

*Vapour-phase Oxidation of Olefins. The Catalysed Oxidation of Diisobutene in the Presence of Selenium.**

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The oxidation of diisobutene [equilibrium mixture of 2 : 4 : 4-trimethylpent-1- and -2-ene, (I) and (II), respectively] with air or oxygen in the vapour phase over a supported copper catalyst at 250—350° in the presence of selenium gave a mixture of 4 : 4-dimethyl-2-methylenepentanal (III) (α -neopentylacraldehyde) and 2 : 4 : 4-trimethylpent-2-enal (IV) as major product. Similar oxidations of (I) containing a little (II), and (II) containing a little (I), indicated that (III) arose mainly from (I), and (IV) mainly from (II).

The methyl ester of 4 : 4-dimethyl-2-methylenepentanoic acid,† derived from (III), could not be polymerised by heating it with benzoyl peroxide under standard conditions.

THE problem of the partial oxidation of olefins in the vapour phase has attracted many investigators. Success depends largely on the use of a selective catalyst which will promote formation of desirable products without causing scission of carbon-carbon bonds and subsequent formation of large proportions of carbon oxides. Metallic silver (suitably supported), which enables good yields of ethylene oxide to be obtained from ethylene, is a typical example of such a catalyst.

Clark and Shutt (U.S.P. 2,383,711) passed propene and other olefins with air over a metallic selenite or tellurite, preferably silver selenite, at 270—320°, and obtained reasonable yields of unsaturated carbonyl compounds containing the same number of carbon atoms per molecule as the corresponding olefins. The addition of metallic oxides, such as cupric oxide, to the silver selenite was recommended but the catalyst, with or without cupric oxide, rapidly lost its activity. Hadley and his co-workers (B.P. 625,330, 648,386, 655,210, 658,179, 658,240) developed an efficient catalyst which consisted essentially of copper and selenium. Since selenium is volatile at the temperatures employed there was need for a continuous transport of it over the copper and it was found best to use the copper in the form of copper aluminate or copper silicate. The present paper describes the application of the oxidation method to diisobutene.

In preliminary experiments with this olefin the catalyst was copper aluminate (for preparation, see Hadley, Heap, and Nichol, B.P. 655,210; example 1 of complete specification); it was then found that copper silicate was a more efficient catalyst, and all subsequent work was carried out with this.

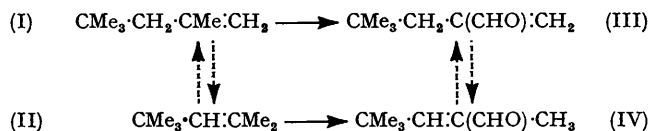
Passage of diisobutene [equilibrium mixture of (I) and (II)], admixed with air and selenium vapour, over the catalyst at 250—350° gave as main product a mixture of C₈ mono-olefinic aldehydes which was shown to consist of 4 : 4-dimethyl-2-methylenepentanal (III) (α -neopentylacraldehyde), b. p. 147—148°, and 2 : 4 : 4-trimethylpent-2-enal (IV), b. p. 162—163°, in the proportions of 3 to 1 approx. When (I) containing 3—4% of (II) was employed in place of the equilibrium mixture of isomers, (III) was the major (78%) constituent of the C₈ aldehyde fraction; (IV) pre-dominated (61%) when (II) containing 5% of (I) was oxidised. The structures of the aldehydes were established by methods described below.

The ready isomerisation of (I) and (II) in the presence of catalysts to give the equilibrium mixture of the isomers is well known [cf. the work of Gallaway and Murray, *J. Amer. Chem. Soc.*, 1948, **70**, 2584, on the isomerisation of (I) and (II) over silica gel at room temperature]. In the present work it was shown that passage of (I) over activated alumina at 275° in the absence of air or oxygen resulted in partial isomerisation to (II); the process was not studied with (II) owing to the limited supplies. Hence the formation of both (III) and (IV) during the oxidation of either (I) or (II) might have been due to partial

* This work is the subject of B.P. 694,353 and 694,362.

† Geneva nomenclature, CO₂H = 1.

isomerisation of the pure olefins, followed by oxidation. The latter must have occurred more readily than the isomerisation, for different proportions of (III) and (IV) were obtained depending on the proportions of (I) and (II) in the starting material. It is also conceivable (although no direct evidence was obtained) that the C₈ aldehydes themselves isomerised to some extent over the catalyst, since this could be slowly effected (concurrently with polymerisation or association) by refluxing the liquids at atmospheric pressure.



