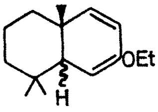
Photochemical Isomerization of the Enol Ether of 4a,8,8-Trimethyl-*trans*-Δ^3-2-octalone to the *cis*-Isomer

By MASAAKI MIYASHITA, HISASHI UDA, and AKIRA YOSHIKOSHI*

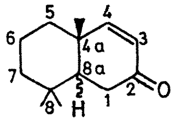
(*Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai, Japan*)

Summary The irradiation of the enol ether of 4a,8,8-trimethyl-*trans*-Δ^3-2-octalone in anhydrous ether yields the *cis*-isomer.

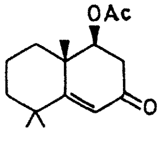
THERE are few precedents[1] for the photofission of 4a,5,6,7,8,8a-hexahydronaphthalene systems and the recyclization of the resulting cyclodecatriene systems, which are of interest as regards synthetic utility[1b] and in connection with a hypothetical pathway for genesis of some sesquiterpenoids.[2] We report on the photolysis of the title compound (I), the enol ether of a *trans*-fused $\alpha\beta$-unsaturated ketone system (III).



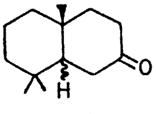
(I) 8aH = α, *trans*
(II) β, *cis*



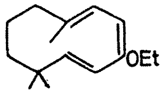
(III) 8aH = α, *trans*
(IV) β, *cis*



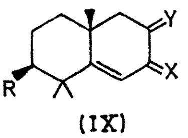
(V)



(VI) 8aH = α, *trans*
(VII) β, *cis*



(VIII)



(IX)
R=H or AcO
X (or Y)=O or $<^{O}_{O}]$

Catalytic hydrogenation (Pd/C–EtOH) of 4-acetoxy-4a,8,8-trimethyl-$\Delta^{1,8a}$-2-octalone (V)[3] gave a single decalone, m.p. 118·0—118·5°, in 86% yield, which was then quantitatively transformed into the desired octalone (III) [ir: ν_{max} (liquid) 1678 and 1610 cm.$^{-1}$, u.v.: λ_{max} (MeOH) 228 nm. (ϵ 8300), n.m.r.†: δ (CCl_4) 5·61 and 6·47 p.p.m. (2H, AB type quartet, J = 10 Hz)], by passing through an alumina column (eliminating acetic acid). The stereochemistry of the *trans*-ring junction in (III) was confirmed by its transformation to the *trans*-decalone (VI), m.p. 36—37°,‡ identical with the authentic sample prepared from the octalone (IX) (R = H, Y = H_2, X = O) by catalytic hydrogenation or lithium–liquid ammonia reduction.[4] Octalone (III) was converted into the enol ether (I) [liquid, 89% pure,§ n.m.r.: δ (CCl_4) 5·51 (2H, narrow quartet) and 4·47 p.p.m. (1H, broad singlet), uv: λ_{max} (Et_2O) 273 nm.] in 76% yield, in the usual manner (triethyl orthoformate–ethanol–toluene-*p*-sulphonic acid).

The irradiation of (I) was carried out in anhydrous ether solution at room temperature under a nitrogen atmosphere using a 450 w high-pressure mercury lamp and a Pyrex

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† 60 MHz, Me_4Si internal standard.

‡ It has been reported that both the racemic[4] and optically active[5] (VI) are liquid, but the racemic one is essentially crystalline compound.

§ As determined by g.l.c. This compound (I) was unstable and could not be purified even by column chromatography or preparative g.l.c. (changed after passing through a detector block), so that it was immediately subjected to photolysis after distillation over potassium hydrogen sulphate.

filter. G.l.c. analysis on an SE-30 column at suitable intervals during irradiation indicated the gradual appearance of a new peak and the diminution of the peak due to (I), and after 3 hr. the new peak had reached over 77% and the peak due to (I) had diminished below 19%. Spectroscopic properties [n.m.r.: δ (CCl_4) 5·63 (2H, narrow quartet) and 4·61 p.p.m. (1H, doublet, J 7 Hz), u.v.: λ_{max} (Et_2O) 273 nm.] clearly showed the photoproduct to be the isomeric, *i.e.*, *cis*-fused enol ether (II), presumably formed by way of photofission–thermal recyclization *via* a cyclodecatriene derivative (VIII) analogous to the previous findings.[1b]

Mild hydrolysis (oxalic acid–dilute ethanol) of (II), without purification, gave the crystalline conjugated ketone (IV) [m.p. 68°, i.r.: ν_{max} (KBr) 1673 and 1640 cm.$^{-1}$, u.v.: λ_{max} (MeOH) 235 nm. (ϵ 7800), n.m.r.: δ (CCl_4) 0·78, 0·96, and 1·22 (3H each, singlets), 6·55, and 5·78 p.p.m. (2H, AB type quartet, J 10 Hz)], not identical with the starting octalone (III), in up to 75% overall yield from (I). The signal due to the C-4 hydrogen (β-hydrogen of the enone system) at 6·55 p.p.m. is further split into doublets (J 2 Hz) (by long-range coupling with the angular C-8a hydrogen); this provides convincing evidence for the assigned structure (IV) having the *cis*-ring fusion and the non-steroidal conformation.[6] The physical properties of the *cis*-fused saturated ketone (VII), m.p. 86—87°, obtained by catalytic hydrogenation (palladium–charcoal–ethanol) of (IV) were also not identical with those of the *trans*-decalone (VI).

Almost identical results were obtained in the photolysis of (I) under various conditions (lower temperature, a Vycor filter, a medium-pressure mercury lamp, *etc.*), and attempts to isolate, trap, or characterize the plausible intermediate cyclodecatriene derivative (VIII) were not successful. However, the formation of the *cis*-fused octalone (IV) in good yield with this method provides synthetic utility for some *cis*-decalone derivatives, because catalytic hydrogenation of the various $\Delta^{1,8a}$-2(or 3)-octalone systems of the type (IX), favours the formation of the *trans*-decalone.[4,7]

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