Photolysis of 2-Ethynylcycloheptanone: a Photochemical Acetylene–allene Rearrangement with Ring Expansion

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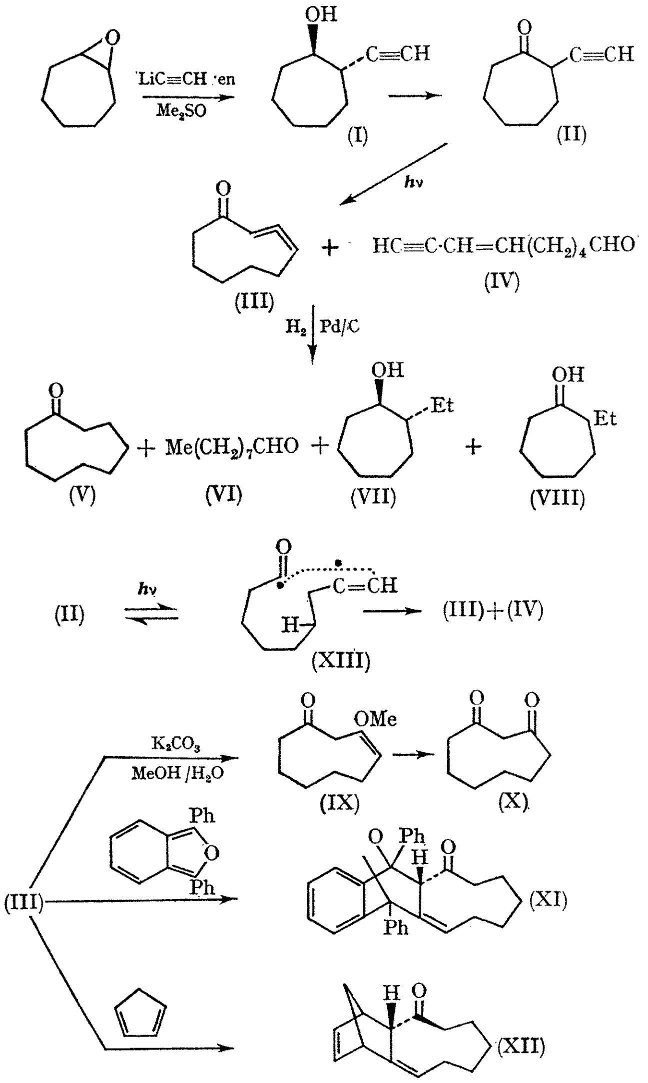
Summary Irradiation of 2-ethynylcycloheptanone gives the unusual allenic ketone, 2,3-cyclononadienone, as the major photochemical product.



IN a continuation of our studies of photochemical rearrangements of medium ring compounds,[1] we have examined the possibility of extending the previously observed[1,2] reversible photochemical ring contraction–ring expansion of β,γ-olefinic ketones to the corresponding β,γ-acetylenic ketones. We report the novel photochemical ring expansion of 2-ethynycycloheptenone (II) to the unstable conjugated allenic ketone, 2,3-cyclononadienone (III). Although we have been unable as yet to isolate (III) in pure form, the evidence outlined below provides strong presumptive evidence for the presence of (III) as the major monomeric product produced in the photolysis of (II).

Treatment of cycloheptene oxide with lithium acetylide–ethylene diamine (en) in dimethyl sulphoxide at room temperature gave *trans*-2-ethynylcycloheptanol (I).† Carefully controlled heterogeneous oxidation[3] of (I) gave 2-ethynylcycloheptanone (II): i.r. 3330 (–C≡C–H) and 1702 cm.$^{-1}$; n.m.r. δ 2·31 p.p.m. (d, 1H, J 3 Hz., –C≡C–H); u.v. (iso-octane) 290 (ϵ 64), 296sh (55) and 308sh nm. (37).

Irradiation‡ of a dilute solution of (II) in benzene through Vycor with 3000 Å lamps was followed by i.r. examination of aliquots which were removed periodically. Irradiation leads to a decrease in the characteristic i.r. bands for the terminal acetylenic hydrogen and saturated carbonyl group of (II) with the simultaneous appearance of new absorptions due to an allene (1940 cm.$^{-1}$) and conjugated carbonyl group (1670 cm.$^{-1}$) consistent with the formation of (III). When the photolysis was stopped after 2 hr. and the crude product was subjected to catalytic hydrogenation over palladium on charcoal, the v.p.c. volatile reduction product consisted of 45% cyclononanone (V), 19% nonyl aldehyde (VI), 12% *trans*-2-ethylcycloheptanol (VII) and 20% 2-ethylcycloheptanone (VIII). When a similar irradiation was carried out under the same conditions, but using hexane as the solvent, the hydrogenated photoproduct contained 74% (V), 10% (VI), 5% (VII), and 10% (VIII). The reaction also occurs when Pyrex optics are used but at somewhat slower rate. The presence of cyclononanone in the reduced photoproduct is consistent with the presence of (III) in the photolysis mixture but numerous attempts to isolate pure (III) have been unsuccessful. Although (III) can be obtained free of contaminants by chromatography, it is stable only in dilute solution and on concentration of these solutions (III) is converted rapidly to higher molecular

