82–86° at 10 mmHg (lit.,¹¹ 93–94° at 15 mmHg), dimethyl nitromalonate,² b.p. 116–118° at 9 mmHg (lit.,¹² 124° at 16 mmHg), acetone cyanohydrin nitrate,⁵ b.p. 70° at 17 mmHg (lit.,⁵ 65–66° at 10 mmHg), methyl 4-bromobutanoate,¹³ b.p. 76–78° at 16 mmHg (lit.,¹⁴ 77° at 15 mmHg), dimethyl α -methoxycarbonylglutarate,¹⁵ b.p. 140° at 10 mmHg (lit.,¹⁶ 147° at 12 mmHg), and dimethyl α -methoxycarbonyl- β -methylglutarate,¹⁷ b.p. 95–96° at 0.3 mmHg (lit.,¹⁷ b.p. 110° at 0.3 mmHg), were prepared by methods described in the literature. Methyl cyclohex-1-enecarboxylate, b.p. 70° at 9 mmHg (lit.,¹⁸ 86° at 15 mmHg) was prepared¹⁸ from bromocyclohexane *via* cyclohexanecarboxylic acid.¹⁹

Preparation of Dimethyl γ -Methoxycarbonyl- γ -nitropimelate.²⁰—Methyl acrylate (6.9 g, 0.084 mol) was added slowly to methyl nitroacetate (5.0 g, 0.042 mol) and Triton B (2 ml) in dioxan (20 ml). The mixture was then maintained at 60–65 °C for 24 h, cooled to room temperature, diluted with dichloromethane (30 ml), and acidified with m-hydrochloric acid. The organic layer was separated, washed with water (3 \times 75 ml), and dried. Distillation gave dimethyl γ -methoxycarbonyl- γ -nitropimelate (7.4 g, 61%), b.p. 164–166° at 0.5 mmHg, ν_{max} 1745 and 1550 cm^{-1} , δ 2.2–2.55 (m, 4 \times CH_2), 3.63 (s, 2 \times Me), and 3.79 [s, $\text{C}(\text{NO}_2)\text{CO}_2\text{Me}$], m/e 260 ($M^+ - \text{OMe}$), 232 ($M^+ - 2 \times \text{OMe}$), and 214 ($M^+ - \text{OMe}$ and NO_2) (Found: C, 45.5; H, 6.0; N, 4.8. $\text{C}_{11}\text{H}_{17}\text{NO}_8$ requires C, 45.4; H, 5.8; N, 4.8%).

Reaction of Dimethyl Nitromalonate with Methyl Acrylate.—(i) Methyl acrylate (8.6 g, 0.1 mol) was added slowly to a stirred solution of dimethyl nitromalonate (8.8 g, 0.05 mol) and Triton B (2.5 ml) in dioxan (20 ml). The mixture was then maintained at 60–65 °C for 24 h, cooled to room temperature, diluted with dichloromethane (30 ml), and acidified with m-hydrochloric acid. The organic layer was separated, washed with water (3 \times 75 ml), dried, and distilled, giving an oil (7.3 g), b.p. 182–200° at 13 mmHg, shown by analytical g.l.c. to contain two products in the ratio 1.3 : 1 (peak areas). Preparative g.l.c. (150–250 °C at 4° min^{-1}) gave dimethyl α -methoxycarbonyl- α -nitroglutarate, ν_{max} 1755 and 1565 cm^{-1} , δ 2.5–2.75 (m, 2 \times

CH_2), 3.68 (s, $\text{CH}_2\text{CO}_2\text{Me}$), and 3.86 [s, $\text{C}(\text{NO}_2)(\text{CO}_2\text{Me})_2$], m/e 232 ($M^+ - \text{OMe}$) and 217 ($M^+ - \text{NO}_2$) (Found: C, 41.3; H, 5.1; N, 5.2. $\text{C}_9\text{H}_{13}\text{NO}_8$ requires C, 41.1; H, 5.0; N, 5.3%) (major product); and dimethyl γ -methoxycarbonyl- γ -nitropimelate, identical (g.l.c., i.r., n.m.r.) with an authentic sample. (ii) A similar condensation using methyl acrylate (4.3 g, 0.05 mol), dimethyl nitromalonate (8.8 g, 0.05 mol), and Triton B (1.25 ml) gave dimethyl α -methoxycarbonyl- α -nitroglutarate (3.8 g, 31%), b.p. 124–125° at 0.2 mmHg. (iii) A similar condensation using methyl acrylate (4.3 g, 0.05 mol), dimethyl nitromalonate (4.4 g, 0.025 mol), and tetramethylguanidine (2 ml), gave dimethyl γ -methoxycarbonyl- γ -nitropimelate (4.2 g, 58%).

