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OLEFINIC AND ACETYLENIC COMPOUNDS.V. THE REGIOSPECIFIC SYNTHESIS OF 1,5-DISUBSTITUTED-CYCLOOCTATETRAENE DERIVATIVES.

By H.P. Figeys*[a], G. Van Lommen[b], M. Belladone[a] and M. Destrebecq[a]
a)Université Libre de Bruxelles, Faculté des Sciences, B-1050 Bruxelles, Belgium. b)Vrije Universiteit Brussel, Dienst Organische Scheikunde, Fakulteit der Wetenschappen, Pleinlaan 2, 1050 Brussel, Belgium.

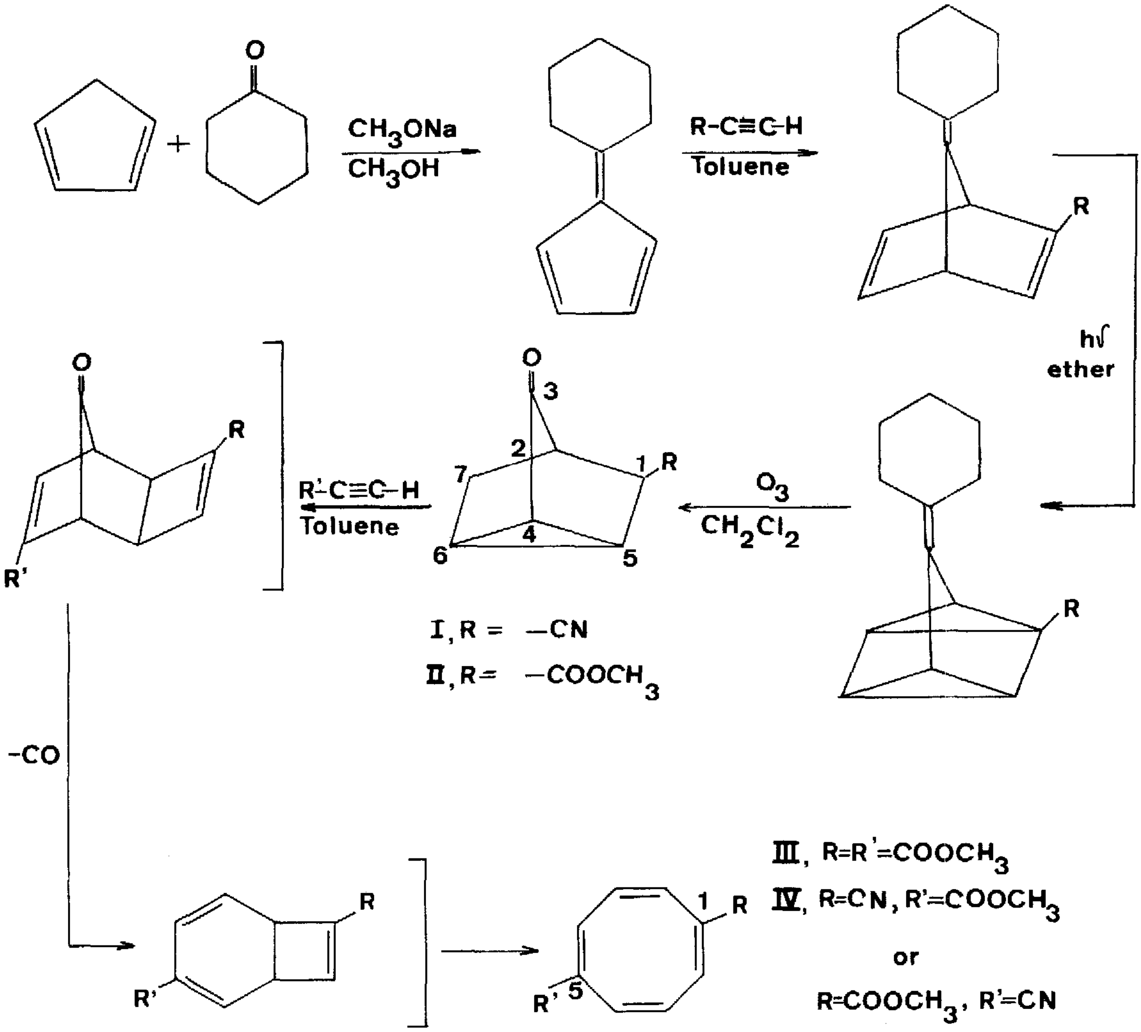
Summary. The Thermally controlled addition of methylpropiolate or cyanoacetylene to 1-methoxycarbonyl-or 1-cyano-quadricyclanone leads in a regiospecific way to the corresponding 1,5-disubstituted cyclooctatetraenes.

We recently reported that the $[{}_{\pi}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s]$ cycloadditions of various monosubstituted acetylenes on 1-methoxycarbonyl- and 1-cyanotetracyclo $[3.2.0.0^{2,7}.0^{4,6}]$ heptane (quadricyclane) are regiospecific reactions(1). Only the isomer corresponding to the orientation of the substituents in the "pseudo-para" positions in the delocalised six-membered cyclic transition state, could in each case be isolated.

On the other hand, Prinzbach et al. have shown that the addition of dimethylacetylenedicarboxylate or methylpropiolate to 1,5-dimethoxycarbonyl-tetracyclo$[3.2.0.0^{2,7}.0^{4,6}]$heptan-3-one (quadricyclanone) leads to the corresponding polysubstituted cycloöctatetraene (COT) derivatives(2,3). In the light of the concept of orbital symmetry conservation(4), this reaction can be described as a $[{}_{\pi}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s]$ cycloaddition, followed by a chelotropic linear loss of carbon monoxide, producing the bicyclic isomer of cycloöctatetraene, which opens then disrotatory to the final product (see scheme I).

