672. *The Reactivity of 2-Bromopent-2-enoic Acid.*

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2-Bromopent-2-enoic acid with methanolic sodium methoxide gives 2-methoxypent-3-enoic acid and smaller amounts of the 2-enoic isomer. The latter is formed from the former.

OWEN and one of us [1] showed that α-bromo-ββ-dimethylacrylic acid (I) with methanolic sodium methoxide gave α-methoxy-ββ-dimethylacrylic acid (II) by reactions involving prototropic changes :

$$\begin{tikzcd}
\text{(I)} & \mathrm{CMe_2{=}CBr{\cdot}CO_2H} \arrow[r] & \mathrm{CH_2{=}CMe{\cdot}CHBr{\cdot}CO_2H} \arrow[d] \\
\text{(II)} & \mathrm{CMe_2{=}C(OMe){\cdot}CO_2H} & \mathrm{CH_2{=}CMe{\cdot}CH(OMe){\cdot}CO_2H} \arrow[l]
\end{tikzcd}$$

and it has been suggested that α-bromocrotonic acid yields α-methoxycrotonic acid by a similar mechanism. The differences shown by these two bromo-acids cannot be related to the position of equilibrium of the unsubstituted acids as crotonic and ββ-dimethylacrylic acid both exist almost wholly in the αβ-form.[2,3] Newman and Owen [4] studied α-bromo*cyclo*hexylideneacetic acid because at equilibrium *cyclo*hexylideneacetic acid affords *ca.* 88%

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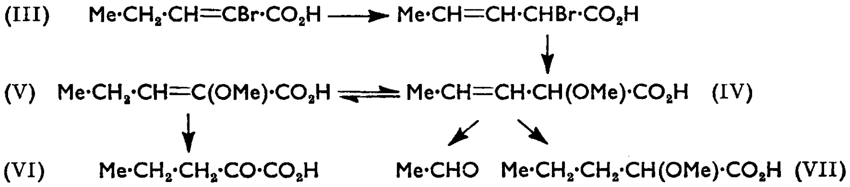
[1] Owen and Sultanbawa, *J.*, 1949, 3089.
[2] Kon and Linstead, *J.*, 1925, **127**, 616.
[3] Linstead and Noble, *J.*, 1934, 614.
[4] Newman and Owen, *J.*, 1952, 4713.

of the βγ-isomer: this bromo-acid gave α-*cyclo*hex-1-enyl-α-methoxyacetic acid which could not be isomerised to αβ-unsaturated α-*cyclo*hexylidene-α-methoxyacetic acid.

Concurrently [5] with the last-mentioned investigation we studied 2-bromopent-2-enoic acid (pent-2-enoic acid at equilibrium affords 32% of the -3-enoic isomer [3]). Liberation of bromide ion from this bromo-acid (III) was complete in 6 hr. in presence of methanolic sodium methoxide at 100° or in 9 hours at 70°, but the yield was better at the lower temperature. The product was shown to be a mixture of 2-methoxypent-3- (IV) and -2-enoic acid (V), as follows. The general nature of the mixture was shown by hydrogenation to 2-methoxypentanoic acid, an authentic sample of which, obtained from 2-bromopentanoic acid by means of sodium methoxide at room temperature, gave an identical *S*-benzylthiuronium salt (although analysis of this salt was unsatisfactory). The presence of 2-methoxypent-2-enoic acid (V) in the mixture was shown by formation of methanol on acid hydrolysis and by formation of the *p*-nitro- and 2 : 4-dinitro-phenylhydrazone of 2-oxopentanoic acid when the mixture was treated with an acid solution of the hydrazine. Ozonolysis of the mixture gave acetaldehyde in amount indicating that 2-methoxypent-3-enoic acid was the main constituent.



$$\begin{tikzcd}
\text{(III)}\ \mathrm{Me{\cdot}CH_2{\cdot}CH{=}CBr{\cdot}CO_2H} \arrow[rr] & & \mathrm{Me{\cdot}CH{=}CH{\cdot}CHBr{\cdot}CO_2H} \arrow[d] \\
\text{(V)}\ \mathrm{Me{\cdot}CH_2{\cdot}CH{=}C(OMe){\cdot}CO_2H} \arrow[d] \arrow[rr, leftarrow, shift right] & & \mathrm{Me{\cdot}CH{=}CH{\cdot}CH(OMe){\cdot}CO_2H}\ \text{(IV)} \arrow[ll, leftarrow, shift right] \arrow[dl] \arrow[d] \\
\text{(VI)}\ \mathrm{Me{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CO_2H} & \mathrm{Me{\cdot}CHO} & \mathrm{Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OMe){\cdot}CO_2H}\ \text{(VII)}
\end{tikzcd}$$

