

### 532. *Reaction of Nitrosylsulphuric Acid with Olefins.*

By D. G. BOLLER and G. H. WHITFIELD.

Crystalline nitrosylsulphuric acid as a suspension in liquid sulphur dioxide reacts with some simple olefins to give hydroxyoximes. For successful reaction the olefinic bond must have at least two alkyl substituents.

NITROSYLSULPHURIC ACID has found use in nitrosation of methylene groups activated by electron-withdrawing substituents on the  $\alpha$ -carbon atom,<sup>1</sup> for diazotisation of amines,<sup>2</sup> and for direct introduction of the diazonium group into the aromatic nucleus.<sup>3</sup> Addition of nitrosylsulphuric acid to the olefinic bond does not appear to have been reported. The results of reactions between nitrosylsulphuric acid and some simple olefins in liquid sulphur dioxide at  $-40^\circ$  are tabulated below.

In the absence of diluent, olefins such as 2-methylbut-2-ene and 2-methylpent-1-ene gave only tars. Moreover, crystalline nitrosylsulphuric acid is insoluble in or reacts with the common organic solvents, and the normal medium for the reagent, concentrated sulphuric acid, would have undesirable secondary effects on the products; liquid sulphur dioxide was found to be a suitable medium. In this medium, at temperatures down to  $-70^\circ$ , nitrosylsulphuric acid forms a white suspension.

2-Methylbut-2-ene was chosen as the simplest olefin likely to react since the electron-donating properties of the methyl groups would facilitate possible electrophilic attack by the nitrosonium ion. From this olefin, a 40% yield of 3-hydroxy-3-methylbutan-2-one oxime could be obtained. When the olefin was added to nitrosylsulphuric acid in sulphur dioxide at  $-40^\circ$ , a fine white suspension was ultimately formed. In initial experiments, the sulphur dioxide was then distilled off and aqueous base added. Ether extraction gave 3-hydroxy-3-methylbutan-2-one oxime (III) and some 3-hydroxy-3-methylbutan-2-one.

<sup>1</sup> Bouveault and Locquin, *Bull. Soc. chim. France*, 1904, **31**, 1049.

<sup>2</sup> Schmidt, *Monatsh.*, 1954, **85**, 424; Blangley, *Helv. Chim. Acta*, 1938, **21**, 1579; Schoutissen, *J. Amer. Chem. Soc.*, 1933, **55**, 4531; De Milt and Van Zandt, *J. Amer. Chem. Soc.*, 1936, **58**, 2044.

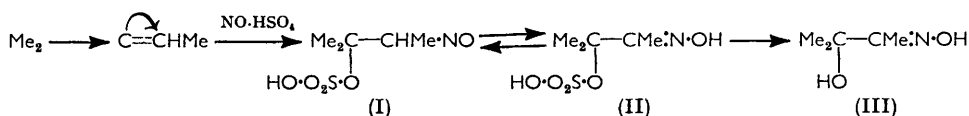
<sup>3</sup> Tedder, *J.*, 1957, 4003.

Effect of crystalline nitrosylsulphuric acid on olefins in liquid sulphur dioxide at  $-40^\circ$ .

Olefin	Mole ratio olefin : $\text{NO} \cdot \text{HSO}_4$	Work-up	Products	Yield (%)
2-Methylbut-2-ene	1	20% aq. NaOH	3-Hydroxy-3-methylbutan-2-one oxime	37
			3-Hydroxy-3-methylbutan-2-one	8
2-Methylbut-2-ene	1	$\text{Ca}(\text{OH})_2$ after filtration of intermediate	2-Hydroxyimino-1,1-dimethylpropyl hydrogen sulphate	54
			3-Hydroxy-3-methylbutan-2-one oxime	29
2-Methylbut-2-ene	1	Liquid $\text{NH}_3$	3-Hydroxy-3-methylbutan-2-one oxime	40
			$(\text{NH}_4)_2\text{SO}_4$	91
Isobutene	1:13	Liquid $\text{NH}_3$	$\alpha$ -Hydroxyisobutyraldoxime	5
			$(\text{NH}_4)_2\text{SO}_4$	72
2-Methylpent-2-ene	1	15% aq. NaOH	2-Hydroxy-2-methylpentan-3-one oxime	13
			2-Hydroxy-2-methylpentan-3-one	9
2-Methylpent-1-ene	1	15% aq. NaOH	2-Methylpent-2-enal oxime	8

It was later found that 3-hydroxy-3-methylbutan-2-one oxime was also produced by dissolving the intermediate white suspension in methanol, allowing the sulphur dioxide to evaporate, and then adding liquid ammonia to the mixture. The oxime which was formed in this instance in 40% yield is believed to be the geometrical isomer of that from the aqueous alkali method, for only the latter depresses the melting point of an authentic sample of oxime.

