

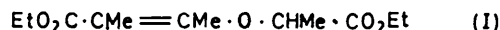
Synthesis and Stereochemistry of Some 3-Substituted 2-Methylbut-2-enoic Acid Derivatives

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U.v. irradiation of diethyl (*E*)-2,4,5-trimethyl-3-oxahex-4-enedioate gives the (*Z*)-isomer. The n.m.r. spectra of these two isomers and of other 3-substituted 2-methylbut-2-enoic acid derivatives are discussed. Diethyl (*E*)-2,4,5-trimethyl-3-oxahex-4-enedioate, identical with a product from the oxidation of ethyl α -methylacetoacetate by lead dioxide, has been synthesised from ethyl (*E*)-3-halogeno-2-methylbut-2-enoates by highly stereoselective substitution reactions, and further reactions of this type are described. The base-catalysed addition of ethanol to ethyl 2-methylbuta-2,3-dienoate is also highly stereoselective and gives ethyl (*E*)-3-ethoxy-2-methylbut-2-enoate.

The oxidation of mixtures of (*E*)- and (*Z*)-3-halogeno-2-methylbut-2-enals is described.

We earlier reported¹ that only one geometrical isomer of diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate (I) is

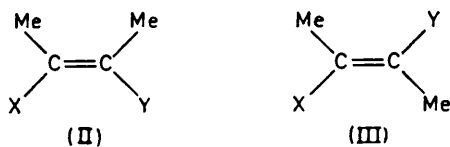


formed in the oxidation of ethyl α -methylacetoacetate with lead dioxide. The configurations of olefinic bonds

in 3-substituted 2-methylbut-2-enoic acid derivatives have been assigned on the basis of the chemical shifts of the protons in the β -methyl groups and the magnitudes of the methyl-methyl homoallylic coupling constants. The value of the homoallylic coupling constant of the

¹ R. Brettle and D. Seddon, *J. Chem. Soc. (C)*, 1970, 3120.

oxidation product (1.36 Hz) falls just below the lower end of the range reported for tetrasubstituted olefins having a transoid arrangement of methyl groups.² However u.v. irradiation of the oxidation product has now given a mixture which n.m.r. spectroscopy has shown to contain both the (*Z*)- and (*E*)-forms of diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate [(II) and (III),

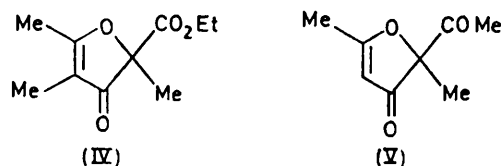


respectively; X = O·CHMe·CO₂Et, Y = CO₂Et]. Since the value of the homoallylic coupling constant of the new isomer (1.0 Hz) falls within the expected range² for a tetrasubstituted olefin having a cisoid arrangement of methyl groups, and since the protons in the β-methyl group of the new isomer absorb at higher field,² the oxidation product must have the (*E*)-configuration.

Reaction of ethyl (*E*)-3-bromo- or -chloro-2-methylbut-2-enoate with ethyl sodiolactate in refluxing benzene gave a low yield of diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate (I). The reactions were highly stereoselective and gave 99% of the (*E*)-isomer (III; X = O·CHMe·CO₂Et, Y = CO₂Et). The almost complete retention of configuration observed in these substitution reactions was also found in the reactions of alkyl (*E*)-3-chloro-2-methylbut-2-enoates with the corresponding alkoxides.³ The configurations of these products follow from the values of the methyl-methyl homoallylic coupling constants, which are very close to those found for diethyl (*E*)-2,4,5-trimethyl-3-oxahex-4-enedioate. We have also observed that in each of the (*E*)-enol ethers (III; X = O·CHMe·CO₂Et, OEt, or OMe, Y = CO₂Et, CO₂Et, or CO₂Me, respectively) the absorption due to the β-methyl group remains the same on changing to an aromatic solvent, but that the absorption due to the α-methyl group is moved to lower field, an effect consistent with a transoid arrangement of the methyl groups.

