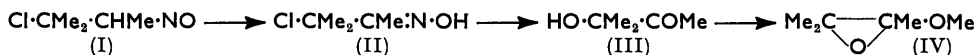


508. *2-Methylbut-2-ene Nitroschloride and its Derivatives.*

By N. THORNE.

The chemical properties of 2-methylbut-2-ene nitrosochloride have been studied. It has been shown that 3-hydroxy-3-methylbutan-2-one can react in the cyclic form since it forms a cyclic methyl ether. The action of sodium ethoxide on 2-methylbut-2-ene nitrosochloride has been investigated. Hydrolysis of 3-methylbut-3-en-2-one oxime has been shown to yield 3-hydroxy-3-methylbutan-2-one, involving a molecular rearrangement.

2-METHYLBUT-2-ENE NITROSOCHLORIDE was prepared by Tilden and Sudborough,¹ Wallach,² and Tornes,³ but its chemical properties were not examined till it was prepared by Schmidt.⁴ Although Schmidt states that the nitrosochloride (I) isomerises to 3-chloro-3-methylbutan-2-one oxime (II) above its melting point, it is now found that this method usually results in an explosive decomposition, and that this change is better effected by heating an ethanolic solution. The white solid dimeric nitrosochloride dissolves in the alcohol to give a blue solution (indicating monomerisation) which when heated becomes yellow as isomerisation occurs.

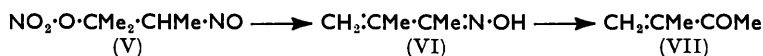


The chloro-oxime (II) can be hydrolysed to 3-hydroxy-3-methylbutan-2-one (III) by hot concentrated hydrochloric acid,⁴ but only in very low yields, and it is now found that yields of over 40% can be obtained if the oxime is simply heated with water. The keto-alcohol structure is proved by formation of a 2:4-dinitrophenylhydrazone and a *p*-nitrobenzoyl derivative. The structure has been further confirmed by conversion by methylmagnesium iodide into pinacol.

According to Bassett and Bell,⁵ many keto-alcohols associate on storage, as shown by an increase in the molecular weight, but 3-hydroxy-3-methylbutan-2-one is now found by molecular-weight determinations to remain monomeric for eight weeks.

Hydroxyacetone exists to an appreciable extent in the monomeric cyclic form and yields a dimeric cyclic methyl ether.⁶ An analogous cyclic ether (IV) was obtained from 3-hydroxy-3-methylbutan-2-one by reaction with methanol and dry hydrogen chloride at room temperature; it was isolated as a crystalline solid, readily hydrolysed by cold dilute hydrochloric acid. The method of preparation and the easy hydrolysis indicate the glucosidic (lactol) ring structure.

Treating 2-methylbut-2-ene nitrosochloride with sodium ethoxide gives a steam-volatile (m. p. 68°) and an involatile substance (m. p. 110°); both, together with a third compound (m. p. 45°), were stated by Wallach⁷ to be formed from 2-methylbut-2-ene nitrosate (V) by sodium ethoxide. Wallach described the three substances as isomeric forms of the oxime (VI), but showed that they exist in solution as monomer, dimer, and trimer, respectively (in order of m. p.s). Repetition of Wallach's work has failed to produce the oxime of m. p. 45°.



Wallach hydrolysed the oxime of m. p. 45° to 3-methylbut-3-en-2-one (VII), which was the expected result. Apparently Wallach made no attempt to hydrolyse the oxime of m. p. 68°; it is now found that this is hydrolysed by dilute acid to 3-hydroxy-3-methylbutan-2-one. Hydration of a double bond αβ to a carbonyl group is not unusual, but the normal result is for the hydroxyl group to become attached to the β-carbon atom, as in

¹ Tilden and Sudborough, *J.*, 1893, **63**, 479.

² Wallach, *Annalen*, 1888, **245**, 246.

³ Tornes, *Ber.*, 1879, **12**, 169.

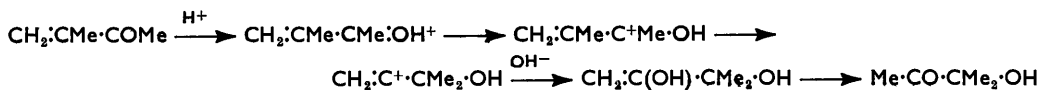
⁴ Schmidt, *Ber.*, 1902, **35**, 3729.

⁵ Bell, M.Sc. Thesis, Wales, 1938, p. 31.

⁶ Kling, *Ann. Chim. Phys.*, 1905, **5**, 510.

⁷ Wallach, *Annalen*, 1891, **262**, 339.

Wurtz's preparation of aldol⁸ from crotonaldehyde by dilute hydrochloric acid at room temperature. The abnormal attachment of the hydroxyl group to the α -carbon atom in the present instance may be explained by a simple molecular rearrangement of the annexed type. In this it is assumed that the first step is the hydrolysis of the unsaturated oxime



(VI) to the corresponding ketone (VII); this was confirmed by hydrolysing a synthetic specimen of the ketone (VII), 3-hydroxy-3-methylbutan-2-one being obtained, as from the oxime. The ketone was synthesised by converting 2:2-dibromopropane by alcoholic potassium hydroxide into 2-bromopropene which with magnesium in the presence of methyl cyanide yields 3-methylbut-3-en-2-one.

EXPERIMENTAL

2-Methylbut-2-ene Nitrosochloride.—Fuming hydrochloric acid (50 c.c.) was added slowly to 2-methylbut-2-ene (30 g.) and pentyl nitrite (50 c.c.) at $<0^\circ$, with stirring during $1\frac{1}{2}$ hr. The liquid became blue immediately, and slowly changed to a paste. The mixture was cooled for a further 30 min., and the nitrosochloride was filtered off, washed with ice-cold ethanol, and thus obtained white (29 g.), m. p. 76° .

