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A NEW REACTION IN THE PYROLYSIS OF β-HYDROXY OLEFINS[1]

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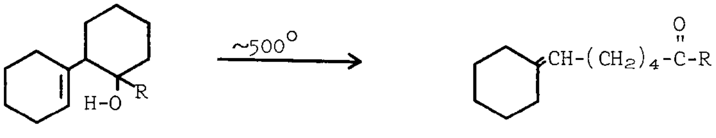
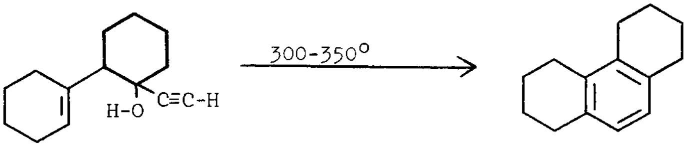
The pyrolysis of β-hydroxy olefins, which normally occurs via a cyclic transition state (2,3) to give olefins and carbonyl compounds, has proven to be a general and reliable transformation and an elegant synthetic method for extending carbon chains(4).

It was earlier shown (5) that the pyrolysis of β-hydroxy olefins of type I (where R=H, CH_3 or C_6H_5) rearrange smoothly at ~500° to give the expected products II.



I II

We wish now to report an initial and unexpected result. In the specific case (III) where R-equals ethinyl (-C ≡ CH), cyclodehydration occurs overwhelmingly to yield octahydrophenanthrene (IV). Indeed, when (III) was heated in an evacuated pyrex tube at 300° for 24 hours (or at 350° for 2 hours), the conversion to octahydrophenanthrene (IV) appeared to be quantitative. Formation of the latter is assumed to occur via an acid-base autocatalyzed reaction.



III IV

The absence of the expected unsaturated ketone was noted by the lack of olefinic protons in the n.m.r. spectrum and the absence of a carbonyl band in the infrared. Octahydrophenanthrene was indicated by the sharp singlet at 3.3 τ (aromatic protons) and aliphatic multiplets at 7.3 and 8.2 τ in the ratio of 2:8:8. The index of refraction [n_D^{20} = 1.5675 (lit. n_D^{20} = 1.5670)(6)], the ultraviolet spectrum [λ_{max} 269, 279 (lit. 269, 279)(7)] and mass spectra (major peaks at M/e, 186, M/e, 158, peak corresponding to successive losses of CH_2 and aromatic peaks, e.g., tropylium ion) fully characterized the pyrolysis product as 1, 2, 3, 4, 5, 6, 7, 8-octahydrophenanthrene. Its m.p. was 16° (lit. m.p. 16.7°)(8).

Approximately equal amounts of two diastereoisomers of compound (III) (based on t.l.c.; two spots, silica gel G, benzene) were formed by treating a stirred suspension of lithium acetylide ethylene diamine complex (92 g, 1 mole) in tetrahydrofuran (500 ml dry nitrogen atmosphere) with 2-(1'-cyclohexenyl)cyclohexanone (89 g, 0.5 mole) at 45° for 16 hours. The mixture of diasteoisomers, isolated as a crude product, was recrystallized several times from petroleum ether (30-40°) to give pure racemate "A" (12 g, m.p. 90.5-91.5°). G.l.p.c. analysis on a SE 30 column at 125° (retention time, 14 min) showed only one peak.

Anal.: Calc'd for $C_{14}H_{20}O$: C, 82.30; H, 9.87

Found: C, 82.52; H, 9.72

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