Dimethyl 2-Methoxycarbonylcyclohexylmalonate.—Methyl cyclohex-1-enecarboxylate (5.0 g, 0.035 mol) was refluxed for 18 h with methanolic 1.4M-dimethyl sodiomalonate (25 ml, 0.035 mol). Methanol was distilled off and the residue, after cooling, was neutralised with aqueous 10% sulphuric acid. The mixture was diluted with ether and filtered, and the ethereal layer was dried (K_2CO_3). Distillation then gave the triester (2.4 g, 25%), b.p. 114–116° at 0.2 mmHg, ν_{max} 1735 cm^{-1} , δ 1.2–2.5 (ring protons), 3.41 [d, J 4 Hz, $\text{CH}(\text{CO}_2\text{Me})_2$], 3.6 (s, CO_2Me), and 3.65 [s, $\text{CH}(\text{CO}_2\text{Me})_2$], m/e 272 (M^+), 241 ($M^+ - \text{OMe}$), 213 ($M^+ - \text{CO}_2\text{Me}$), and 210 ($M^+ - 2 \times \text{OMe}$), which ran as a single peak on analytical g.l.c. (Found: m/e , 272.1260. $\text{C}_{13}\text{H}_{20}\text{O}_6$ requires M , 272.1260).

Dimethyl α -Methoxycarbonyladipate.—Methyl 4-bromobutanoate (18.3 g, 0.1 mol) was added dropwise to methanolic 2M-dimethyl sodiomalonate (50 ml, 0.1 mol). The mixture was then refluxed for 7 h, cooled, and poured into 2M-hydrochloric acid (200 ml). Extraction with ether then gave dimethyl α -methoxycarbonyladipate (12.7 g, 55%), b.p. 111–114° at 0.2 mmHg, ν_{max} 1735 cm^{-1} , δ 1.4–1.95 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 2.22 (t, J 7 Hz, MeO_2CCH_2), 3.26 (t, J 7 Hz, CH), 3.52 (s, MeO_2CCH_2), and 3.60 [s, $\text{CH}(\text{CO}_2\text{Me})_2$], m/e 233 ($M^+ + 1$), 232 (M^+), 201 ($M^+ - \text{OMe}$), and 172 ($M^+ - \text{CO}_2\text{Me}$) (Found: C, 51.9; H, 7.1. $\text{C}_{10}\text{H}_{16}\text{O}_6$ requires C, 51.7; H, 6.9%).

Reactions of Triesters with Fuming Nitric Acid.—(i) Dimethyl α -methoxycarbonylglutarate (5.0 g, 0.023 mol) was placed in a three-necked flask fitted with a dropping funnel, a thermometer dipping into the liquid, and a water condenser protected by a calcium chloride tube. Fuming nitric acid (10 ml) was added dropwise, with stirring, at a rate which maintained the temperature in the range 5–15 °C, and the stirring was continued for 3½ h. The solution was then poured into ice-water (500 ml) and the mixture was extracted with toluene (3 \times 100 ml). The combined extracts were washed with water (2 \times 100 ml) and then with portions (150 ml) of aqueous 5% urea (until a starch-potassium iodide test for nitrogen oxides in the aqueous layer was negative), dried, and distilled to give an oil (1.8 g), b.p. 140–142° at 0.7 mmHg, shown by analytical

¹⁰ F. L. M. Pattison, R. L. Buchanan, and F. H. Dean, *Canad. J. Chem.*, 1965, **43**, 1700.

¹¹ K. Schank and N. Moell, *Chem. Ber.*, 1969, **102**, 71.

¹² K. Osugi, *J. Pharm. Soc. Japan*, 1955, **75**, 1549.