3-Chloro-3-methylbutan-2-one Oxime.—A solution of the nitrosochloride (5 g.) in ethanol (50 c.c.) was heated to its b. p.; the solution boiled for a few minutes without further heating, and its blue colour gradually changed to yellow. The alcohol was removed, and the ketoxime was obtained as colourless crystals (4.5 g.), m. p. 50° .

3-Hydroxy-3-methylbutan-2-one.—2-Methylbut-2-ene nitrosochloride (19 g.) and water (400 c.c.) were heated under reflux for $1\frac{1}{2}$ hr. The mixture was steam-distilled till 200 c.c. of distillate had been collected. The distillate was saturated with potassium carbonate and extracted several times with ether. After drying (K_2CO_3), the ethereal solution was distilled, giving the colourless ketol (6.4 g.), b. p. $138\text{--}140^\circ$ [Found: M (cryoscopic in benzene and bromoform), 102.3, 103.0. Calc. for $\text{C}_5\text{H}_{10}\text{O}_2$: M , 102]. With 2:4-dinitrophenylhydrazine in warm sulphuric acid and alcohol this gave the 2:4-dinitrophenylhydrazone, orange-red crystals (from benzene), m. p. 192° (Found: C, 47.2; H, 5.0; N, 19.6. $\text{C}_{11}\text{H}_{14}\text{O}_5\text{N}_4$ requires C, 46.8; H, 5.0; N, 19.9%).

p-Nitrobenzoyl chloride, by the Schotten-Baumann procedure, gave the *p*-nitrobenzoyl derivative, m. p. 194° (from ethyl acetate) (Found: C, 56.9; H, 5.2; N, 5.9. $\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}$ requires C, 57.4; H, 5.2; N, 5.6%).

To a filtered, cold solution from magnesium (5.2 g.), ether (150 c.c.), and methyl iodide (29.5 g.), 3-hydroxy-3-methylbutan-2-one (6.5 g.) in ether (20 c.c.) was added. The mixture was then heated under reflux for 30 min., cooled, and decomposed with dilute sulphuric acid. Removal of the ether gave pinacol hydrate (5.5 g.), m. p. 48° .

2-Methoxy-2:3:3-trimethyloxiran (IV).—3-Hydroxy-3-methylbutan-2-one (7 g.) was kept for 4 hr. in dry methanol (25 c.c.) containing a little hydrogen chloride, then neutralised with silver carbonate, and filtered. Distillation gave the ether (2 g.), b. p. $85^\circ/100$ mm., which solidified overnight, then having m. p. 23° [Found: C, 62.1; H, 10.2%; M (cryoscopic in benzene), 116.8. $\text{C}_6\text{H}_{12}\text{O}_3$ requires C, 62.05; H, 10.35%; M , 116].

3-Methylbut-3-en-2-one Oxime.—2-Methylbut-2-ene nitrosochloride (33 g.) in ethanol (90 c.c.) was added in small portions to sodium (5.7 g.) dissolved in absolute ethanol (100 c.c.). The mixture was refluxed for 2 hr., then poured into water, and the whole was steam-distilled till no more oil passed over. Distillation gave the ketoxime (18 g.), b. p. $102\text{--}104^\circ/15$ mm., m. p. 68° [Found: C, 60.2; H, 9.2; N, 14.4%; M (cryoscopic in benzene and bromoform), 231.6, 200.7. Calc. for $(\text{C}_5\text{H}_9\text{ON})_2$: C, 60.6; H, 9.1; N, 14.15%; M , 198].

A small amount of oil, remaining in the flask after the steam-distillation, crystallised (0.2 g.; m. p. 110°) from alcohol (Wallach's γ -oxime, m. p. 111°).

Under the same conditions, the nitrosate (30 g.) yielded the ketoxime (10.5 g.) and a small residue, m. p. 110° .

The oxime (18 g.) was heated under reflux with dilute sulphuric acid (150 c.c.) for 1 hr. The resulting solution was steam-distilled till 200 c.c. of distillate had been collected. The distillate

⁸ Wurtz, *Bull. Soc. chim. France*, 1884, **42**, 286.

was saturated with potassium carbonate and extracted several times with ether. The ethereal solution was dried (K_2CO_3) and distilled, 3-hydroxy-3-methylbutan-2-one (5 g.), b. p. 138—140°, being obtained. It was identified as its 2 : 4-dinitrophenylhydrazone and *p*-nitrobenzoate.

3-Methylbut-3-en-2-one.—A solution of 2-bromopropene (15 g.) in ether (20 c.c.) was added dropwise to a mixture of magnesium (3.3 g.), ether (50 c.c.), and methyl cyanide (6.5 g.). The resulting solution was heated for 30 min. and then decomposed with dilute sulphuric acid. The ethereal layer was dried (K_2CO_3) and distilled, giving 3-methylbut-3-en-2-one (1.5 g.), b. p. 98—100°/762 mm., 36—38°/70 mm.; n_D^{20} 1.4168. Brant⁹ gives b. p. 98.5°/735 mm., 37—38°/75 mm., n_D^{20} 1.4163.

Hydrolysis of 3-Methylbut-3-en-2-one.—The ketone (1.5 g.) was heated under reflux with dilute sulphuric acid (30 c.c.) for 3 hr. The resulting solution was saturated with potassium carbonate and extracted several times with ether. The ethereal solution was dried (K_2CO_3) and distilled, giving 3-hydroxy-3-methylbutan-2-one (1 g.), b. p. 138—140°, identified as 2 : 4-dinitrophenylhydrazone and *p*-nitrobenzoate.

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⁹ Brant, *J. Amer. Chem. Soc.*, 1942, **64**, 2224.