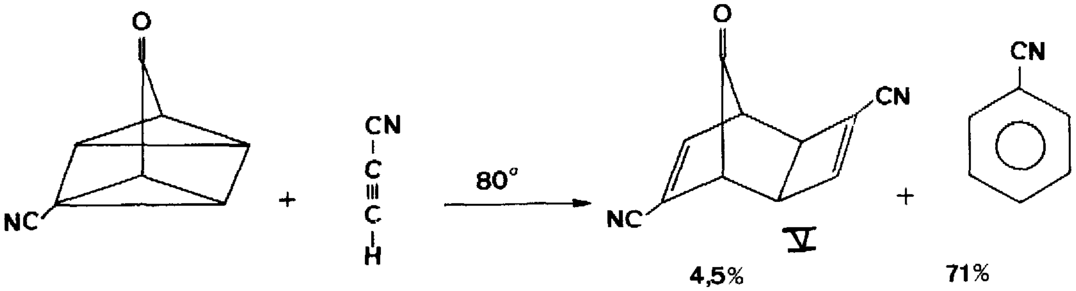
The possibility thus arose that this reaction scheme could be used as a regiospecific entry to cycloöctatetraenes polysubstituted in well-known and preselected positions; this problem is far from being resolved and has up to now not received a satisfactory solution(5).

1-methoxycarbonyl(II)-and 1-cyano-quadricyclanone(I) were prepared by the method described by Prinzbach et al.(6,7) for the synthesis of (II)(Scheme I). The Knoevenagel condensation of cyclopentadiene with cyclohexanone ($NaOCH_3/CH_3OH$; 2 h, 50°C) led to 6,6'-hexamethylene-fulvene (yield:39%)(8); after Diels-Alder reaction with methylpropiolate (in refluxing toluene, 24 h, oily product, yield 43%) or cyanoacetylene (toluene at 120° under pressure, 15 h, yield 61%, mp : 98°), photochemical $[{}_{\pi}2_s + {}_{\pi}2_s]$ cycloaddition (medium pressure Hg-lamp, 150 Watt, pyrex, ether) of the resulting norbornadiene derivative (for II: 8h., 93%, mp:85°; for I : 12h., 89%, mp:104°) and ozonolysis (CH_2Cl_2, -40°C) of the remaining double bond, 1-methoxycarbonyl and 1-cyano-quadricyclanone are obtained in respectively 78% and 80% (mp 45°) yield. The use of cyclohexanone in this reaction scheme instead of benzophenone or acetone as originally described by Prinzbach, avoided both low photochemical yields and the manipulations of unstable oily products(6).



Scheme I

Reaction of II with methylpropiolate and with cyanoacetylene in toluene at 130° under pressure for 14hrs yielded respectively 1,5-dimethoxycarbonyl-COT (III) (yield 35%, together with 27% of methylbenzoate) and 1-cyano-5-methoxycarbonyl-COT (IV) (yield 26%, 34% of methylbenzoate) as the only detectable isomers. Methylbenzoate is the known thermal degradation product of II(7), formally produced by a forbidden $2\sigma \rightarrow 2\pi$ ring-opening of the quadricyclane nucleus, with simultaneous or subsequent loss of carbon monoxyde(2). The same compound IV was obtained when I was made to react with methylpropiolate under the same conditions; the yield however dropped to 3.5% and 80% of benzonitrile was produced during the reaction. This seems to indicate that the presence of strong electron withdrawing groups like the cyano group at the 1,5,6 and/or 7 positions of the quadricyclane nucleus favors considerably the ring-opening process; a similar observation has been made by J.R. Edman and H.E. Simmons(9) on 1,5-dicyano-quadricyclane; a theoretical interpretation has been given by R. Hoffmann(10). In an attempt to reduce the importance of this thermal degradation, I was made to react with cyanoacetylene at 80° (instead of 130°) for 14h; benzonitrile (yield 71%) and the adduct V (Scheme II, yield 4.5%) could be isolated from the reaction mixture by preparative t.l.c., thus confirming the reaction sequence outlined in Scheme I.



Scheme II

The NMR-spectra of III and IV at -70°C and 270 MHz confirmed the 1,5-structure (ABX pattern for III with $\delta_A = 6.105$, $\delta_B = 6.177$, $\delta_X = 7.129$ ppm, $J_{AB} = 11.49$ Hz and $J_{AX} = 3.53$ Hz; two overlapping ABX systems for IV, which could be computer-analyzed(11) with the following results and attributions : $\delta_A = 6.196$, $\delta_B = 5.891$, $\delta_X = 7.118$ ppm, $J_{AB} = 11.051$ and $J_{AX} = 3.980$ Hz; $\delta_{A'} = 6.004$, $\delta_{B'} = 6.219$, $\delta_{X'} = 6.720$ ppm, $J_{A'B'} = 11.057$ and $J_{A'X'} = 3.538$ Hz) (Figure I); at room temperature, a dynamical bond shift takes place.

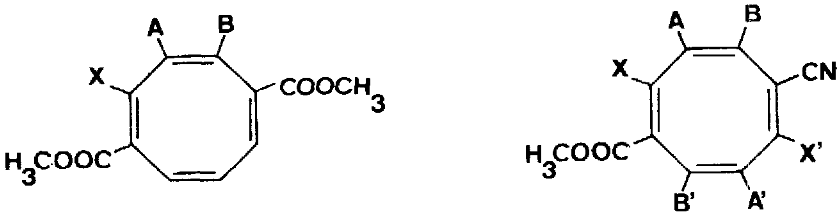


Figure I

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