A minor product from the reaction of ethyl (*E*)-3-chloro-2-methylbut-2-enoate with ethyl sodiolactate was identified as ethyl 2,3-dihydro-2,4,5-trimethyl-3-oxofuran-2-carboxylate (IV) from analytical data and from its spectroscopic (u.v., i.r., n.m.r.) properties, many of which were closely analogous to those reported for 2-acetyl-2,5-dimethylfuran-3(2*H*)-one (V).⁴ Compound

(IV) is the Dieckmann cyclisation product from (I) and we have shown by a separate experiment that treatment



of the (*E*)-form of (I) with ethanolic sodium ethoxide gives (IV) and an unidentified product also formed in the reactions of the ethyl (*E*)-3-halogeno-2-methylbut-2-enoates with ethyl sodiolactate. This cyclisation involves a change in the configuration of the double bond, which could occur in the strongly basic reaction medium as a result of the loss of a proton from the β-methyl group, or by an addition-elimination process.

The addition of ethanol to ethyl 2-methylbuta-2,3-dienoate with a low concentration of ethoxide ion as catalyst gave ethyl (*E*)-3-ethoxy-2-methylbut-2-enoate and two trace products identical with the major and trace products formed by the action of ethoxide ion on ethyl (*E*)-3-chloro-2-methylbut-2-enoate. A similar stereospecificity has recently been reported for the addition of hydrogen iodide to the same allenic ester.^{2a} We have been unsuccessful in attempts to prepare diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate (I) by an analogous base-catalysed addition of ethyl lactate to the allenic ester.

In connection with the foregoing studies employing alkyl 3-halogeno-2-methylbut-2-enoates we have sought alternative routes to such compounds, and particularly to the (*Z*)-forms. Oxidation of the readily available mixture of the two 3-chloro-2-methylbut-2-enals containing ca. 35% of the (*Z*)-form (II; X = Cl, Y = CHO) with silver oxide⁵ gave the corresponding acids (II and III; X = Cl, Y = CHO) in 47% yield, but the mixture contained only ca. 5% of the (*Z*)-acid. Other oxidising agents gave very low overall yields. Oxidation of the corresponding cyanohydrins in methanol with manganese dioxide⁶ gave a mixture of the methyl 3-chloro-2-methylbut-2-enoates (II and III; X = Cl, Y = CO₂Me) in only 20% yield and the (*Z*)-isomer accounted for only ca. 10% of the mixture. 3-Bromo-2-methylbut-2-enal, easily obtainable from butanone,⁷ is also now shown to be a mixture, containing ca. 40% of the (*Z*)- and ca. 60% of the (*E*)-form. The mixture deteriorates much more rapidly than the corresponding mixture of chloroaldehydes,^{8a} but oxidation with silver oxide gave a 10% yield of (*E*)-3-bromo-2-methylbut-2-enoic acid. Con-

² (a) J.-C. Chalchat, P. Duteurtre, F. Therón, and R. Vessiere, *Compt. rend.*, 1971, **273** C, 832; (b) M. Verny, *Bull. Soc. chim. France*, 1970, 1942; R. Seux, G. Morel, and A. Foucand, *Tetrahedron Letters*, 1972, 1003; T. C. Clarke, D. R. Kelsey, and R. G. Bergmann, *J. Amer. Chem. Soc.*, 1972, **94**, 3626; R. H. Summerville and P. von R. Schleyer, *ibid.*, p. 3628; A. J. Waring, M. R. Morris, and M. M. Islam, *J. Chem. Soc. (C)*, 1971, 3274; A. J. Waring, personal communication.

³ (a) D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 1960, 2349; (b) J. A. Edwards, V. Schwarz, J. Fojkos, M. L. Maddox, and J. H. Fried, *Chem. Comm.*, 1971, 292.

⁴ R. Shapiro, J. Hackmann, and R. Wahl, *J. Org. Chem.*, 1966, **31**, 2710.

⁵ A. I. Nanov, V. G. Vinokurov, T. V. Protopopova, and A. P. Skoldinov, *J. Gen. Chem. (U.S.S.R.)*, 1964, **34**, 352.

⁶ E. J. Corey, N. W. Gilman, and B. E. Ganem, *J. Amer. Chem. Soc.*, 1968, **88**, 5616.

⁷ Z. Arnold and A. Holy, *Coll. Czech. Chem. Comm.*, 1961, **26**, 3059 (*Chem. Abs.*, 1962, **56**, 15,329).