The reaction mechanism was established by the methods used earlier.[1] Treatment of the distilled reaction product with 2 : 4-dinitrophenylhydrazine showed it to contain *ca.* 10% of 2-methoxypent-2-enoic acid (V). Heating the product with 5N-sodium hydroxide increased this proportion to 35%, but this fell to 20% when the alkali-treated mixture was distilled. This change during distillation was confirmed by a change in the ultraviolet absorption maximum from ε 5550 at 220 mμ to ε 2290 at 210 mμ, and may have been due to decarboxylation [6] (this may also have accounted for Newman and Owen's failure [4] to isolate α-*cyclo*hexylidene-α-methoxyacetic acid).

EXPERIMENTAL

M. p.s were determined on a hot stage.

Pent-2-enoic acid (prepared [7] from propaldehyde and malonic acid in pyridine containing a trace of piperidine), b. p. 71—73°/1·5 mm., with bromine in carbon disulphide at −10° in sunlight or ultraviolet light gave a crude dibromide whence Bachmann's method [8] afforded 2-bromopent-2-enoic acid, needles [from light petroleum (b. p. 40—60°)], m. p. 49—50°, ultraviolet absorption max. at 228 mμ (ε 6500) in EtOH.

Reaction of 2-Bromopent-2-enoic Acid with Methanolic Sodium Methoxide.—(*a*) The bromo-acid (0·9 g.) and methanolic sodium methoxide (3 equivs.) were heated at 70° or 100° for the times stated below. The methanol was then removed under slightly diminished pressure, the residue acidified (Congo-red) with 5N-sulphuric acid and extracted with ether, the aqueous layer neutralised with calcium carbonate, and bromide ion determined by titration with silver nitrate (chromate indicator). Results are tabulated.

	100°						70°	
Concn. (N) of NaOMe	1·0	1·0	1·8	2·7	2·7	5·5	2·7	2·7
Time (hr.)	2	6	2	3	6	3	6	9
Reaction (%)	70	98	70	97	100	98	90	94

(*b*) The bromo-acid (18·0 g.) was heated with methanolic 1·35N-sodium methoxide (136 c.c.) at 70—75° for 9 hr. with occasional shaking. After evaporation in a vacuum, the residue was

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[5] Cf. Alles and Sultanbawa, *Proc. Ceylon Assoc. Adv. Sci.*, 1950, **6**, II, 27.
[6] Cf. Arnold, Elmer, and Dodson, *J. Amer. Chem. Soc.*, 1950, **72**, 4359.
[7] Goldberg and Linstead, *J.*, 1928, 2343.
[8] Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 4279.

dissolved in ice-cold 5N-sulphuric acid and extracted with ether. The dried ($MgSO_4$) extracts, on evaporation, gave an oil (8·5 g., 66%) which by fractionation afforded a mixture (A) (5·7 g., 44%), b. p. 69—70°/0·5 mm., n_D^{30} 1·4474, u.v. absorption max. at 210 mμ (ε 2280), of 2-methoxypent-2- and -3-enoic acid, which gave faulty analyses (Found: C, 56·3, 56·1; H, 7·25, 7·8%; equiv., 130·3. Calc. for $C_6H_{10}O_3$: C, 55·4; H, 7·75%; equiv., 130·1). The mixture afforded a S-*benzylthiuronium salt*, needles (from ethanol), m. p. 151—152° (Found: C, 56·9; H, 6·6; N, 9·3. $C_{14}H_{20}O_3N_2S$ requires C, 56·7; H, 6·8; N, 9·45%).

Hydrogenation of the Mixture (A).—In water (40 c.c.) containing sodium carbonate (1·2 g.) and Raney nickel (0·5 g.), the oil (1·3 g.) absorbed 230 c.c. (30°/760 mm., 0·93 mol.) of hydrogen. After filtration the solution was extracted with ether which removed 2-*methoxypentanoic acid* (0·6 g.), b. p. 72—74°/1 mm., n_D^{30} 1·4185 (Found: C, 54·5; H, 9·1. $C_6H_{12}O_3$ requires C, 54·5; H, 9·2%). The *S*-benzylthiuronium salt, needles (from ethanol), m. p. 134°, gave poor analyses (Found: C, 57·4; H, 7·5. Calc. for $C_{14}H_{22}O_3N_2S$: C, 56·3; H, 7·4%).