¹³ W. J. Bailey and R. A. Baylouny, *J. Amer. Chem. Soc.*, 1959, **81**, 2126.

¹⁴ H. Gilman and E. A. Zoellner, *J. Amer. Chem. Soc.*, 1931, **53**, 1945; H. Gilman and R. H. Kirby, *Org. Synth.*, Coll. Vol. 1, 1941, p. 361.

¹⁵ Cf. N. J. Leonard and G. L. Schoemaker, *J. Amer. Chem. Soc.*, 1949, **71**, 1763.

¹⁰ V. M. Rodionov, E. V. Mashinskaya, and V. M. Belikov, *Zhur. obshchei Khim.*, 1948, **18**, 917 (*Chem. Abs.*, 1949, **43**, 127).

¹¹ H. Feuer, H. B. Hass, and K. S. Warren, *J. Amer. Chem. Soc.*, 1949, **71**, 3078.

¹² F. Arndt and J. D. Rose, *J. Chem. Soc.*, 1935, 1.

¹³ A. W. D. Avison and A. L. Morrison, *J. Chem. Soc.*, 1950, 1471.

¹⁴ E. S. Ferninandi and G. Just, *Canad. J. Chem.*, 1971, **49**, 1070.

g.l.c. to contain two products in the ratio 7 : 6 (peak areas). Preparative g.l.c. gave $\gamma\gamma$ -bis(methoxycarbonyl)- γ -butyrolactone, ν_{\max} 1 815 and 1 755 cm^{-1} , δ 2.58 (A_2B_2 , $\text{CH}_2\cdot\text{CH}_2$) and 3.82 (s, $2 \times \text{CO}_2\text{Me}$), m/e 175 ($M^+ - \text{CO}$ and H), 158 ($M^+ - \text{CO}_2$), and 143 ($M^+ - \text{CO}_2\text{Me}$) [Found: C, 47.7; H, 5.2. $\text{C}_8\text{H}_{10}\text{O}_6$ requires C, 47.5; H, 4.9(5)%] (major product); and dimethyl α -methoxycarbonyl- α -nitroglutarate, identical (i.r. and n.m.r. data) with a sample isolated as described above. (ii) Reaction of dimethyl α -methoxycarbonyl- β -methylglutarate (5.4 g) with fuming nitric acid similarly gave material (3.0 g), b.p. 120–140° at 0.6 mmHg, shown by analytical g.l.c. to contain two products in the ratio 3 : 2 (peak areas), together with some of the starting triester. Preparative g.l.c. gave $\gamma\gamma$ -bis(methoxycarbonyl)- β -methyl- γ -butyrolactone, ν_{\max} 1 810 and 1 750 cm^{-1} , δ 1.4 (d, J 7 Hz, CHMe), 2.1–2.8 (AB of ABX, $\text{CH}_A\text{H}_B\cdot\text{CH}_X\text{Me}$), 2.9–3.25 (X of ABX), and 3.82 (s, $2 \times \text{CO}_2\text{Me}$), m/e 217 ($M^+ + 1$), 216 (M^+), and 157 ($M^+ - \text{CO}_2\text{Me}$) [Found: C, 50.0; H, 5.6(5)]. $\text{C}_9\text{H}_{12}\text{O}_6$ requires C, 50.0; H, 5.5(5)% (major product); and dimethyl α -methoxycarbonyl- β -methyl- α -nitroglutarate, ν_{\max} 1 765, 1 750, and 1 560 cm^{-1} , δ 1.2 (d, J 7 Hz, CHMe), 2.1–2.86 (AB of ABX, $\text{CH}_A\text{H}_B\cdot\text{CH}_X\text{Me}$), 3.1–3.3 (X of ABX), 3.65 (s, $\text{CH}_2\cdot\text{CO}_2\text{Me}$), and 3.85 [s, $\text{C}(\text{CO}_2\text{Me})_2$]; m/e 246 ($M^+ - \text{OMe}$) [Found: C, 43.4; H, 5.5(5); N, 4.9. $\text{C}_{10}\text{H}_{15}\text{NO}_8$ requires C, 43.3; H, 5.4; N, 5.0(5)%]. (iii) Reaction of dimethyl 2-methoxycarbonylcyclohexylmalonate (1.9 g) with fuming nitric acid similarly gave an oil, b.p. 160–170° at 2 mmHg, shown by analytical g.l.c. to be essentially a single product. Preparative g.l.c. gave dimethyl 9-oxo-8-oxabicyclo[4.3.0]nonane-7,7-dicarboxylate (3) (0.7 g, 39%), ν_{\max} 1 815 and 1 745 cm^{-1} , δ 1.1–2.3 (ring protons) and 3.82 (s, $2 \times \text{CO}_2\text{Me}$), m/e 197 ($M^+ - \text{CO}_2\text{Me}$) and 169 ($M^+ - \text{CO} - \text{CO}_2\text{Me}$) [Found: C, 56.3(5); H, 6.5. $\text{C}_{12}\text{H}_{16}\text{O}_8$ requires C, 56.2(5); H, 6.2(5)%]. (iv) Reaction of dimethyl α -methoxycarbonyladipate (5.0 g) with fuming nitric acid similarly gave material (1.9 g), b.p. 110–130° at 0.2 mmHg, shown by analytical g.l.c. (100–300 °C at

