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2:3.7:8-DIBENZOTRICYCLO[$3.3.1.0^{4,6}$]NONA-2.7-DIEN-9-ONE

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In a previous paper (1) we reported the synthesis of the tricyclo[$3.3.1.0^{4,6}$]nonan-9-one by an intramolecular addition to the isolated double bond of the α-ketocarbene generated from the corresponding diazoketone following the method described by Stork and Ficini (2).

In the present work we have extended this reaction to the dibenzocycloheptatriene system which has been recently investigated in our institute (3). For this purpose we prepared the diazomethylketone I by treatment of 1:2.5:6-dibenzocycloheptatrien-7-carboxylic acid chloride

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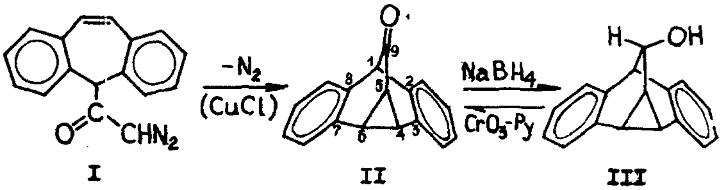
[1] V. Ioan, M. Popovici, E. Moşanu, M. Elian and C.D. Nenitzescu, Rev. Roumaine Chim. 10, 185 (1965).

[2] G. Stork and J. Ficini, J.Amer.Chem.Soc. 83, 4678 (1961).

[3] E. Ciorănescu, A. Bucur, M. Elian, M. Banciu, M. Voicu and C.D. Nenitzescu, Rev. Roumaine Chim. 10, 161 (1965).

(4) with an ethereal solution of diazomethane. The crude diazoketone, a yellowish-red solid with m.p. 123-127° (dec.) (ν 1650 (C=O), 2110 (N_2) cm^{-1}) was used in the next step without further purification.



The decomposition was carried out by a gradual addition of the solid diazoketone (4.0 g) into a suspension of cuprous chloride (1.5 g) in boiling cyclohexane (400 ml) or by heating a 1% solution of I in benzene under reflux in the presence of 0.5% finely powdered copper for 8-10 hours. From the residue left after filtration of the catalyst and evaporation of solvent, the ketone II i.e. the 2:3.7:8-dibenzotricyclo$[3.3.1.0^{4,6}]$nona-2.7-dien-9-one was isolated, by recrystallization from methanol, in 30% of the theoretical yield ; m.p. 168.5-169°. (Anal. Calcd. for $C_{17}H_{12}O$: C, 87.90 ; H, 5.21 ; mol. wt. 232. Found : C, 87.97 ; H, 5.50 ; mol. wt. 224 (Rast's Method). Semicarbazone, m.p. 224-225° (from methanol). (Found : C, 74.86 ; H, 5.45 ; N, 14.73. $C_{18}H_{15}N_3O$ requires C, 74.72 ; H, 5.23 ; N, 14.52). Oxime, m.p. 219-220° (from 70% ethanol). (Found : C, 82.38 ; H, 5.33 ; N, 5.74. $C_{17}H_{13}NO$

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[4] M. A. Davis, S. O. Winthrop, R. A. Thomas, F. Herr, M. P. Charest and R. Gaudry, J. Med. Chem. 7, 88 (1964).

requires C, 82.57 ; H, 5.30 ; N, 5.66).

The ketone was assigned the structure II on the basis of its spectral properties. The infrared spectrum exhibits normal absorption for the ketone carbonyl (ν 1721 cm^{-1} with satellites at 1700 and 1753 cm^{-1}). The n.m.r. spectrum (5) shows absorption at τ 2.92 (multiplet, 8 protons), 5.92 (doublet, 1 proton), 6.98 (doublet, 2 protons), 7.50 (multiplet, 1 proton) ; no vinylic protons can be observed. The signals at τ 5.92, 6.98 and 7.50 may be rationalized in terms of an AB_2X spectrum (6) with J_{AB} = 8.0, J_{AX} = 2.1, J_{BX} = 0 cps and with τ 7.50 = A, 6.98 = B_2, 5.92 = X. The J_{AB} = 8 cps is exactly the value expected for a <u>cis</u>-cyclopropane hydrogen coupling constant (7). Consequently the n.m.r. spectrum confirms the structure II.

Reduction of ketone II with sodium borohydride in methanol afforded the alcohol III, m.p. 135.5-136° (from 50% methanol). (<u>Anal</u>. Calcd. for $C_{17}H_{14}O$: C, 87.15 ; H, 6.02. Found : C, 86.92 ; H, 6.23). The infrared spectrum exhibits characteristic absorptions at ν 1037 (C-OH) and 3590 (O-H) cm^{-1}.

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[5] 60 Mc ; in CCl_4.

[6] H_A, H_B and H_X being the protons in the respective positions 5, 4 (=6) and 1.

[7] J. D. Graham and M. T. Rogers, <u>J.Amer.Chem.Soc</u>. 84, 2249 (1962).

Oxidation of III with chromium trioxide in pyridine regenerated the starting ketone (mixed m.p. without depression and identical infrared spectra).

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