Small amounts of α -methylacraldehyde were isolated from all the oxidations and probably arose from the *isobutene* formed by thermal fission of the *diisobutene*. The other main by-products were carbon dioxide and materials of high molecular weight. The amount of the latter varied with the severity of heating of the crude product during fractionation and was reduced by distillation in steam or under reduced pressure. Small amounts of the C₈ aldehydes were produced by thermal decomposition of these compounds of high molecular weight, for example, during distillation.

In the above preliminary experiments difficulty was experienced in condensing the C₈ aldehydes completely in cold traps, either because they formed aerosols or because the exit gases were readily supersaturated with them. As an increase of contact time over the catalyst beyond the optimum caused little further oxidation of the C₈ aldehydes a re-cycle system was tried (see p. 1419): the main feature of this was that part of the gas leaving the reaction vessel was fed back to the entrance of this vessel after being replenished with oxygen, *diisobutene*, and selenium. By re-cycling, the concentration of product in the gas leaving the apparatus was increased and the loss due to incomplete condensation was reduced.

The structures of the aldehydes (III) and (IV) were established in the following way. Elementary analyses and ultra-violet absorption properties of the substances and their derivatives demonstrated that they were $\alpha\beta$ -unsaturated C₈ carbonyl compounds. Hydrogenation of each gave, first, the known 2:4:4-trimethylpentanal and then 2:4:4-trimethylpentan-1-ol, and oxidation with silver oxide in alkaline media or, in one case, with molecular oxygen, gave the corresponding unsaturated C₈ carboxylic acids which on hydrogenation furnished the same saturated acid, 2:4:4-trimethylpentanoic acid. From these facts it followed that the aldehydes possessed the isomeric structures (III) and (IV). Assignment of (III) to the aldehyde of b. p. 147–148° and of (IV) to that of b. p. 162–163° was indicated by infra-red studies and proved by ozonolysis: the higher-boiling compound gave the expected trimethylacetaldehyde and methylglyoxal, whereas the isomer gave formaldehyde, *tert.*-butylacetic acid, and traces of glyoxal. The formation of *tert.*-butylacetic acid is in accord with the fact that Whitmore and Church (*J. Amer. Chem. Soc.*, 1932, 54, 3710) obtained this acid in small amounts from the ozonolysis of the corresponding isomer of *diisobutene*, namely, (I). It presumably arose in both cases by a similar mode of decomposition of the intermediate ozonide. However, the production of formaldehyde in high yield from (III) is evidence that the latter contains a methylene group, although it is possible that not all of the formaldehyde obtained arose from this group.

Although (III) and (IV) were both new compounds when first prepared by us, (III) has recently been described by Smith, Norton, and Ballard (*ibid.*, 1951, 73, 5284) who stated that it was made by Hearne and Adams (U.S.P. 2,486,842). No details of (III) were given, however, in this patent specification.

The unsaturated acids derived from (III) and (IV) were clearly 4:4-dimethyl-2-methylenepentanoic acid and 2:4:4-trimethylpent-2-enoic acid, respectively. The methyl ester of the former, prepared *via* the acid chloride, could not be induced to polymerise on being heated with benzoyl peroxide; the bulky α -*neopentyl* grouping presumably exerted a strong steric hindrance.

EXPERIMENTAL

Preparation of Copper Silicate Catalyst.—A solution of commercial sodium metasilicate (1 part, containing about 50% w/w of Na_2SiO_3) in water (20 parts) was added during 2 min. to a vigorously stirred solution of cupric nitrate trihydrate (2 parts) in cold water (about 10 parts). The resulting light blue precipitate was collected on a Buchner funnel and sucked as dry as possible. The filter cake was dried at 80–100°, heated in a stream of air at about 300° in order to decompose any excess of copper nitrate, and then formed into cylindrical pellets, $\frac{1}{8}$ in. in diameter by $\frac{1}{8}$ in. long. Finally the pellets were heated at 600° for 1½ hr. The final heat treatment and the avoidance of washing of the filter cake were essential for an efficient catalyst.