The position of the hydroxyimino-group on the final product (III) suggests that the reaction proceeds by way of electrophilic attack of the nitrosonium ion  $\text{NO}^+$  on the secondary carbon atom, which by virtue of the  $+I$  effects of the methyl substituents is relatively electron rich. This is presumably followed by nucleophilic attack of the sulphate anion to give the intermediate (I), which on isomerisation to the hydroxyimino form, gives the hydrogen sulphate (II). The ester group is then hydrolysed to the final product.



The isolation of 2-hydroxyimino-1,1-dimethylpropyl hydrogen sulphate (II) in an experiment with 2-methylbut-2-ene supports this mechanism. At  $-40^\circ$  this intermediate was filtered off; it decomposed violently after 3 hours at room temperature. Its identity was confirmed by infrared spectroscopy and microanalysis, and by hydrolysis with aqueous sodium carbonate to 3-hydroxy-3-methylbutan-2-one oxime.

Propene failed to react with nitrosylsulphuric acid even at  $-15^\circ$ , the double bond being less activated towards electrophilic attack. With isobutene, only 5% of pure  $\alpha$ -hydroxyisobutyraldoxime could be isolated, the bulk of the product being complex. Treatment of the reaction product from 2-methylpent-2-ene with aqueous base gave 2-hydroxy-2-methylpentan-3-one oxime in 13% yield, and some 2-hydroxy-2-methylpentan-3-one. From reaction with 2-methylpent-1-ene a complex mixture was again obtained from which only the  $\alpha\beta$ -unsaturated oxime, 2-methylpent-2-enal oxime could be isolated in 8% yield. In all these reactions most of the product consisted of unidentifiable tars. Reactions with oct-1-ene, butadiene, di-isobutene, cyclohexene, and styrene gave only tar.

It is apparent from the experiments with 2-methylbut-2-ene that nitrosylsulphuric acid can add across the olefinic bond in a manner analogous to nitrosyl chloride, obeying the

Markownikoff rule. Since propene failed to react, it is concluded that, for addition, the double bond must have at least two alkyl substituents.

### EXPERIMENTAL

**Materials.**—2-Methylbut-2-ene (Light & Co.) was redistilled, and then had b. p. 38°. Isobutene was produced by cracking of naphtha and analysed as 98% isobutene, 1.6% but-1-ene and but-2-ene, and 0.2% n-butane. 2-Methylpent-1-ene was obtained by triethyl aluminium-catalysed dimerisation of propene<sup>4</sup> at 60° and 300 atmos. and was redistilled; it had b. p. 60.7°. 2-Methylpent-2-ene was prepared from 2-methylpent-1-ene by isomerisation with Raney nickel at 300° for 60 hr. The fraction of distillate boiling at 66° was taken. Nitrosylsulphuric acid was prepared in the usual manner to give crisp white crystals, m. p. 73–75°, which were stored in a vacuum desiccator over concentrated sulphuric acid.<sup>5</sup>

**Reaction of Nitrosylsulphuric Acid with 2-Methylbut-2-ene.**—(a) *Sodium hydroxide neutralisation.* 2-Methylbut-2-ene (23.2 g., 0.33 mole) was added dropwise during 10 min. to a stirred suspension of nitrosylsulphuric acid (43.3 g., 0.33 mole) in dry liquid sulphur dioxide at –40°. The mixture was stirred for 30 min., the sulphur dioxide allowed to evaporate, and 20% aqueous sodium hydroxide added to the residual oil until neutral. The mixture was warmed at 45° for 20 min., the oily layer separated, and the ether-soluble portion of this dried (MgSO<sub>4</sub>). Removal of the ether gave a solid which on crystallisation from ligroin gave 3-hydroxy-3-methylbutan-2-one oxime (6.1 g.), m. p. 88° (lit.,<sup>6</sup> m. p. 85–86°) (Found: C, 51.3; H, 9.7; N, 12.1. Cal. for C<sub>5</sub>H<sub>11</sub>NO<sub>2</sub>: C, 51.2; H, 9.5; N, 12.0%). From the ether-insoluble portion of the oily layer was obtained by distillation 3-hydroxy-3-methylbutan-2-one (2.8 g.), b. p. 30°/30 mm. [dinitrophenylhydrazone, m. p. 136° (lit.,<sup>7</sup> b. p. 139°; dinitrophenylhydrazone, m. p. 138–139°)] and unidentified oil (2.8 g.). Continuous ether extraction of the aqueous mother-liquor gave some crystalline material, which on sublimation gave more (8 g.) 3-hydroxy-3-methylbutan-2-one oxime, m. p. 87–88°.