2-Methoxypentanoic acid was prepared by treating 2-bromopentanoic acid (1·8 g.) with methanolic 4·5N-sodium methoxide (7·5 c.c.) at 30° for 3 weeks. Acidification with 5N-hydrochloric acid, extraction with ether, and drying ($MgSO_4$) and evaporation of the extract gave the acid (1·4 g.), b. p. 70—74°/1 mm., n_D^{30} 1·4205, whose *S*-benzylthiuronium salt formed needles, m. p. 134° alone or mixed with the salt described in the preceding paragraph.

Hydrolysis of the Mixture (A).—(*a*) Hydrolysis of the mixture with 5N-sulphuric acid and subsequent distillation gave a distillate affording a positive resorcinol test for methanol.

(*b*) When the mixture (A) was kept with *p*-nitrophenylhydrazine in 5N-hydrochloric acid overnight, a yellow solid separated which on crystallisation from ethanol had m. p. 186° alone or mixed with the *p*-nitrophenylhydrazone, m. p. 186—187° (Found: N, 16·3. Calc. for $C_{11}H_{13}O_4N_3$: N, 16·7%), of 2-oxopentanoic acid which had been prepared from ethyl 3-ethoxycarbonylpentanoate by Adickes and Andresen's method.[9] The authentic ester had b. p. 86—87°/0·7 mm. and gave a 2 : 4-dinitrophenylhydrazone, m. p. 99°; the authentic acid gave a 2 : 4-dinitrophenylhydrazone, m. p. 167°.

(*c*) With a 1% solution of 2 : 4-dinitrophenylhydrazine the mixture A gave a 2 : 4-dinitrophenylhydrazone, m. p. 166—167° (from ethanol) alone or mixed with that described in (*b*).

Ozonolysis of Mixture A.—The mixture (0·5 g.) was ozonised in carbon tetrachloride (15 c.c.) at −10° for 3 hr. After evaporation the residue was distilled in steam. The distillate afforded the dimedone derivative, m. p. and mixed m. p. 141°, and 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 146—147°, of acetaldehyde. The non-volatile residue gave an unidentified bis-2 : 4-dinitrophenylhydrazone.

Experiments bearing on the Reaction Mechanism.—(*a*) The mixture A (100 mg.) with an excess of 2 : 4-dinitrophenylhydrazine in 4N-sulphuric acid gave 2-(2 : 4-dinitrophenylhydrazono)pentanoic acid (20 mg.), corresponding to *ca.* 10% of 2-methoxypentanoic acid.

(*b*) The mixture A (2·0 g.) was heated with 5N-sodium hydroxide (10 c.c.) for 20 hr. at 100°. The mixture was cooled, acidified (Congo-red) with cold 5N-hydrochloric acid, and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The residue had b. p. 70—82°/0·5—1 mm., n_D^{30} 1·4500 (0·75 g.). Part (100 mg.) of the distillate gave, as above, 2-(2 : 4-dinitrophenylhydrazono)pentanoic acid (50 mg., *ca.* 20%).

(*c*) Experiment (*b*) was repeated except that the product was not distilled. The product, $\lambda_{max.}$ 220 mμ (ε 5550), gave 90 mg. (*ca.* 35%) of the above-mentioned phenylhydrazone.

(*d*) 2-Bromopent-2-enoic acid (0·45 g.) was heated with methanolic 2·25N-sodium methoxide (3·4 c.c.) for 7 hr. at 70—75°. The solution was cooled, acidified with dilute sulphuric acid, and treated with 2 : 4-dinitrophenylhydrazine in 4N-sulphuric acid (100 c.c.). After 6 weeks at *ca.* 30° 0·246 g. (*ca.* 33%) of the above-mentioned 2 : 4-dinitrophenylhydrazone was collected.

(*e*) Experimentation as in (*d*), but with 32 hours' heating, gave 0·657 g. (*ca.* 88%) of hydrazone.

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[9] Adickes and Andresen, *Annalen*, 1944, **555**, 55.