⁸ (a) J. M. F. Gagan, A. G. Lane, and D. G. M. Lloyd, *J. Chem. Soc. (C)*, 1970, 2454; (b) W. R. Benson and A. E. Pohland, *J. Org. Chem.*, 1965, **30**, 1126.

figurations for these pairs of halogeno-compounds were assigned on the basis of their n.m.r. spectra, details of which for those cases not fully discussed in the literature are given in the Table. The spectra are analogous to

N.m.r. spectra (τ values; solvent CDCl_3 ; $\Delta = \delta(\text{C}_6\text{H}_6) - \delta(\text{CDCl}_3)$ in p.p.m.; J in Hz)

	$\beta\text{-Me}$		$\alpha\text{-Me}$		$J_{\text{Me, Me}}$
	τ	Δ	τ	Δ	
(II; X = Cl, Y = CHO) ^a	7.63 (q)	+0.43	8.21 (q)	+0.21	1.0
(III; X = Cl, Y = CHO) ^b	7.40 (q)	+0.46	8.16 (q)	0.00	1.4
(II; X = Br, Y = CO ₂ H)	7.76 (q)	+0.58	8.01 (q)	+0.41	1.1
(III; X = Cl, Y = CO ₂ H) ^c	7.42 (q)	+0.26	7.93 (q)	+0.12	1.5
(II; X = Br, Y = CHO)	7.51 (q)	+0.54	8.29 (q)	+0.26	1.0
(III; X = Br, Y = CHO)	7.27 (q)	+0.60	8.17 (q)	+0.02	1.5
(II; X = Cl, Y = CO ₂ Me)	7.82 (q)	+0.31	8.08 (q)	+0.20	1.1
(III; X = Cl, Y = CO ₂ Me) ^d	7.55 (q)	+0.07	7.99 (q)	+0.04	1.6
(III; X = OMe, Y = CO ₂ Me) ^e	7.64 (q)	+0.03	8.24 (q)	-0.24	1.4
(III; X = OEt, Y = CO ₂ Et) ^f	7.66 (q)	0.00	8.20 (q)	-0.34	1.35
(II; X = O-CHMe-CO ₂ Et, ^g Y = CO ₂ Et)	8.10 (q)		8.22 (q)		1.0
(III; X = O-CHMe-CO ₂ Et, Y = CO ₂ Et) ^h	7.73 (q)	-0.02	8.15 (q)	-0.24	1.36

Other absorptions [$\tau(\text{CDCl}_3)$]: ^a -0.15 (s, CHO). ^b -0.02 (s, CHO). ^c -2.4 (s, CO₂H). ^d 6.28 (s, CO₂Me). ^e 6.28 (s) and 6.34 (s) (MeO and CO₂Me). ^f 5.86 (q, CO₂CH₂), 6.24 (q, O-CH₂Me), 8.73 (t) and 8.75 (t) (2 \times Me). ^g 5.80 (q) and 5.88 (q) (CO₂CH₂), 5.47 (q, O-CH-Me-CO₂), 8.50 (d, O-CHMe-CO₂), 8.74 (t, 2 \times MeCH₂). ^h 5.80 (q) and 5.83 (q) (CO₂CH₂), 5.28 (q, O-CHMe-CO₂), 8.53 (d, O-CHMe-CO₂), and 8.74 (2 \times MeCH₂). All J 7 Hz.

previously reported spectra for compounds of types (II) and (III) with respect to the magnitudes of the methyl-methyl homoallylic coupling constants,² the chemical shifts of the methyl groups,^{2,8} and the nature of the aromatic solvent-induced shifts.^{8a}

EXPERIMENTAL

General Directions.—M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra (solvent EtOH) were measured with a Perkin-Elmer 137 spectrophotometer and i.r. spectra (for liquid films) on a Perkin-Elmer 137 or a Pye Unicam SP 200 spectrophotometer. N.m.r. spectra were obtained with a Perkin-Elmer R12, a Varian A60, or a Varian HA 100 instrument for solutions in deuteriochloroform or perdeuteriobenzene containing tetramethylsilane as internal standard. The integrations were in every case in agreement with the proton assignments. Homoallylic coupling constants were the average of six peak separations

* The chemical shifts for the protons in the terminal methylene group and the 2-methyl group do not agree with those recorded¹³ but are in agreement with values for several related compounds; e.g., J. Pansard and M. Gaudemar (*Bull. Soc. chim. France*, 1968, 3332) give $\tau(\text{CDCl}_3)$ 4.85 and 8.13 (J 3 Hz) for the analogous protons in the corresponding acid.