Oxidation of Diisobutene.—Preliminary experiments were carried out in the helical glass tubing reaction vessel shown in Fig. 1. The diisobutene was introduced into the air stream by allowing the air to bubble through liquid diisobutene in a vessel kept in a water-bath maintained at $15^\circ \pm 0.5^\circ$, while the selenium vapour was introduced by suspending a small cup (*A*)

FIG. 1.

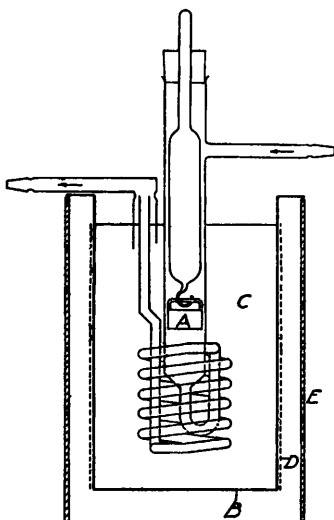
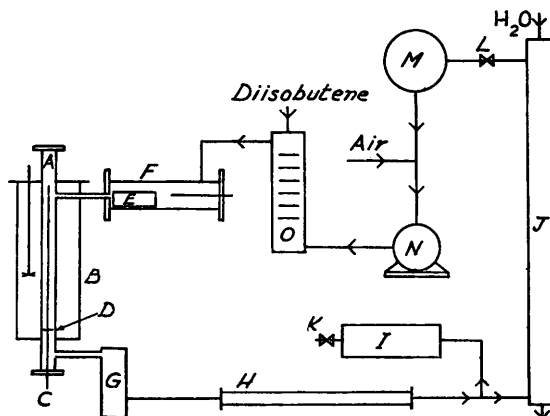


FIG. 2.



containing molten selenium in the entrance chamber of the reaction vessel. The reaction vessel, including the larger part of the entrance chamber, was immersed in a heating bath (*B*) containing a molten mixture (*C*) of sodium nitrite and potassium nitrate electrically heated by the winding (*D*) and lagged by a cylinder (*E*) of asbestos-cement and thermostatically kept at a temperature of $320^\circ \pm 2^\circ$.

The products of the reaction were collected in three traps in series, the first at room temperature, the second cooled in solid carbon dioxide-acetone, and the third in liquid air. At the end of a run, the contents of the traps were mixed and steam-distilled, and the upper layer in the distillate was separated and fractionated at atmospheric pressure through a column (40 cm. long, 1.5 cm. diam.) packed with single-turn glass helices. Samples of gas taken after the first trap were analysed for carbon dioxide in a Bone and Wheeler apparatus. An aliquot portion of the aqueous layer of the steam-distillate was titrated with hydroxylamine reagent for carbonyl content.

In a typical run, air (20 l. at room temperature and pressure), diisobutene (1.65 g., equilibrium mixture of isomers), and selenium vapour (0.025 g.) were passed per hour over the copper silicate catalyst (16 g.) at 320° for 56 hr. After exhaustive steam-distillation of the combined products and separation of the two layers in the steam-distillate an upper (oil) layer of 77.8 g. was obtained. The aqueous layer contained carbonyl compounds equivalent to 6.4 g. of α -methylacetaldehyde. Some resinous material (5 g. approx.) was not steam-volatile.

Distillation of the upper layer afforded fractions: (i) b. p. 60–90° (6.2 g.); (ii) b. p. 90–110° (23.5 g.); (iii) b. p. 110–140° (4.3 g.); (iv) b. p. 140–165° (31.9 g.); and residue (10 g.).

Re-fractionation of (i) gave α -methylacraldehyde (odour), b. p. 65–75°, which rapidly polymerised in the absence of inhibitor, and (ii) was mainly unchanged diisobutene containing a little α -methylacraldehyde. Re-fractionation of the main bulk of (iv) gave first pure α -neopentylacraldehyde (III) (4 : 4-dimethyl-2-methylenepentanal) as a pale yellow liquid, b. p. 147–148°, n_D^{20} 1.4363 (Found: C, 76.35; H, 11.15. Calc. for $C_8H_{14}O$: C, 76.15; H, 11.2%); ultra-violet absorption max. in EtOH: 2240 and 3150 Å (ϵ 6000 and 36, respectively). (Smith *et al.*, *loc. cit.*, gave b. p. 149–150°, n_D^{20} 1.4363, d_4^{20} 0.840.) This was followed by 2 : 4 : 4-trimethylpent-2-enal (IV), b. p. 162–163°, n_D^{20} 1.4527 (Found: C, 76.0; H, 11.15. $C_8H_{14}O$ requires C, 76.15; H, 11.2%); ultra-violet absorption max. in EtOH: 2300 and 3080 Å (ϵ 11000 and 43, respectively). The proportions of (III) and (IV) were 3 to 1 approx.

