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Reaction of Fatty Acids with Hydroxy-radicals

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In the presence of hydroxy-radicals, palmitic, oleic, and linoleic acids are partially transformed into the corresponding C_{2n-2} hydrocarbon and a C_{n-1} alcohol. The double bonds in unsaturated acids may be preserved by performing the reaction in a heterogeneous system.

CHROMATOGRAPHY of linoleic acid that had been autoxidised in the presence of ammonia vapour in the dark for 14 weeks revealed that one of the components was a hydrocarbon which gave *n*-tetratriacontane when catalytically hydrogenated. Formation of a C_{2n-2} hydrocarbon from a C_n acid strongly suggested that the acid had been decarboxylated and that the residual alkyl radical had dimerised. Presumably these reactions are initiated by the transfer of an electron from a carboxylate ion to a hydroxy-radical formed during autoxidation. This hypothesis was tested as follows.

A methanolic solution of palmitic acid was brought to pH 11 and mixed with an excess of aqueous hydrogen peroxide. Some hours later the mixture was worked up. T.l.c. revealed the presence of three components: n-triacontane (17%), n-pentadecanol (71%), and starting material (2%).

Dilute hydrogen peroxide was added to an emulsion prepared by shaking together oleic acid, cyclohexane, and aqueous sodium hydroxide. Next day the organic compounds were recovered. T.l.c. indicated the presence of a hydrocarbon and an alcohol. The alcohol was isolated and chromatographed alongside olevl alcohol on a chromatostrip impregnated with silver nitrate;¹ the $R_{\rm F}$ values were the same and were much lower than that of n-octadecanol, which suggested that the unknown alcohol contained one double bond. In reversed-phase partition chromatography² the alcohol had a slightly higher $R_{\rm F}$ value than did oleyl alcohol, which suggested that it was heptadecenol. The chain-length and the position of the double bond in the unknown alcohol were established by degradation. Olevl alcohol was treated similarly so that the products could be compared. The samples were treated with ozone and the products were reduced with lithium aluminium hydride; the resultant mono- and di-ols were examined separately. The diols were identified chromatographically; the unknown alcohol gave octane-1,8-diol whereas oleyl alcohol gave nonane-1,9-diol. The monohydroxy-compounds were identified by chromatography on damp Kieselguhr³ and also as their 3,5-dinitrobenzoates; both the unknown alcohol and oleyl alcohol gave n-nonanol. Because the unknown alcohol gives rise to octane-1,8-diol and n-nonanol it must contain 17 carbon atoms and an 8,9-double bond, *i.e.* it is n-heptadec-8-en-1-ol.

These results show that an aliphatic acid is converted into a hydrocarbon and an alcohol by the action of hydroxy-radicals; the ratio of the products depends on the concentration of hydroxy-radicals in the system.

¹ L. J. Morris, Chem. and Ind., 1962, 1238.

² H. P. Kaufmann and Z. Makus, Fette, Seifen, Anstrichm., 1960, 62, 1014.

In an autoxidising system the concentration of hydroxyradicals will be small, so the main product will be a hydrocarbon, a fact that is significant in theories of the origins of petroleum.⁴

Small amounts of reference hydrocarbons and alcohols may be prepared as follows. The acid is placed along the origin line of a chromatoplate which is then transferred to a tank containing weakly ammoniacal hydrogen peroxide, as for chromatographic development. When the advancing front has just covered the sample, the plate is withdrawn from the tank and set aside until the next day. A two-stage development of the chromatogram, first in cyclohexane for a distance of 16 cm. and then in benzene-methanol (9:1) for a distance of 12 cm. places the hydrocarbon and the alcohol in suitable positions for recovery.

EXPERIMENTAL

Silica gel G (Merck) was used for t.l.c., $300 \mu m$. thick for normal work and $650 \mu m$. for preparative work; developing tanks were lined with filter paper saturated with solvent. I.r. spectra were determined for potassium bromide discs for solids and for liquid films for oils.

Autoxidation of Linoleic Acid.—Linoleic acid was purified by chromatography on silica gel with benzene-ethanol (9:1) as eluant. Test chromatostrips of the purified acid in the same solvent showed only one component. A thin layer of linoleic acid contained in a Petri dish was placed in a large glass tank with a beaker containing a few drops of aqueous ammonia. The tank was sealed and set aside in the dark. After 14 weeks the material was brownish yellow. A sample was taken up in methanol, acidified with dilute hydrochloric acid, and examined by t.l.c. under various conditions; at least five components were detected, of which the least polar had the properties of a hydrocarbon. Tests (on the adsorbent) for carboxy-, amino-, ester, hydroxy-, and carbonyl groups were negative.

Hydrocarbon.—The hydrocarbon was extracted into cyclohexane from a 2% aqueous methanolic solution of autoxidised linoleic acid (ca. 3 g.); removal of the solvent left a colourless liquid (160 mg.), v_{max} 980 (C=C) and 730 (long chain) cm.⁻¹. When catalytically hydrogenated, the substance took up 179 ml./g. at S.T.P. (calc. for tetratriacontatetraene, 190 ml./g.). The product gave white plates of n-tetratriacontane, m.p. 72.5° (from cyclohexane) (lit.,⁵ 73°) (Found: C, 85.4; H, 14.6%. Calc. for C₃₄H₇₀: C, 85.25; H, 14.75%).