^a A. Koll, *Annalen*, 1888, **249**, 303.

¹⁰ H. Scheiber and W. Bube, *Ber.*, 1915, **48**, 1445.

measured from spectra run at 100 Hz sweep width with a Varian HA 100 instrument. Mass spectra were recorded with an A.E.I. MS-9 instrument.

Analytical g.l.c. was carried out with an F and M 720 or a Griffin and George D6 instrument, and preparative g.l.c. with a Varian Aerograph A-700 instrument. The carrier gas was either nitrogen-hydrogen (9:1) (F and M and A-700) or nitrogen (D6). Column packings (on Chromosorb) were either 10% (D6, F and M) or 30% (A-700) and are abbreviated thus: SO (silicone oil), SR (silicone rubber), C (Carbowax), DEGS (diethylene glycol succinate). Column lengths were 2 (F and M; DEGS and SR), 6 (D6, F and M, C and SR), and 20 ft (A-700).

Starting Materials.—3-Chloro-2-methylbut-2-enoic acid, prepared^{2a,3a} from ethyl α -methylacetoacetate, had m.p. 65–66° (lit.,^{2a} 68–69°) and was mainly the (*E*)-form but contained (n.m.r.) about 2% of the (*Z*)-form.^{2a} 3-Chloro-2-methylbut-2-enal, b.p. 44° at 20 mmHg (lit.,^{5b} 54–56° at 23 mmHg), was shown by g.l.c. (F and M; C; 80°) to contain the (*Z*)- and (*E*)-forms, t_R 24.2 and 34.8 min [(*Z*):(*E*) 35:65], and had an n.m.r. spectrum in agreement with the published data.^{8a} Ethyl (*E*)-3-chloro-2-methylbut-2-enoate^{2a,9} had b.p. 70° at 18 mmHg, n_D^{25} 1.4548 (lit.,^{3a} 61.1° at 10 mmHg, n_D^{25} 1.4551), and ran as essentially one component on g.l.c. (D6; SO and C; 93°). Methyl (*E*)-3-chloro-2-methylbut-2-enoate¹⁰ had b.p. 50–52° at 22 mmHg (lit.,¹⁰ 159–161°) and ran as essentially one component on g.l.c. (F and M; 6 ft; SR; 210°). (*E*)-3-Bromo-2-methylbut-2-enoic acid,^{2a,11} m.p. 93–94° (lit.,¹² 94–95°), on esterification (EtOH-H₂SO₄) gave ethyl (*E*)-3-bromo-2-methylbut-2-enoate, b.p. 87–89° at 19 mmHg (lit.,^{2a} 73–74° at 10 mmHg). Ethyl 2-methylbuta-2,3-dienoate¹³ had b.p. 54° at 13 mmHg (lit.,¹³ 52° at 11 mmHg), ν_{max} 1960, 1940, 1720, 850, and 780 cm⁻¹, τ (CDCl₃) 4.91 (q, J 3 Hz, CH₂=C), 5.76 (q, J 7 Hz, ester CH₂), 8.10 (t, J 3 Hz, =CMe), and 8.70 (t, J 7 Hz, ester Me) [lit.,¹⁴ ν_{max} 1960, 1940, and 840 cm⁻¹, τ (CDCl₃) 5.0].*

Photoisomerisation of Diethyl (*E*)-2,4,5-Trimethyl-3-oxahex-4-enedioate.—Diethyl (*E*)-2,4,5-trimethyl-3-oxahex-4-enedioate (230 mg) in benzene (25 ml) was irradiated for 85 min in a 1200 W Rayonet Photochemical Reactor at 254 nm. After evaporation of the benzene, g.l.c. (D6; SO; 142°) indicated that the residue contained both forms of diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate [(*Z*):(*E*) 2:3], t_R 23.6 and 27.4 min, respectively, identified by their n.m.r. spectra (see Table).

