Synthesis of Dodeca-1:11-diene-3:5:7:9-tetrayne

E. R. H. JONES, J. M. THOMPSON AND
M. C. WHITING

The University, Manchester, England

One of the substances identified by Sørensen and Sørensen¹ in the roots of several *Coreopsis* species shows a characteristic absorption spectrum, which was found to be very similar to that of synthetic tetradeca-2:12-diene-4:6:8:10-tetrayne². The volatility of the natural product, and the relative positions of the absorption maxima, suggested that the natural product might be even simpler than this hydrocarbon. Accordingly we have now synthesized dodeca-1:11-diene-3:5:7:9-tetrayne by oxidative coupling of hex-1-ene-3:5-diyne³. This extremely unstable hydrocarbon has m.p. 38–40°, whereas the *Coreopsis* product subsequently¹ obtained pure, darkens on heating above 43° without melting. A comparison of infra-red absorption spectra left little doubt that the two hydrocarbons are not identical. The ultra-violet absorption maxima of the synthetic compound lie at wavelengths 16–28 Å shorter than those of the *Coreopsis* compound, whereas the estimated experimental error of our values is about 10 Å, and of Prof. Sørensen's only about 5 Å. That these small differences are real was confirmed by measurements made at Manchester on a sample of the natural hydrocarbon kindly supplied by Professor Sørensen. The ultra-violet absorption spectrum, intermediate between those of the two synthetic hydrocarbons, suggests a mono-alkyl-diene-tetrayne chromophore. The presence of three linear C₁₁ polyenynes^{4,5} in related species supports the view that the *Coreopsis* hydrocarbon is trideca-1:11-diene-3:5:7:9-tetrayne.

This conclusion contrasts with the earlier one of Sørensen and Sørensen¹, based upon extremely difficult experiments with minute quantities of a very unstable substance, that the natural compound was the C₁₈ hydrocarbon now synthesised. It is hardly necessary to mention that the identification of saturated hydrocarbons such as dodecane and tridecane on a milligramme scale is by no means an easy task.

Experimental. A solution of hex-1-ene-3:5-diyne in liquid ammonia was prepared from 5.85 g of 1:6-dichlorohex-4-ene-2-yne², and

extracted with isobutane, and the isobutane was replaced by acetone (10 ml). Cuprous chloride (10 g) and ammonium chloride (16 g) in water (50 ml) were added, giving a clear red solution. Hydrogen peroxide (15 ml, 30 %) was introduced⁶ below the surface of the liquid, with external cooling to below 10°, during 20 minutes, followed by 50 ml of hydrochloric acid (1:3). From this point all operations were carried out at –5° in weak artificial light. The mixture was extracted with ether, and the extract at once evaporated under reduced pressure to less than 5 ml. The residue was dissolved in pure hexane (30 ml), and the mixture chromatographed on 50 g of alumina, which was eluted with 150 ml of hexane. Evaporation of the eluate to 10 ml and cooling to –75° gave crystalline dodeca-1:11-diene-3:5:7:9-tetrayne, which after four recrystallisations formed pale yellow needles (ca. 0.3 g), m.p. 38–40° in an evacuated capillary tube. It blackened at once in light even at –5°, and absorbed oxygen so rapidly that analysis or even normal weighing for spectrographic examination was impossible; for the latter purpose a little was sublimed at 30° (bath temp.)/10^{–4} mm on to a cold finger and dissolved at once in hexane, absolute intensities being found approximately by evaporating an aliquot and weighing the residue in nitrogen. Hydrogenation gave *n*-dodecane, m.p. –10––9°, in agreement with literature values¹. The observed uptake (8.8 moles) was low, probably because of partial polymerisation.

U.V.-spectrum in hexane:

ϵ_{max}	8 600	14 000	12 000	7 350
λ_{max}	3 880	3 600	3 350	3 140 Å
ϵ_{max}	115 000	160 000	99 000	85 500
λ_{max}	2 850	2 690	2 560	2 440 — 2 460 Å

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