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PROPELLANES IV.[1] THE PHOTOCHEMICAL REALIGNMENT OF 12-OXA[4.4.3]PROPELLA-2,4,7,9-TETRAENE AND OF 12-METHYL-11,13-DIOXO-12-AZA[4.4.3]PROPELLA-2,4,7,9-TETRAENE: DERIVATIVES OF TETRACYCLO$[4.4.0.0^{2,10}.0^{5,7}]$DECA-3,8-DIENE

Esther Babad, David Ginsburg and Mordecai B. Rubin
Department of Chemistry, Israel Institute of Technology, Haifa

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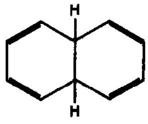
The energy surface corresponding to hydrocarbons of the formula $(CH)_{10}$ encompasses a multitude of shallow potential wells into which may fall interconvertible, more, or less elusive members of the series. These hydrocarbons are related through a complex array of electrocyclic processes and may be accessible either photochemically or thermally.

The variegated species related to cis-9,10-dihydronaphthalene 1 include bullvalene, Nenitzescu's hydrocarbon-tricyclo$[4.2.2.0^{2,5}]$deca-3,7,9-triene, bicyclo[4.2.2]deca-2,4,7,9-tetraene 2, tricyclo$[5.3.0.0^{4,8}]$deca-2,5,9-triene, tetracyclo$[4.4.0.0^{1,5}.0^{2,8}]$deca-3,9-diene, and various substituted derivatives.[2-7] The missing link in this series of fluxional isomers has been the oft-cited[3,5,7] but never isolated tetracyclo$[4.4.0.0^{2,10}.0^{5,7}]$deca-3,8-diene 3.



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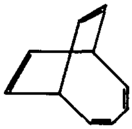

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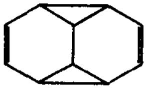

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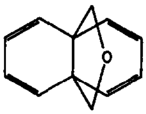

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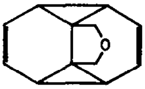

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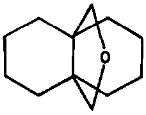

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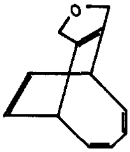

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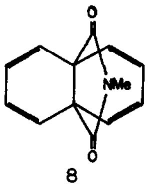

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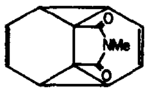

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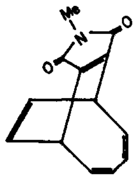

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We wish to report that photoirradiation[8] of 12-oxa[4.4.3]propella-2,4,7,9-tetraene 4[1,9] at 2537 Å affords 12-oxa-pentacyclo[$4.4.0.0^{2,10}.0^{5,7}$]trideca-3,8-diene 5, a 1-6 bridged derivative of 3, in about 95% yield (accompanied by about 5% of an insoluble polymer). Its remarkably simple NMR spectrum ($CDCl_3$; 60 MHz) determined at -25°C consisted of 3 lines of equal intensities at 361 Hz ($W_{1/2}$= 4 Hz; vinylic protons), 255 Hz ($W_{1/2}$= 1.5 Hz; $C\underline{H}_2O$) and 88 Hz ($W_{1/2}$= 4 Hz; allylic cyclopropyl protons).[10] Irradiation at 88 Hz resulted in appreciable sharpening of the line at 361 Hz ($W_{1/2}$= 1.5 Hz) and vice versa. The UV spectrum of 5 (in MeOH) showed only strong end absorption (λ 220nm; ε 3000). Further support for the structure of 5 was obtained by catalytic hydrogenation at room temperature (platinum oxide in methanol) which quantitatively afforded the known[11] 12-oxa[4.4.3]propellane 6.

Upon standing at room temperature in deuteriochloroform or in methanol solution, 5 was quantitatively converted into the tetraene 7,[12] m.p. 85.5-86.5°, a derivative of 2. Its spectroscopic properties were in good agreement with those reported for 2.[7] UV (MeOH): λ_{max} 286(sh), 272, 265 nm; ε_{max} 2200, 3300, 3400. NMR ($CDCl_3$; 60MHz): 2 proton doublet centered at 367 Hz (ethylene bridge); 4 proton multiplet centered at 342 Hz (diene bridge); a pair of lines at 269 and 267.5 Hz (diastereotopic $C\underline{H}_2O$) and a broad 2 proton multiplet at 193 Hz (allylic protons). Irradiation at 193 Hz caused collapse of the 367 Hz doublet and of the 347 Hz multiplet to broad singlets. The half-life for the conversion 5→7 in methanol solution at 22°C was ca. 2 hours.

Photoirradiation[8] of the tetraenic imide 8[13] was even more dramatic in that the product 9, analogous to 5, had a half-life of ca. 3 hours in methanol solution at 60° for the conversion 9→10. The spectroscopic properties of 9 and 10 were: 9[12], UV (MeOH): λ 220 nm; ε 7500. NMR ($CDCl_3$; 60MHz): 2 lines of equal intensities at 360 Hz ($W_{1/2}$= 4 Hz; 4 vinylic protons) and 133 Hz ($W_{1/2}$= 4 Hz; 4 allylic cyclopropyl protons) and a third line at 189 Hz (3H; $NC\underline{H}_3$). Irradiation at 133 Hz resulted in appreciable sharpening of the line at 360 Hz ($W_{1/2}$= 1.5 Hz), and vice versa. 10,[12] m.p. 205.5-206°, UV(MeOH): λ_{max} 293 (sh), 248 nm; ε_{max} 2600, 13200. NMR($CDCl_3$; 60 MHz): 2 proton doublet centered at 444 Hz (ethylene bridge), 4 proton multiplet centered at 347 Hz (diene bridge), a broad 2 proton multiplet at 215 Hz (allylic protons) and a sharp 3 proton singlet at 184 Hz($NC\underline{H}_3$).

Irradiation at 215 Hz caused collapse of the 444 Hz doublet and of the 347 Hz multiplet to broad singlets.

The failure of other workers to observe 3 or its derivatives may be due to the reaction conditions employed or to factors for which the additional ring present in 5 and in 9, is responsible. This question as well as the further photochemical behavior of 7 and 10 are being investigated.

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