Reaction of Ethyl Sodiolactate with Ethyl (*E*)-3-Halogeno-2-methylbut-2-enoates.—(a) Sodium hydride (1.78 g, 0.074 mol) was added to ethyl lactate (8.6 g, 0.074 mol) in benzene (150 ml). When the initial reaction was over ethyl (*E*)-3-chloro-2-methylbut-2-enoate (12.0 g, 0.074 mol) was added, and the solution was stirred under reflux for 4 days. The precipitated sodium chloride was then collected and washed with a little benzene. The combined filtrate and washings were dried (CaCl₂) and distilled, to give three fractions: (i), b.p. 60–100° at 15 mmHg (7.12 g), (ii), b.p. 100–136° at 13 mmHg (1.20 g), and (iii), b.p. 136–170° at 13 mmHg (2.92 g). Analytical g.l.c. (D6; SO; 142°)

¹¹ J. Wislicenus and M. Henze, *Annalen*, 1900, **313**, 243; R. E. Buckles and C. V. Mock, *J. Org. Chem.*, 1950, **15**, 680; W. J. Le Noble, *Tetrahedron Letters*, 1969, 895.

¹² P. Pfeiffer, *Z. phys. Chem. (Leipzig)*, 1904, **48**, 40.

¹³ H. J. Bestmann and M. Hartung, *Chem. Ber.*, 1966, **99**, 1198.

¹⁴ G. R. Harvey and K. W. Ratts, *J. Org. Chem.*, 1966, **31**, 3907.

revealed that (i) was essentially a mixture of the starting esters and that (ii) and (iii) contained diethyl (*E*)-2,4,5-trimethyl-3-oxahex-4-enedioate (t_R 27.4 min) and a trace of the (*Z*)-form (t_R 23.6 min) together with two minor products, (t_R 9.6 and 15.8 min). Redistillation of material from a duplicate experiment gave diethyl (*E*)-2,4,5-trimethyl-3-oxahex-4-enedioate (10% yield), b.p. 160–163° at 16 mmHg (lit.,¹ 91–93° at 0.04 mmHg), identical (i.r., n.m.r.) with the previously reported material.¹ The compound having t_R 9.6 min was collected by preparative g.l.c. (A-700; SR; 150–165°) and identified spectroscopically as ethyl 2,3-dihydro-2,4,5-trimethyl-3-oxofuran-2-carboxylate, λ_{max} 271.5 nm (ϵ 8860), ν_{max} 1750, 1705, and 1640 cm^{-1} , τ (CDCl₃) 5.83 (q, J 7 Hz, ester CH₂), 7.77br and 8.34br (2 \times s, MeC=CMe), 8.49 (s, tertiary Me), and 8.72 (t, J 7 Hz, ester Me) (Found: C, 60.8; H, 7.25%; m/e 198. C₁₆H₁₄O₄ requires C, 60.6; H, 7.1%; M , 198).

(b) The analogous reaction with ethyl (*E*)-3-bromo-2-methylbut-2-enoate gave the same four products, including diethyl 2,4,5-trimethyl-3-oxahex-4-enedioate [(*Z*):(*E*) 1:130], together with a further product, t_R 38.0 min (D6; SO; 142°).

Cyclisation of Diethyl (E)-2,4,5-Trimethyl-3-oxahex-4-enedioate.—Sodium hydride (0.069 g, 0.0029 mol) was added to a solution of diethyl (*E*)-2,4,5-trimethyl-3-oxahex-4-enedioate (0.698 g, 0.0029 mol) in ethanol (20 ml) and the mixture was heated under reflux for 4 h. The ethanol was removed and the residue treated with 2*N*-hydrochloric acid and extracted (\times 3) with ether. The combined extracts were washed with water, dried (Na₂SO₄), and evaporated. G.l.c. of the residue (D6; SO; 142°) showed the presence of the ester (IV) (t_R 9.6 min) and a second product (t_R 15.8 min; see before) in the ratio 3:2.

Alkyl 3-Alkoxy-2-methylbut-2-enoates.—Ethyl (*E*)-3-ethoxy-2-methylbut-2-enoate, b.p. 85° at 13 mmHg (lit.,^{3a} 82° at 10 mmHg), was prepared as described earlier^{3a} by the action of ethanolic sodium ethoxide on ethyl (*E*)-3-chloro-2-methylbut-2-enoate. G.l.c. (F and M; 6 ft SR; 60–200° at 5° min⁻¹) showed the major product (t_R 13.7 min) to be contaminated by traces of two other products (t_R 6.6 and 9.1 min).