The α -neopentylacraldehyde readily gave a 2 : 4-dinitrophenylhydrazone, which crystallised from 95% ethanol as red prisms, m. p. 163° (Found: C, 54.95; H, 5.85. $C_{14}H_{18}O_4N_4$ requires C, 54.9; H, 5.9%); ultra-violet absorption max. in EtOH: 3720 Å (ϵ 2.1×10^4), and a semicarbazone, which separated from aqueous alcohol as white crystals, m. p. between 202° and 209° (depending on the rate of heating) (Found: C, 58.65; H, 9.2; N, 22.9. $C_9H_{17}ON_3$ requires C, 58.95; H, 9.35; N, 22.9%).

The 2 : 4 : 4-trimethylpent-2-enal readily gave a 2 : 4-dinitrophenylhydrazone, which separated from ethyl acetate-ethanol in long, thin, red rods, m. p. 203–204° (Found: C, 55.15; H, 5.8; N, 18.3. $C_{14}H_{18}O_4N_4$ requires C, 54.9; H, 5.9; N, 18.3%), light absorption max. in EtOH: 3780 Å (ϵ 2.7×10^4), and a semicarbazone, which separated from aqueous ethanol in long flattened needles, m. p. 170–171° (Found: C, 59.45; H, 9.35; N, 23.0. $C_9H_{17}ON_3$ requires C, 58.95; H, 9.35; N, 22.9%).

Analysis of the original fractions (i)–(iv) from the distillation of the oil layer of the steam-distillate (see above) showed that they contained the following (total quantities): (a) unchanged diisobutene (25.4 g.); (b) C_8 mono-olefinic aldehydes (34.0 g.); and (c) α -methylacraldehyde (6.5 g.) (a further 6.4 g. were present in the aqueous layer of the steam-distillate). The yields, based on an input of 93 g. of diisobutene, were thus: diisobutene recovered, 28%; α -methylacraldehyde, 11%; C_8 mono-olefinic aldehydes, 32.5%; high-boiling residues, 12–15% (calc. as C_8 aldehyde). The exit gases contained 3.7% of carbon dioxide, equivalent to a yield of 7%. Fraction (iv), on analysis by infra-red spectroscopy, was shown to contain 68% of α -neopentylacraldehyde and 23% of 2 : 4 : 4-trimethylpent-2-enal.

Other mixtures of the two isomers were similarly oxidised. In each case the fraction of the product boiling between 140° and 165° was analysed by infra-red spectroscopy. The results are summarised in the Table.

The impurities present in the 140–165° fractions analysed by infra-red spectroscopy were not identified.

Variation of isomeric composition of C_8 aldehyde with variation of isomeric composition of feedstock.

Composition of feedstock, %		Composition of C_8 aldehyde, %	
Trimethylpent-1-ene	Trimethylpent-2-ene	α -neopentylacraldehyde	2 : 4 : 4-Trimethylpent-2-enal
96–97	3–4	78	18
80	20	68	23
5	95	17	61

Partial Isomerisation of 2 : 4 : 4-Trimethylpent-1-ene.—Nitrogen (20 l./hr.) was saturated at 15° with 2 : 4 : 4-trimethylpent-1-ene (1.65 g./hr.; 95% purity) and then passed through the standard glass helical reaction vessel (see above) which contained activated alumina (20 g., 8–18 mesh) and was kept at 275°. The effluent gases were passed through a trap cooled in solid carbon dioxide-acetone. After 24 hr. the condensate was removed and distilled without fractionation, and the distillate analysed by infra-red spectroscopy. It contained 70% of trimethylpent-1-ene and 30% of trimethylpent-2-ene.