Reaction of n-Hexadecanoic Acid with Hydrogen Peroxide. —The pH of a solution of palmitic acid (65 mg.) in methanol (20 ml.) was adjusted to 11 with methanolic sodium hydroxide, and the solution was mixed with 6% aqueous hydrogen peroxide (1 ml.). Some hours later, the mixture was acidified with dilute hydrochloric acid and the organic

³ S. J. Purdy and E. V. Truter, J. Chromatog., 1964, 14, 62.

⁴ R. Robinson, Nature, 1967, 214, 263.

compounds were extracted with ether. The extract was dried (Na₂SO₄) and reduced to a small volume. Chromatograms showed the presence of three components; they were recovered separately after preparative t.l.c. on eight plates with benzene-methanol (19:1) as eluant. The least polar component gave white plates of n-triacontane (11 mg.), m.p. $64\cdot5--65\cdot5^{\circ}$ (from ether) (lit.,⁵ 66°), v_{max} 740 and 730 (long chain) cm.⁻¹ (Found: C, 85·4; H, 14·55%. Calc. for $C_{30}H_{62}$: C, 85·2; H, 14·8%).

The intermediate component yielded n-pentadecanol (46 mg.) as a waxy solid, m.p. 43—44° (from ether) (lit.,⁵ 44°), ν_{max} 1065 (C–O) and 728 (long chain) cm.⁻¹ (Found: C, 78·85; H, 14·05%. Calc. for C₁₅H₃₂O: C, 78·9; H, 14·1%).

The most polar compound was palmitic acid (2 mg.), m.p. $64 \cdot 5 - 65 \cdot 5^{\circ}$.

Heterogeneous Reaction between Oleic Acid and Hydrogen Peroxide.-Chromatographically pure oleic acid (38 mg.), water (25 ml.), cyclohexane (1 ml.), and 10n-sodium hydroxide (0.25 ml.) were shaken together. Hydrogen peroxide (6%; 1 ml.) was dispersed in the emulsion which was then set aside. After the cyclohexane had evaporated (next day), the cloudy solution was acidified and the organic compounds were extracted with ether. The extract was dried (Na_2SO_4) and reduced to a small volume. T.l.c. with benzene-methanol (9:1) as eluant showed the presence of a hydrocarbon, an alcohol, oleic acid, and a component which was more polar than oleic acid. The alcohol was isolated by preparative t.l.c. (seven plates) with benzenemethanol (9:1) as eluant, to yield heptadecenol as a colourless oil (Found: C, 80.3; H, 13.4%. Calc. for C₁₇H₃₄O: C, 80·3; H, 13·4%).

Heptadecenol.—Chromatography on a layer of silica gel impregnated with 5% silver nitrate¹ with benzenemethanol (33:7) as eluant gave the following $R_{\rm F}$ values: n-octadecanol 0.95, oleyl alcohol 0.30, and heptadecenol 0.30. Reversed-phase partition chromatography on a layer of silica gel impregnated with 15% decane, with methyl cyanide-acetic acid (3:1) 90% saturated with decane² as eluant, gave the following $R_{\rm F}$ values: oleyl alcohol 0.40 and heptadecenol 0.54.

Heptadecenol (10 mg.) in ethyl acetate (20 ml.) was treated with ozone at room temperature. When ozonolysis was complete the solution was reduced in volume, water (0.1 ml.) was added, and the solvent was evaporated off. The residue was dissolved in pyridine, treated with lithium aluminium hydride, and worked up in the normal way. A sample of oleyl alcohol was processed in the same way. Chromatograms showed that both products contained monoand di-ols; these were isolated separately by preparative t.l.c. (one plate for each product) with benzene-methanol (9:1) as eluant. Samples of the diol fractions were chromatographed together with reference compounds by the continuous elution technique for 5 hr., (solvent traverse 17 cm.) with benzene-methanol (39:1) as eluant. The following sample traverses were observed: octan-1,8-diol 125 mm., decan-1,10-diol 153 mm., diol from oleyl alcohol (nonan-1,9-diol) 139 mm., and diol from heptadecenol 126 mm.

Samples of the monohydroxy-compound fractions were chromatographed together with reference compounds on damp Kieselgur G (Merck) with cyclohexane as eluant; ³ $R_{\rm F}$ values: n-octanol 0.85, n-decanol 0.70, monohydroxy-compound from oleyl alcohol (n-nonanol) 0.75, and monohydroxy compound from heptadecenol 0.75. The monohydroxy-compound from heptadecenol was converted into pale yellow microcrystals of n-nonyl 3,5-dinitrobenzoate, m.p. and mixed m.p. 51.5—52° (from methanol).

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⁵ "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1965.