The identity of the oxime was confirmed by comparison of its i.r. and u.v. spectra with those of an authentic sample prepared from the corresponding ketone with hydroxylamine, and also by refluxing the oxime with 10% oxalic acid solution for 90 min. This gave 3-hydroxy-3-methylbutan-2-one, b. p. 139° (dinitrophenylhydrazone, m. p. 136–137°).

(b) *Isolation of 2-hydroxyimino-1,1-dimethylpropyl hydrogen sulphate.* In an experiment similar to the above the mixture was stirred, after olefin addition, for 90 min. at –40° and the white suspension filtered off. Evaporation of residual sulphur dioxide gave the *hydrogen sulphate* (34.9 g., 54%) as a white solid (Found: C, 30.5; H, 5.7; N, 7.1; S, 16.3. C<sub>5</sub>H<sub>11</sub>NO<sub>5</sub>S requires C, 29.6; H, 5.8; N, 6.6; S, 16.5%). The sulphur dioxide mother-liquor was treated with excess of calcium hydroxide, the liquid removed by evaporation, and the residue extracted with ether. Removal of solvent gave crude 3-hydroxy-3-methylbutan-2-one oxime.

2-Hydroxyimino-1,1-dimethylpropyl hydrogen sulphate (4.8 g.) was dissolved in water (10 ml.) and, with cooling, potassium carbonate added till slightly alkaline. This solution was then saturated with sodium chloride and continuously extracted with ether to give 3-hydroxy-3-methylbutan-2-one oxime (0.9 g.), m. p. 86.5°.

(c) *Liquid ammonia neutralisation.* In a further experiment with 2-methylbut-2-ene (70 g.) the mixture was stirred for 30 min. after addition of the olefin and methanol (1 l.) added at below –20°. Sulphur dioxide was then removed under reduced pressure at –20 to –15° and excess of anhydrous liquid ammonia added. Ammonium sulphate (100 g., 91%) was removed by filtration and the residual ammonia allowed to evaporate. After removal of methanol at reduced pressure, the yellow-green residue was Soxhlet-extracted with benzene; evaporation of this solvent gave semi-crystalline solid (69.3 g.). Further extraction with ethanol of the remaining residue produced semi-solid material (22.5 g.) and viscous oil (5 g.). Recrystallisation from benzene of the combined solids gave 3-hydroxy-3-methylbutan-2-one oxime (34.7 g.), m. p. 88–90° (Found: C, 51.1; H, 9.8; N, 12.3. Calc. for C<sub>5</sub>H<sub>11</sub>NO<sub>2</sub>: C, 51.2; H, 9.5; N, 12.0%). Acid hydrolysis of this oxime gave 3-hydroxy-3-methylbutan-2-one. Evaporation of benzene from the mother-liquor left semi-crystalline material (48 g.) which on

<sup>4</sup> Goddard and Smith, B.P. 858,187.

<sup>5</sup> Elliot, Kleist, Wilkins, and Webb, *J.*, 1926, 1219.

<sup>6</sup> Favorski, *J. prakt. Chem.*, 1913, **88**, 662.

<sup>7</sup> Aston and Greenburg, *J. Amer. Chem. Soc.*, 1940, **62**, 2594.

sublimation gave more 3-hydroxy-3-methylbutan-2-one oxime (11.2 g.). The total yield was 45.9 g. (40%). The remainder of the product consisted of tar.

The mixed m. p. of the oxime with the one of m. p. 87–88° obtained from the sodium hydroxide neutralisation method was 62–65°. Its mixed m. p. with a synthetic sample of the oxime (m. p. 88–91°) prepared from the ketone by hydroxylamine, was 64–67°. It is probable that the hydroxy-oximes produced by the two methods are geometrical isomers.