Oxidation of Diisobutene in a Re-cycle Apparatus.—Fig. 2 is a diagram of the apparatus. The reaction vessel (A) was a vertical, $\frac{3}{8}$ -inch bore, stainless-steel tube, which protruded through the bottom of a 5-in. diameter bath (B) of the same material. The liquid in the bath, which was about 30 in. deep, contained the same mixture as that described for Fig. 1; it was heated electrically by a winding on the outside of the container and thermostatically controlled. Vigorous stirring ensured a uniform temperature. A thermocouple pocket (C) carried, at a point 3 in. from the bottom of the bath, a grid (D), which supported the catalyst. Gas entered the top of the reaction vessel after passing over molten selenium contained in a tray (E) having a horizontal, rectangular, cross-section of 1 × 6 in. The selenium tray was placed in an

electrically heated chamber (*F*) thermostatically controlled at 300°, and the selenium transport was adjusted by altering the area of tray covered by a sliding lid. Gas leaving the reaction vessel passed downwards through a metal vessel (*G*) of 12 sq. in. cross section and 12 in. in height in which selenium (together with some selenium dioxide and unidentified resinous material) condensed. The gas issued from the selenium collector at about 100° and then passed through an air-cooled condenser (*H*) at the end of which part of the gas stream was vented *via* a trap (*I*), cooled in a solution of solid carbon dioxide in alcohol, while the remainder passed up a packed tower (*J*) down which a stream of water flowed. The liquid condensing in (*H*) ran down into the base of (*J*). The proportioning of flow between main stream and vent was effected by means of valves *K* and *L*. On emerging from the top of the tower, the recycled gas passed through a gas meter (*M*) and a pump (*N*) into the diisobutene evaporator (*O*) which contained a series of filter-papers spaced vertically, at intervals, on to which diisobutene was dripped at a measured rate. Subsequently the gas entered the selenium evaporator. At the end of a run the liquid effluent from (*J*) and the condensate in (*I*) were combined, and the products recovered by steam-distillation.

In a typical run with 2 : 4 : 4-trimethylpent-1-ene (96% purity, the other 4% being the 2-ene isomer) the following conditions were employed : ratio of re-cycle gas to make-up gas, 4 to 1; temp. of bath, 320°; max. temp. in catalyst bed, 334°; vol. of gas entering reactor, 400 l. per hr.; concn. of olefin in gas entering reactor, 2.1% v/v; wt. of selenium evaporated, 0.39 g. per hr.; weight of copper silicate catalyst, 170 g. (130 ml.); duration of run, 25 hr. The yields calculated on olefin fed to the system were : C₈ aldehydes, 36%; α-methylacraldehyde, 2%; carbon dioxide, 6%. The efficiency of conversion of olefin into C₈ aldehyde was 64%, and 12% of the olefin fed was unaccounted for.

The products from several oxidations similar to the above were combined and distilled through a 100-plate column, to give α-neopentylacraldehyde, b. p. 147—148° (92% of total C₈ aldehyde) and 2 : 4 : 4-trimethylpent-2-enal, b. p. 162—163° (8%).

Hydrogenation of α-neopentylacraldehyde to 2 : 4 : 4-Trimethylpentanal.—A solution of α-neopentylacraldehyde (6.9 g.) in ethanol (35 c.c.) was shaken with Raney nickel (2 g. of "paste") to remove traces of selenium, the mixture filtered, and the catalyst washed with a little ethanol. The combined filtrate and washings were hydrogenated at atmospheric pressure and temperature over fresh Raney nickel (2 g. of "paste") until slightly more than 1 mol. of hydrogen had been absorbed. Interruption of the reaction, filtration, and isolation of the product by fractional distillation afforded 2 : 4 : 4-trimethylpentanal (2.0 g.), b. p. 39°/9 mm., n_D^{20} 1.4155 (Hickinbottom, *J.*, 1948, 1331, gives b. p. 149—151°, n_D^{20} 1.4180), which readily gave a 2 : 4-dinitrophenylhydrazone, bright yellow needles, m. p. 145°, from ethanol (Byers and Hickinbottom, *ibid.*, p. 1328, give m. p. 143—144°), and a semicarbazone, m. p. 115°, from aqueous ethanol (Hickinbottom, *loc. cit.*, gives m. p. 118—120°).

