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PHOTOCHEMICAL REARRANGEMENT OF BENZONORCARADIENE DERIVATIVES

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The photochemical rearrangement of benzonorcaradiene derivatives has been attracting interests in recent years, and studied by several workers, but neither study on the stereochemical course of the rearrangement nor the reaction with 7-alkyl substituted derivatives was reported.[1,2,3]

Now we wish to report the rearrangement of methyl 2,3-benzonorcaradien-7-yl-acetate (Ib) proceeding in similar fassion to unsubstituted benzonorcaradiene (Ia), with highly stereospecific manner.

Irradiation of a methanolic solution of 6,7-benzobicyclo[3.2.2]nona-2,6,8-trien-4-one (II)(Ushio high pressure Hg lamp, Pyrex filter) for 10 min. gave mainly endo-Ib as reported by Chapman[4] and Kende,[5] but prolonged irradiation (1 hr.) gave a mixture of compounds. The mixture was found by glc (Apiezon L, 20 ft.) to be composed of at least five components, from which naphthalene, methyl 2-naphthylacetate (III) and three isomeric methyl esters [A(mass spectrum, m/e 214(9.1), 154(31), 141(100), 128(39), 115(29); $\nu_{\max}^{\text{Liq. film}}$ cm^{-1} 3035, 2930, 1735, 1250, 1162, 757, 730), B(m/e 214(37), 155(100), 154(45), 153(23), 142(20), 141(62), 115(21); $\nu_{\max}^{CCl_4}$ cm^{-1} 3035, 2960, 1735, 1245, 1160, 1115) and C(m/e 214 (22), 155(25), 154(28), 141(100); $\nu_{\max}^{\text{Liq. film}}$ cm^{-1} 3015, 2950, 1735, 1250, 1162, 808, 770, 753)] were isolated by preparative glc (A : B : C = 20 : 65 : 15).

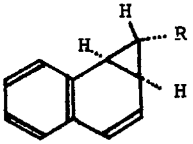
Compound A showed uv spectrum [$\lambda_{\max}^{EtOH}$ nm.(log ε) 262$^{\text{infl.}}$, 268.5(3.12), 275 (3.15)] similar to those of benzocyclobutene[6] or benzocyclopentene.[7] Its nmr spectrum[δ ppm.(CCl$_4$) 7.08(4H,s), 6.29(1H,d), 6.15(1H,bd), 4.23(1H,b), 3.63(3H, s), 3.44(1H,b), 3.26(1H,b), 2.41(2H,m)] showed the presence of only two olefinic protons, whose coupling constant (J=2.7 Hz) corresponded to that of cyclobutene system.[8] The structure IVb or IVc rather than V was assigned for this compound by comparison of the spectrum with the reported one of IVa;[8] the structure IVb was confirmed by independent synthesis of IVc. An olefinic triester (VI), mp. 120-121°, was prepared from indenone ethylene ketal by three steps; sensitized photocycloaddition with maleic anhydride[9] (76 %), subsequent esterification of the acid anhydride and hydrolysis of the ethylene ketal by refluxing in benzyl alchohol in the presence of p-TsOH (40 %), followed by Wittig reaction with methyl diethylphosponoacetate in glyme (70 %). Catalytic hydrogenation (Pd-C/H_2) proceeded with attack of hydrogen from less hindered side of the molecule to double-bond accompanied with hydrogenolysis of the benzyl esters to give crude VII (95 %). Decarboxylative dehydrogenation of VII was effected by electrolysis in aq. pyridine (Et_3N)[10] to give IVc as a colourless liquid (glc separation, 35 %)[m/e 214(10.7), 154(29), 141(100), 128(38), 115(25); δ ppm.(CCl_4) 7.03(4H,s), 6.40(1H,d), 6.05(1H,bd), 4.16(1H,b), 4.0-3.2(2H,b), 3.67(3H,s), 2.62(2H,m); $\nu_{max}^{liq.\ film}$ cm^{-1} 3040, 2950, 1733, 1250, 1160, 770, 750; λ_{max}^{EtOH} nm.(log ε) 263(2.99), 268(3.08), 275(3.08)]. Virtual identity of the mass spectrum of IVb with that of IVc sufficiently supports the structure of IVb.

