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TRICYCLO[4.1.0.0^{2,7}]HEPT-4-EN-3-ONE : A SIMPLE SYNTHESIS AND ^{13}C-NMR SPECTRUM

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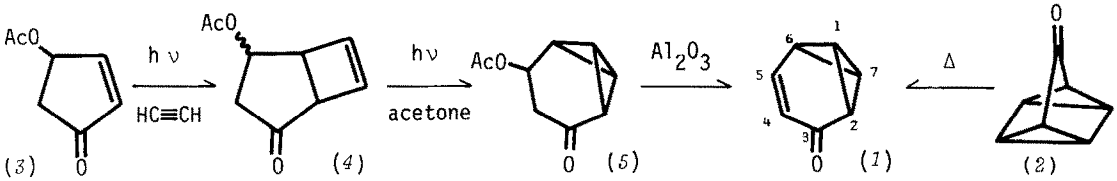
Although tricyclo[4.1.0.0^{2,7}]hept-4-en-3-one (tropovalene) (*1*), a valence isomer of tropone, has recently been synthesized by Prinzbach$^{1)}$ through thermolysis of quadricyclanone (*2*),$^{2)}$ neither the low yield of the thermolysis nor the multistep sequence permitted the production of *1* in quantities sufficient for a detailed investigation. We now report a facile procedure for synthesizing *1* which makes this intriguing compound easily accessible.

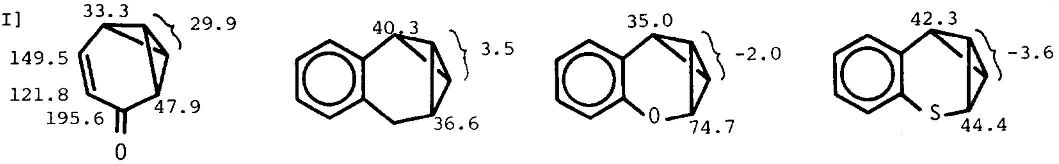
It seemed practical to build up *1* from 4-acetoxycyclopenten-2-one (*3*) following the scheme, previously developed by Ipaktschi,$^{3)}$ for the construction of tricyclo[4.1.0.0^{2,7}]heptan-3-one ring system.



Thus, a solution of 4-acetoxycyclopenten-2-one (*3*)$^{4)}$ [3 g] in dry acetone [200 ml] cooled with dry ice-ethanol bath was irradiated using a 100 w Hanovia high pressure mercury lamp for 4 h while acetylene was blown through. Usual work-up was followed, then, careful distillation gave a mixture of stereoisomeric cycloadducts (*4*)$^{5)}$ in 54.5% yield. The adduct (*4*) [800 mg] was dissolved in 130 ml of dry acetone and irradiated with a 450 w high pressure mercury lamp for 5 h. After removal of the solvent in vacuo at 0°C, the product (*5*)$^{6)}$ when chromatographed on alumina deactivated with 10% water was smoothly converted into the desired *1* in 61% yield (based on *4*). The spectral data of *1* are completely identical with those reported.[1]

The carbon chemical shifts of *1*[7] are compared in Chart-I with those of a series of benz-annelated tricyclo[4.1.0.0^{2,7}]heptenes.[8] It is worthnoting that the compound *1* shows significant shift to lower field (ca.30 ppm) for the bridgehead carbons of the bicyclobutane moiety of *1*. This finding indicates decreased electron density at these carbons and it is consistent with the downfield chemical shift of the C$_1$ and C$_7$ protons (δ=3.35) observed in the ^{1}H-nmr spectrum of *1*.[1] This deshielding could be explained by the ground-state conjugation effect between the carbonyl group and the bicyclobutane ring.

[Chart-I]



References and Notes

1) H. Prinzbach, H. Babsch, and H. Fritz, *Tetrahedron Lett.*, 2129 (1976).

2) P. G. Gassman and D. S. Patton, *J. Am. Chem. Soc.*, 90, 7276 (1968).

3) J. Ipaktschi, *Chem. Ber.*, 105, 1996 (1972).

4) C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, 29, 3505 (1964).

5) ^{1}H-Nmr spectrum of *4* displays one proton doublet at δ 5.21 (J=5.2 Hz, H-4) overlapping with 0.4 proton multiplet and three protons singlet at δ 2.0 accompanied with 1.2 protons sharp singlet at δ 2.02 indicating a ratio of *exo/endo* isomers is 1:0.4.

6) ^{1}H-Nmr spectrum of *5* (bp 35°C/0.04 Torr) shows one proton triplet of doublet at δ 5.36 (J=7.0, 3.5 Hz, H-5) and two protons pseudo triplet at δ 2.50 (H-1, and -7).

7) These assignments can be made on the basis of relative signal intensity, splitting patterns in the off-resonance decoupled spectrum, and comparison with spectra of some suitable reference compounds. (δ-values from TMS).

8) M. Uyegaki, S. Ito, Y. Sugihara, and I. Murata, *Tetrahedron Lett.*, 4473(1976).