*Reaction of Nitrosylsulphuric Acid with Isobutene.*—Dry isobutene (63 g.) was added during 1 hr. to a stirred suspension of nitrosylsulphuric acid (127 g.) in anhydrous sulphur dioxide at –40°, giving a blue-green coloration with each fresh addition. The mixture was cooled to –75° and left overnight. The fine white suspension was dissolved in methanol (500 ml.) at –40° and the sulphur dioxide removed at –20°. Excess of liquid ammonia was then passed in and the precipitated ammonium sulphate (91 g.) filtered off. Removal of methanol by distillation at reduced pressure left white solid (55 g.) (consisting of products from ammonia-sulphur dioxide and unidentified organic residues) and yellow oil (44.8 g.). Fractional distillation of this oil gave a series of fractions boiling between 67°/5 and 90°/5 mm. The fraction (5.3 g.) with b. p. 88–90°/5 mm.,  $n_D^{24}$  1.4596, was identified as  $\alpha$ -hydroxyisobutyraldoxime (Found: C, 46.8; H, 9.1; N, 13.9. Calc. for  $C_4H_9O_2N$ : C, 46.6; H, 8.8; N, 13.6%). Franke<sup>8</sup> gives b. p. 110°/19 mm. Infrared spectral analysis of the earlier fractions (combined weight, 24.3 g.) indicated the presence of hydroxyimino and tertiary-hydroxyl functions and carbon-carbon unsaturation.

*Reaction of Nitrosylsulphuric Acid with 2-Methylpent-2-ene.*—2-Methylpent-2-ene (28.5 g., 0.34 mole) was added dropwise during 2 hr. to a stirred suspension of nitrosylsulphuric acid (43.3 g., 0.34 mole) in anhydrous liquid sulphur dioxide at –40°. The sulphur dioxide was removed by evaporation and 15% aqueous sodium hydroxide added until slightly alkaline; a dark red oil (13.4 g.) separated. Continuous ether extraction of the aqueous layer yielded more oil (14.7 g.). Repeated fractional distillation of these oils eventually gave: (i) 2-hydroxy-2-methylpentan-3-one (3.4 g.), b. p. 40–45°/6 mm.,  $n_D^{20}$  1.4238 [semicarbazone m. p. 131–133° (aqueous methanol)] (lit.,<sup>7</sup> b. p. 154°,  $n_D^{14.5}$  1.4238; semicarbazone, m. p. 131.5–132°); (ii) clear liquid (5.7 g.), b. p. 80–86°/1 mm.,  $n_D^{20}$  1.4700, which partially crystallised. The infrared spectrum was consistent with that expected for 2-hydroxy-2-methylpentan-3-one oxime although satisfactory microanalysis figures were not obtained. Hydrolysis of this oxime with oxalic acid gave 2-hydroxy-2-methylpentan-3-one,  $n_D^{15}$  1.4250; semicarbazone, m. p. 130°. The residue was a tar.

*Reaction of Nitrosylsulphuric Acid with 2-Methylpent-1-ene.*—2-Methylpent-1-ene (38 g.; 0.45 mole) was added dropwise during 20 min. to a suspension of nitrosylsulphuric acid (57.5 g., 0.45 mole) in anhydrous liquid sulphur dioxide at –40°, and the mixture stirred for 2 h. After sulphur dioxide had evaporated, 15% aqueous sodium hydroxide (300 ml.) was added, and the mixture refluxed on a water-bath at 40° for 30 min. A top oily layer was then separated and bulked with liquid that was continuously ether-extracted from the aqueous layer to give 30.4 g. of oil. Repeated fractional distillation of this oil gave: (i) complex mixture (14.3 g.) containing carbonyl, nitrile, tertiary hydroxyl and hydroxyimino functions, b. p. 37–84°/10 mm.; (ii) clear liquid (4 g.), b. p. 62°/2 mm., which slowly crystallised (m. p. 48°) and was shown by i.r. and u.v. spectra to be 2-methylpent-2-enal oxime (lit.,<sup>9</sup> m. p. 48–48.8°) (Found: C, 64.3; H, 9.7; N, 13.2. Calc. for  $C_6H_{11}NO$ : C, 63.7; H, 9.7; N, 12.4%); (iii) higher-boiling residues containing the amide group.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, HEAVY ORGANIC CHEMICALS DIVISION,  
RESEARCH DEPARTMENT, BILLINGHAM, CO. DURHAM. [Received, September 27th, 1963.]

<sup>8</sup> Franke, *Monatsh.*, 1890, **21**, 214.

<sup>9</sup> Goethals, *Bull. Soc. chim. belges.*, 1937, **46**, 415.