Hydrogenation of α-neopentylacraldehyde to 2 : 4 : 4-Trimethylpentan-1-ol.—A solution of α-neopentylacraldehyde (10 g.) in ethanol (50 c.c.) which had been pre-treated with Raney nickel (2 g. of "paste") as described above was hydrogenated at room pressure and temperature over fresh Raney nickel (2 g. of "paste"). When the rate of hydrogenation became slow the temperature was raised gradually to 55° and kept thereat until absorption of hydrogen ceased. Isolation of the product afforded 2 : 4 : 4-trimethylpentan-1-ol (7.0 g.), b. p. 68—69°/12 mm., n_D^{20} 1.4260 (Whitmore *et al.*, *J. Amer. Chem. Soc.*, 1941, 63, 643, give b. p. 78—80°/22 mm., n_D^{20} 1.4278—1.4285), which readily gave a 3 : 5-dinitrobenzoate, m. p. 73—74°, on recrystallisation from 95% ethanol (Whitmore *et al.*, *loc. cit.*, give m. p. 72.5—73.5°).

Oxidation of α-neopentylacraldehyde to 4 : 4-Dimethyl-2-methylenepentanoic acid.—(A) A solution of sodium hydroxide (6 g.) in water (300 c.c.) was added dropwise to a stirred mixture of silver oxide (from 15 g. of nitrate), α-neopentylacraldehyde (5 g.), and water (50 c.c.); the resultant mixture was shaken mechanically overnight and filtered, and the solid washed with water. The combined filtrate and washings were extracted with ether, the ether extracts were discarded, and the aqueous solution was acidified strongly with sulphuric acid. The oil which separated was taken up in ether, the ethereal extract was washed with water, dried (Na₂SO₄), and evaporated. The oil (4.15 g.) obtained solidified, and on fractional distillation *in vacuo* afforded 4 : 4-dimethyl-2-methylenepentanoic acid (α-neopentylacrylic acid) as a colourless oil (2.55 g.), which rapidly solidified to a crystalline solid, m. p. 39° (Found : C, 67.2; H, 9.85%; equiv., 144. C₈H₁₄O₂ requires C, 67.55; H, 9.9%; equiv., 142.2). The acid formed a p-bromophenacyl ester which separated from 90% ethanol in rosettes of needles, m. p. 56° (Found : C, 56.35; H, 5.4. C₁₆H₁₉O₃Br requires C, 56.65; H, 5.65%).

(B) α-neopentylacraldehyde (126 g.) was stirred vigorously at 15° for 20 hr. while oxygen

was passed in at the rate of 2 l./hr. The liquid product (140 g.) was fractionated under reduced pressure to give: (i) b. p. $<105^{\circ}/70$ mm. (48 g.); (ii) b. p. $<105^{\circ}/10$ mm. (13 g.); (iii) b. p. $105\text{--}115^{\circ}/10$ mm. (50 g.); (iv) b. p. $50\text{--}100^{\circ}/1$ mm. (3 g.); and residue (26 g.). Fraction (i) was substantially pure α -neopentylacraldehyde, and fraction (ii) was a mixture of this with 4 : 4-dimethyl-2-methylenepentanoic acid and acids of lower molecular weight. Fraction (iii) was substantially pure 4 : 4-dimethyl-2-methylenepentanoic acid, m. p. 37° . By melting, cooling, and draining the partially crystalline mass, the m. p. was raised to 44° (Found : equiv., 142.5). The infra-red absorption spectrum of the pure material was consistent with the assigned constitution.

The acid was converted by means of thionyl chloride into the acid chloride, and this on treatment with methanol in the presence of pyridine afforded methyl 4 : 4-dimethyl-2-methylenepentanoate (57% overall yield), b. p. $95^{\circ}/70$ mm., n_D^{20} 1.4303 (Found : C, 69.7; H, 10.0%; sap. equiv., 157; unsaturation, $1.02H_2$. $C_9H_{16}O_2$ requires C, 69.2; H, 10.3%; sap. equiv., 156). The infra-red absorption spectrum of the pure ester was consistent with the assigned structure.

Hydrogenation of the acid (0.8 g.) in ethanol (25 c.c.) over Adams's platinum oxide catalyst (0.1 g.) at room temperature and pressure resulted in the absorption of 1.0 mol. of hydrogen. Isolation of the product afforded 2 : 4 : 4-trimethylpentanoic acid as an oil which was converted *via* the acid chloride ($SOCl_2$ -benzene) into the anilide (m. p. $118\text{--}119^{\circ}$, from methanol-water) and the amide [needles, m. p. $123\text{--}124^{\circ}$, from light petroleum (b. p. $60\text{--}80^{\circ}$)]. Whitmore *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 2028) give m. p. $117\text{--}118^{\circ}$ and m. p. 123° for the anilide and amide, respectively, of 2 : 4 : 4-trimethylpentanoic acid.