10° min^{-1}) to contain two products in the ratio 2 : 1 (peak areas) together with the starting triester. Preparative g.l.c. gave dimethyl α -hydroxy- α -methoxycarbonyladipate, ν_{\max} 3 250 (OH) and 1 740 cm^{-1} (ester CO), δ 1.5–1.7 (m, $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$), 1.85–2.05 (m, $\text{CH}_2\cdot\text{CO}_2\text{Me}$), 2.27 [t, J 7 Hz, $\text{CH}_2\cdot\text{C}(\text{OH})$], 3.6 (s, $\text{CH}_2\cdot\text{CO}_2\text{Me}$), and 3.76 [$2 \times$ s, HO and $\text{C}(\text{OH})(\text{CO}_2\text{Me})_2$], m/e 216 ($M^+ + 1 - \text{OMe}$) and 188 ($M^+ + 1 - \text{CO}_2\text{Me}$) [Found: C, 48.2; H, 6.7. $\text{C}_{10}\text{H}_{16}\text{O}_7$ requires C, 48.4; H, 6.4(5)%] (major product); and dimethyl α -methoxycarbonyl- α -nitroadipate, ν_{\max} 1 745 and 1 560 cm^{-1} , δ 1.71–2.0 (m, $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$), 2.32–2.56 ($\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$), 3.67 (s, $\text{CH}_2\cdot\text{CO}_2\text{Me}$), and 3.88 [s, $\text{C}(\text{CO}_2\text{Me})_2$], m/e 246 ($M^+ - \text{OMe}$) and 199 ($M^+ + 1 - \text{OMe} - \text{NO}_2$) [Found: C, 43.5; H, 5.6; N, 4.9. $\text{C}_{10}\text{H}_{15}\text{NO}_8$ requires C, 43.3; H, 5.4; N, 5.0(5)%].

Nitration of Dimethyl α -Methoxycarbonylglutarate with Acetone Cyanohydrin Nitrate.—Dimethyl α -methoxycarbonylglutarate (6.5 g, 0.03 mol) in dry tetrahydrofuran (25 ml) was added slowly to a slurry of sodium hydride (0.72 g, 0.03 mol) in tetrahydrofuran (25 ml). The mixture was then stirred and refluxed for 0.5 h and then cooled to room temperature. A solution of acetone cyanohydrin nitrate (1.3 g, 0.01 mol) in tetrahydrofuran (25 ml) was added slowly and the mixture was stirred and refluxed for 2 h. Unchanged hydride was decomposed with ethanol, and the mixture was then poured onto ice (500 g) and 10M-hydrochloric acid (25 ml). Extraction with ether gave an oil, which on distillation gave a fraction (4.5 g), b.p. 100–110° at 0.2 mmHg, shown by analytical g.l.c. to be essentially the starting triester containing 1% of a product. Preparative g.l.c. (10 ft Carbowax 20 M; 180 °C) gave a sample of the product, identified (i.r., n.m.r.) as dimethyl α -methoxycarbonyl- α -nitroglutarate.

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