Methyl (*E*)-3-chloro-2-methylbut-2-enoate (5.6 g) was heated under reflux for 2 h with methanolic sodium methoxide [from sodium (0.875 g) in methanol (35 ml)] to give essentially pure (g.l.c.; F and M; 6 ft SR; 80–200° at 7.5° min⁻¹) methyl (*E*)-3-methoxy-2-methylbut-2-enoate (2.5 g, 46%), b.p. 68–70° at 11 mmHg. A sample collected by semipreparative g.l.c. (same conditions) showed m/e 144.0787 (C₇H₁₂O₃ requires M , 144.0786).

Addition of Ethanol to Ethyl 2-Methylbuta-2,3-dienoate.—Ethyl 2-methylbuta-2,3-dienoate (2.2 g, 0.017 mol) in ethanol (5 ml) was added during 2 h to a stirred solution of

sodium ethoxide in ethanol [from sodium (21 mg) and ethanol (100 ml)] maintained below 0° by an ice-salt bath. After 72 h at room temperature most of the ethanol was evaporated off. Ether (50 ml) and water (10 ml) were added and the ethereal layer was separated, washed with water, and dried (Na₂SO₄). Distillation then gave essentially pure ethyl (*E*)-3-ethoxy-2-methylbut-2-enoate (1.75 g, 58%), b.p. 80° at 8 mmHg. G.l.c. (F and M; 6 ft SR; 60–200° at 5° min⁻¹) showed that the major product (t_R 13.7 min) was contaminated by the two minor products (t_R 6.6 and 9.1 min) present in the sample prepared by the alternative synthesis already described.

Oxidation of 3-Chloro-2-methylbut-2-enal.—Sodium hydroxide (25 g) in water (333 ml) was added dropwise to a mixture of freshly distilled 3-chloro-2-methylbut-2-enal [(*Z*):(*E*) 35:65] (22.4 g) and silver nitrate (72 g) in aqueous ethanol (H₂O, 70 ml; EtOH, 180 ml) and the mixture was vigorously stirred for 20 h. Solid was filtered off; acidification of the filtrate then gave 3-chloro-2-methylbut-2-enoic acid [(*Z*):(*E*) 5:95] (10.6 g, 47%), m.p. 63–65°.

Methyl 3-Chloro-2-methylbut-2-enoates.—3-Chloro-2-methylbut-2-enal [(*Z*):(*E*) 37:63; 5.0 g] and sodium cyanide (8.0 g) were added to a stirred suspension of active manganese dioxide¹⁵ (57.5 g) in acetic acid (3.0 g) and methanol (300 ml), and the mixture was then stirred at room temperature for 12 h. The bulk of the solid was removed by filtration and the remainder by centrifugation. Evaporation left the crude product, which was taken up in chloroform. The solution was dried (Na₂SO₄) and distilled, affording methyl 3-chloro-2-methylbut-2-enoate (1.2 g, 20%) [(*Z*):(*E*) 10:90], b.p. 50° at 10 mmHg.

Oxidation of 3-Bromo-2-methylbut-2-enal.—3-Bromo-2-methyl-2-enal [(*Z*):(*E*) 40:60] had b.p. 52° at 10 mmHg [lit.,⁸ 30° (bath) at 0.25 mmHg] and decomposed at room temperature overnight to a black tarry mass. A solution of sodium hydroxide (12.5 g) in water (167 ml) was added dropwise, with vigorous stirring, to a mixture of the aldehydes (16.1 g) and aqueous ethanolic silver nitrate (AgNO₃, 36 g; H₂O, 90 ml; EtOH, 35 ml), and the stirring was continued for 20 h. Solid was filtered off and the filtrate was concentrated and then acidified with dilute nitric acid, affording the crude acid (1.3 g, 10%), m.p. 83–85°. Several crystallisations [light petroleum (b.p. 60–80°) (charcoal)] gave (*E*)-3-bromo-2-methylbut-2-enoic acid, m.p. and mixed m.p. 91–93°.

We thank J. W. Hancox for some exploratory experiments and the S.R.C. for an award (to D. S.).

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¹⁵ J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1952, 1094.