Ozonolysis of α -neoPentylacraldehyde.—Ozonised oxygen (containing about 4% w/v of ozone) was passed into a solution of α -neopentylacraldehyde (2 g.) in redistilled methylene dichloride (50 c.c.), which was cooled in alcohol-solid carbon dioxide, until ozone appeared in the exit gas. The latter was bubbled through ice-cold water (50 c.c.; A) throughout the experiment. The methylene dichloride solution was evaporated *in vacuo* below room temperature and the bright greenish-yellow liquid remaining was dissolved in acetic acid (10 c.c.). The solution was added cautiously to a mixture of zinc dust (1.05 g.) and water (10 c.c.) which was shaken vigorously. The resultant mixture was steam-distilled until about 35 c.c. of distillate (B) had been collected. The residual liquid in the distilling flask was cooled, filtered, and set aside (C).

Liquid A above gave no precipitate with a solution of 2 : 4-dinitrophenylhydrazine in aqueous 2N-hydrochloric acid. With this reagent a test portion of liquid B gave a precipitate of formaldehyde 2 : 4-dinitrophenylhydrazone which crystallised from 95% ethanol as brownish-yellow crystals, m. p. and mixed m. p. 167° . A test portion of liquid C was heated with a solution of 2 : 4-dinitrophenylhydrazine in 6N-hydrochloric acid, and the small amount of derivative which separated was collected, washed with dilute hydrochloric acid, and recrystallised from glacial acetic acid. Red crystals, m. p. 314° (decomp.), were obtained (Found : C, 40.5; H, 2.4. Calc. for $C_{14}H_{10}O_8N_8$: C, 40.2; H, 2.4%) which gave an intense blue colour with alcoholic sodium hydroxide. The m. p. was undepressed on admixture of the crystals with authentic glyoxal bis-2 : 4-dinitrophenylhydrazone.

The main bulk of liquid C was extracted with ether, and the extract was washed with a little water, dried (Na_2SO_4), and evaporated *in vacuo* to give a colourless oil (0.95 g.) which gave no carbonyl reactions and appeared to be acidic. It was combined with a similar oil from another ozonolysis on the above scale and the mixture was fractionated to give, after removal of acetic acid, a colourless acid (0.4 g.), b. p. $170\text{--}180^{\circ}$, n_D^{20} 1.4081 (Found : equiv., 115. Calc. for $C_6H_{12}O_2$: equiv., 116). The acid formed a *p*-bromophenacyl ester, which crystallised from 95% ethanol as plates, m. p. $81\text{--}82^{\circ}$, and an amide, which crystallised from light petroleum (b. p. $100\text{--}120^{\circ}$) as leaflets, m. p. 132° (lit. : m. p. 132° for *tert.*-butylacetamide). The m. p. of the *p*-bromophenacyl ester was not depressed on admixture of the ester with an authentic specimen of *p*-bromophenacyl *tert.*-butylacetate.

In a subsequent experiment on a similar scale the total amount of formaldehyde formed on decomposition of the ozonide was estimated by the neutral sulphite method and amounted to 0.46 g. (theory for one CH_2 group, 0.48 g.).

Hydrogenation of 2 : 4 : 4-Trimethylpent-2-enal to 2 : 4 : 4-Trimethylpentan-1-ol.—A solution of the aldehyde (5 g.) in absolute ethanol (50 c.c.) was hydrogenated over Raney nickel "paste" (5 g.) at room temperature and pressure until no more hydrogen was absorbed. It afforded 2 : 4 : 4-trimethylpentan-1-ol (3.35 g.), b. p. $84^{\circ}/25$ mm., whose 3 : 5-dinitrobenzoate (from 95% ethanol), had m. p. $73\text{--}74^{\circ}$, undepressed on admixture with the derivative obtained above from the hydrogenation of α -neopentylacraldehyde.

