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ARYNIC CONDENSATION OF KETONE ENOLATES. VIII*

ONE STEP SYNTHESIS OF DIBENZOTRICYCLO $\left[4,2,2,1^{2,5}\right]$ UNDECA-8,10-DIENE-1-OL

STRUCTURE ELUCIDATION BY ^{13}C AND ^{1}H NMR

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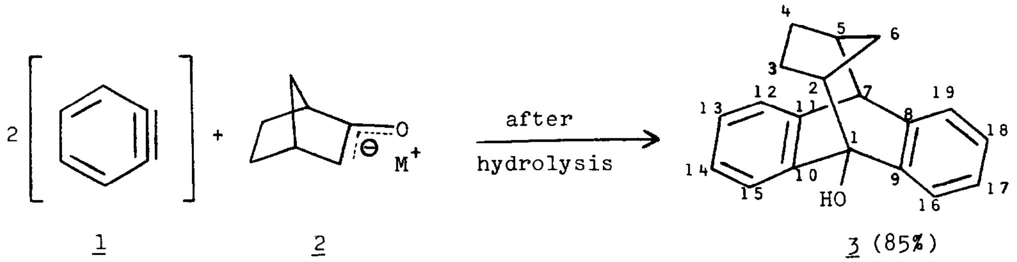
We have shown previously[1] that the condensation of benzyne, in aprotic medium, with some ketone enolates may be a route to anthranols. This reaction carried out with suitable bicyclic ketones might lead to syntheses of polycyclic derivatives, difficult to prepare by other ways. The result obtained with bicyclo [2,2,1] heptanone-2 is summarized in the following scheme :



(1 is formed by action of $NaNH_2$-2 on PhBr).

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* Part VII : P. CAUBERE, G. GUILLAUMET and M.S. MOURAD ; Tetrahedron, in the press

To our knowledge, the compound 3* (m.P. 174°) has never been described and the spectroscopic data about this type of compound are very scarce[2]. Since the reaction of benzyne with ketone enolates may give several ways of condensation[1,3], it was essential to prove the structure **of product 3 decisively.** In this purpose ^{13}C and ^{1}H NMR were used.

^{13}C NMR spectra have been recorded with a bruker HX 90 operating at 22.63 MHz in the Fourier transform mode with complete proton decoupling. The features of the ^{13}C NMR spectra of product 3 (dibenzotricyclo $[4,2,2,1^{2,5}]$ undeca-8,10-diene-1-ol) are summarized in the table :

Table

^{13}C chemical shifts$^{(a)}$ of 3 and $\Delta\delta$ ^{13}C shifts produced by Eu(DPM)$_3$

Position	δ ^{13}C (b)	$\Delta\delta$ ^{13}C (c)	$\Delta\delta$ ^{13}C (d)
C_1	79.62	2.10	3.80
C_2	48.74	0.70	1.80
C_3	28.20	0.39	0.85
C_4	27.90	0.04	0.20
C_5	37.23	0.25	0.50
C_6	37.04	0.32	0.95
C_7	49.65	0.30	0.85
$C_8+C_{11}$$^{(e)}$	142.5 ; 140.1	0.30 ; 0.40	0.80 ; 1.00
$C_9+C_{10}$$^{(e)}$	147.0 ; 144.9	0.50 ; 0.60	1.20 ; 1.40
$C_{12}+C_{13}+C_{14}$ (e) $+C_{17}+C_{18}+C_{19}$	126.7 ; 126.4 ; 126.0 125.4 ; 125.1 ; 124.7	0.10 to 0.30	0.30 to 0.60
$C_{15}+C_{16}$ (e)	121.7 ; 119.8	0.50	1.00

(a) Chemical shifts are given in ppm from TMS

(b) ^{13}C chemical shifts of 3 in $CDCl_3$ (0.15 mol/l)

(c)(d) Same sample with progressively added Eu(DPM)$_3$; 0.01 and 0.03 mol/l

(e) Separate assignment for these carbons is impossible

* Satisfactory analytical data were obtained for this product.

Partial assignments were first established on the basis of an off resonance experiment (No attempt was made to differentiate the carbons numbered 12, 13, 14, 17, 18 and 19). The use of Eu(DPM)$_3$ shift reagent[4] allowed to raise the remaining ambiguities (see table). These assignments establish the proposed structure. Furthermore the given attribution is in agreement with the literature data ; the effect of a benzylic alcohol function is to increase the chemical shift of the ^{13}C bearing the function[5] while it decreases the chemical shift of the other cyclic carbons. For the saturated cycle, chemical shifts of the same order of magnitude as ours have been found previously[6] in compounds of similar configuration.

The structure was further confirmed with PMR homodecoupling experiments ; irradiation of H_7 $[\delta$ (CDCl$_3$) 4.02 ppm$]$ or H_5 $[\delta = 2.42$ to 2.67 ppm$]$ evidenced a coupling of 9 Hz between these two protons. The C_1-C_2 junction was demontrated on the basis of the shift induced by Eu(DPM)$_3$ on H_2 $[\delta = 2.20$ to 2.42 ppm$]$.

Besides the molecular peak, the mass spectrum shows many fragments, among which the peak corresponding to the loss of the five membered ring is found.

The UV spectrum shows : λ_{max} (EtOH) 276.5 (log ε 3.11) ; 268 (3.02) and 261.5 (2.85).

Reaction procedure :

25 mM of norcamphor in 10 cm^3 of tetrahydrofuran (THF) were added dropwise to a stirred solution of 25 mM trityl lithium, from triphenyl methane and BuLi in THF[7,8]. Stirring was continued at 40° for 1 h, a solution of 25 mM of bromobenzene was added and then a suspension of NaNH$_2$ (50 mM) in the THF. The reaction was continued at 40° for 6 h, and then the reaction mass was treated in the usual way[3].

We thenk G. TELLER, Laboratory of organic chemistry (Strasbourg) for the mass spectrum.

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