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† All new compounds gave satisfactory analytical results.

‡ Irradiations were conducted under nitrogen in a vessel mounted in the centre of a Rayonet Photochemical Reactor equipped with RPR-3000 Å or RPR-2537 Å lamps. The temperature inside the reactor was *ca.* 35°.

weight products. Spectral results for (III); n.m.r. (dilute solution) δ 5·78 (1H, d of t, J 8·5 and 6·5 Hz., H-4) and 5·52 p.p.m. (1H, m, H-2). U.v. (iso-octane): 204 (ϵ 14,900), 220sh (7,800) and 287 nm. (ϵ 380). The following experiments clearly establish (III) as the precursor of cyclononanone in the reduced photoproduct.

TABLE

Composition of reduced photolysis product from irradiation of (II)[a]

Solvent	U.v. source	Reaction vessel	% Products (V)	(VI)	(VII)	(VIII)
Hexane	3000 Å	Vycor	75	9	2	11
Acetone[b]	3000 Å	Vycor	4	1	2	90
Hexane[c]	3000 Å	Vycor	75	9	3	10
Hexane	2537 Å	Quartz	28	3	2	65
Acetone[d]	2537 Å	Quartz	2	1	1	94

[a] All photolyses were conducted in duplicate using the merry-go-round technique and for a period of 2 hr. [b] 0·044M in (II) [c] 0·020M in (II) and 0·01M in di-t-butyl nitroxide. [d] 0·050M in (II).

Treatment of the crude photoproduct with basic aqueous methanol at room temperature gave the enol ether (IX) which was readily converted to the known[4] 1,3-cyclononanedione (X). The formation of (IX) from (III) is consistent with previous studies of the base catalysed addition of methanol to allenic ketones.[5]

When a chloroform solution of the crude photoproduct was treated with 1,3-diphenylisobenzofuran at room temperature the crystalline *endo*-adduct (XI), m.p. 181—182°, was obtained in 30% yield. Adduct (XI) exhibits i.r. absorption at 1688 cm.$^{-1}$ and the n.m.r. spectrum shows, *inter alia*, an eight-line multiplet at δ 5·52 for the vinyl proton and a partially resolved doublet at δ 4·28 (J 2 Hz.) for the *exo*-methinyl hydrogen, which collapsed to a sharp singlet when the vinyl proton was irradiated in a spin decoupling experiment. On similar irradiation of the *exo*-methinyl proton, the absorption at δ 5·52 collapsed to a doublet of doublets (J 10 and 6 Hz.) corresponding to coupling of the vinyl proton with the two adjacent non-equivalent allylic protons.[6] Similarly, the crystalline adduct (XII), 49—50°, was obtained in 25% yield by treatment of the crude photoproduct with cyclopentadiene at room temperature.

All of the above evidence clearly indicates the presence of (III) in the photolysis mixture. Irradiation of (II) apparently leads to a type (I) cleavage of the C-1–C-2 bond to give the diradical (XIII) which can either reclose to (II) or (III) or undergo an intramolecular hydrogen abstraction to give the enyne aldehyde (IV). Irradiation of samples of (III) gives no products containing a seven-membered ring indicating the reaction is irreversible. Although in most free radical reactions allenic products are rarely obtained in appreciable quantities when propargyl radicals are generated,[7] recent studies have shown that under appropriate conditions an equilibrium can be established between the allenic and propargyl system .[8]

Attempts to sensitize the reaction with acetone or to quench the reaction with di-t-butyl nitroxide[9] were unsuccessful (see Table). These sensitization and quenching results are consistent with the reaction proceeding by way of a singlet excited state as has been indicated for the rearrangement of the corresponding β,γ-olefinic ketones.[2c]

This study indicates the photochemistry of β,γ-acetylenic ketones parallels that of the corresponding β,γ-olefinic ketones and provides a novel method of considerable utility for the preparation of the unusual conjugated allenic ketones in medium-sized rings in high yield.

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