Compound B had a uv spectrum [λ_{max}^{EtOH} nm.(log ε) 220(4.27, end abs.), 275 (3.83), $308^{infl.}$(3.19)] characteristic to benzonorcaradiene. Since its nmr spectrum [δ ppm.(CCl_4) 7.35-6.86(4H,m), 6.18(2H,s), 3.60(3H,s), 2.38(2H,m), 2.30 (1H,q,J_{ab}= 9.0 Hz. J_{ac}= 5.4 Hz.), 1.42(1H,q, J_{ab}= 9.0 Hz. J_{bc}= 3.6 Hz.), -0.05 (1H,q, J_{ac}=5.4 Hz. J_{bc}= 3.6 Hz.)] showed that two olefinic protons did not couple with adjacent protons, the only structure VIII was suitable for B.

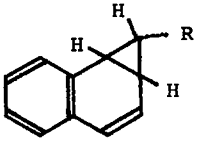
Compound C had a uv absorption [λ_{max}^{EtOH} nm.(log ε) 228.5(4.62), $257^{infl.}$ (3.74)] similar to that of 4,5-benzotropilidene[11] and the corresponding signals of the tropilidene olefinic protons [δ ppm.(CCl_4) 7.23(4H,m), 6.52(2H,d, J_{ab}= 10.5 Hz.), 5.65(2H,q, J_{ab}= 10.5 Hz. J_{bx}= 5.2 Hz.), 3.62(3H,s), 2.6-3(1H,m), 2.48 (2H,m)] in nmr spectrum, and hence structure IX was proposed to this compound.

In order to inquire into the reaction sequence, II, VIII and IX, independently dissolved in CD_3OD, were irradiated in an nmr tube at about 0°C and the reactions were followed by nmr spectroscopy. These experiments clarified that initially formed endo-Ib is photochemically converted to a mixture of the endo and exo isomers of Ib (ca. 2 : 1), followed by slow, concurrent transformations into naphthalene, IVb and IX; the last compound is rapidly isomerized to VIII, which expels methylene to form III.

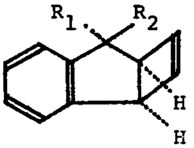
In order to establish the stereochemical course of the rearrangement of Ib to IVb, we resolved Ic in optically active forms using brucine as a base, and obtained a (+)-acid, $[\alpha]_D^{20}+150^\circ$(c=1, 95%EtOH), mp. 125-126°. A (+)-Ic($[\alpha]_D^{23}+142^\circ$)



(I)-exo



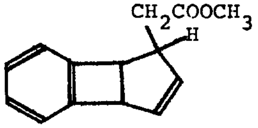
(I)-endo



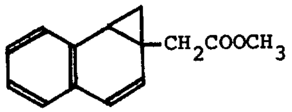
(IV)

Ia, R = H
Ib, R = CH_2COOCH_3
Ic, R = COOH
Id, R = $COCHN_2$

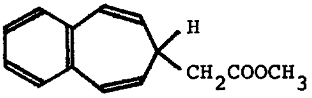
IVa, $R_1 = R_2$ = H
IVb, $R_1 = CH_2COOCH_3$, R_2 = H
IVc, R_1 = H, $R_2 = CH_2COOCH_3$



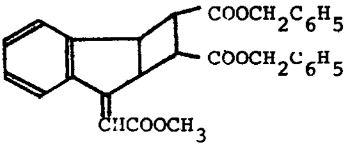
(V)



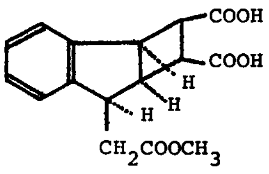
(VIII)



(IX)



(VI)



(VII)

was converted to a diazoketone (Id), which was photolyzed in methanol to give a methyl acetate (Ib). After purification (silicic acid/ ether-hexane(5:95)) and equilibration by heating, the endo-exo mixture Ib (1:2) had an optical rotation, $[\alpha]_D^{23}+23.5^{\circ}$(c=1,MeOH). Photolysis of these in methanol gave IVb as a colourless liquid with an optical rotation, $[\alpha]_D^{25}-117^{\circ}$(c=0.5, MeOH).[12] These experiments show that the reaction of Ib to IVb proceeds in highly stereospecific manner. The determination of the absolute configurations of (+)-Ic and (-)-IVb would reveal the stereochemical course of the photochemical reaction, and we are now under extensive investigation along this line.

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12) Using optically impure (-)-Ic ($[\alpha]_D-63.2^{\circ}$), the same reaction gave (-)-Ib ($[\alpha]_D-10.3^{\circ}$) and then (+)-IVb ($[\alpha]_D+57^{\circ}$). As expected, the ester VIII, isolated in these experiments, was optically inactive.