Hydrogenation of 2 : 4 : 4-Trimethylpent-2-enal to 2 : 4 : 4-Trimethylpentanal.—A solution of 2 : 4 : 4-trimethylpent-2-enal (1 g.) in absolute ethanol (30 c.c.) was hydrogenated at room temperature and pressure over Raney nickel "paste" (1 g.) until slightly more than one mol. of hydrogen had been absorbed, then filtered. The solution readily gave yellow needles (from ethanol) of 2 : 4 : 4-trimethylpentanal 2 : 4-dinitrophenylhydrazone, m. p. 144—145°, undepressed on admixture with the derivative obtained earlier from the hydrogenation of α -neopentylacetaldehyde.

Oxidation of 2 : 4 : 4-Trimethylpent-2-enal to 2 : 4 : 4-Trimethylpent-2-enoic Acid.—A solution of sodium hydroxide (12 g.) in water (600 c.c.) was added slowly to a stirred, cooled mixture of silver oxide (from 45 g. of nitrate), 95% ethanol (50 c.c.), water (50 c.c.), and 2 : 4 : 4-trimethylpent-2-enal (10 g.), and the resultant mixture was stirred overnight. The product was filtered, the solid was washed with water and ethanol, the combined filtrate and washings were concentrated *in vacuo* to ca. 100 c.c., extracted with ether, and the extract was discarded. The aqueous layer was acidified strongly with sulphuric acid and the oil which separated was extracted with ether. The ethereal extracts were washed with water, dried (Na_2SO_4), and evaporated *in vacuo*, to give crystals (9.65 g.) which were then fractionally distilled in a microstill. 2 : 4 : 4-Trimethylpent-2-enoic acid was obtained as a colourless oil (8.1 g.), b. p. 124.5/11.5 mm., m. p. 45—46°. Recrystallisation from light petroleum (b. p. 60—80°), cooled in solid carbon dioxide-alcohol, afforded a white microcrystalline solid, m. p. 47—48° (Found: C, 67.95; H, 10.0%; equiv., 143. $\text{C}_8\text{H}_{14}\text{O}_2$ requires C, 67.55; H, 9.9%; equiv., 142.2). The acid gave a *p*-bromophenacyl ester which separated from 90% ethanol-10% water as sheaves of thin needles, m. p. 79—80° (Found: C, 56.55; H, 5.75; Br, 23.95. $\text{C}_{16}\text{H}_{19}\text{O}_3\text{Br}$ requires C, 56.65; H, 5.65; Br, 23.55%). On hydrogenation of the acid (0.5 g.) in ethanol (10 c.c.) over Adams's catalyst (0.1 g.) at room temperature and pressure, 1.0 mol. of hydrogen was rapidly absorbed. Isolation of the product afforded 2 : 4 : 4-trimethylpentanoic acid, identified as described above.

Ozonolysis of 2 : 4 : 4-Trimethylpent-2-enal.—Ozonised oxygen (containing about 4% w/v of ozone) was passed through a solution of the aldehyde (2 g.) in redistilled methylene dichloride (50 c.c.) at the rate of about 30 c.c. per min. The aldehyde solution was cooled in a solid carbon dioxide-alcohol bath, and the gas leaving the solution was bubbled through ice-cold water (the resulting liquid was found to contain only traces of carbonyl compounds). When ozone appeared in the exit gas (after about 6 hr.) ozonolysis was stopped, the methylene dichloride solution was evaporated *in vacuo* below room temperature, and the bright greenish-yellow oil obtained was dissolved in acetic acid (10 c.c.). The solution was added cautiously, with shaking, to a mixture of zinc dust (1.05 g.) and water (10 c.c.) and the resultant mixture was diluted with water and distilled until about 7 c.c. of liquid had been collected. With 2 : 4-dinitrophenylhydrazine sulphate solution the distillate gave a copious precipitate of trimethylacetaldehyde 2 : 4-dinitrophenylhydrazone, needles (from ethanol-ethyl acetate), m. p. 209—210°, undepressed on admixture with an authentic specimen.

The liquid remaining in the distilling-flask was filtered and on treatment with 2 : 4-dinitrophenylhydrazine in dilute hydrochloric acid gave a precipitate of methylglyoxal bis-2 : 4-dinitrophenylhydrazone, which formed small brick-red crystals, m. p. and mixed m. p. 298—300° (decomp.), from pyridine (Found: C, 41.65; H, 3.05; N, 26.4. Calc. for $\text{C}_{15}\text{H}_{12}\text{O}_8\text{N}_8$: C, 41.65; H, 2.8; N, 25.9%), and gave an intense blue colour with alcoholic sodium hydroxide.

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