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PHOTOLYSIS OF 3,4:6,7-DIBENZOBICYCLO[3.2.2]NONA-3,6,8-TRIENE SYSTEM

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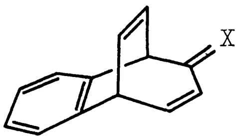
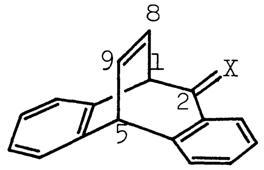
Photolysis of 3,4:6,7-dibenzobicyclo[3.2.2]nona-3,6,8-trien-2-one (3) afforded exclusively 3,4-benzo-4a,9a-dihydrofluorenone (5) by way of [1,3]-acyl migration. Compound (4), exomethylene counterpart of the ketone (3), was regiospecifically isomerized to (7) by both the direct and sensitized irradiations.

Recent papers on the photochemistry of 6,7-benzobicyclo[3.2.2]nona-3,6,8-trien-2-one (1)[1] and 2-methylene-6,7-benzobicyclo[3.2.2]nona-3,6,8-triene (2)[2] has prompted us to report our study on the dibenzo annelated analogs of the bicyclo[3.2.2]nona-3,6,8-triene system.



(1) : X = O

(2) : X = CH_2



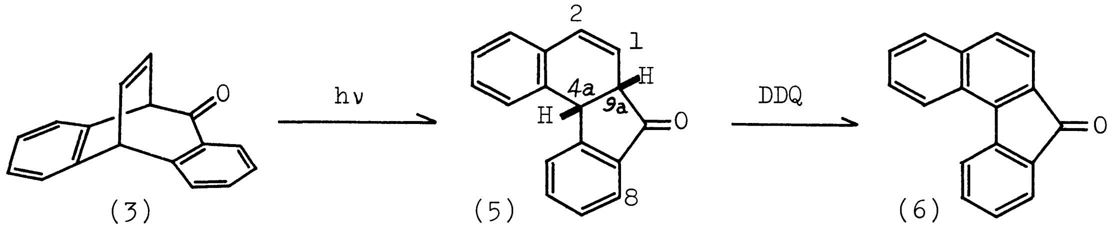
(3) : X = O

(4) : X = CH_2

Compound (3), 3,4:6,7-dibenzobicyclo[3.2.2]nona-3,6,8-trien-2-one[3], was prepared by thermal addition of benzyne to 2,3-benzotropone.[4] Thus, when 2,3-benzotropone and isoamyl nitrite were treated with anthranilic acid in dichloromethane and tetrahydrofuran at 40°C for 6hr, and the product was purified by chromatography over silica gel (benzene elution) and recrystallization from ether afforded a colorless crystalline adduct with mp 104-105°C in 62 % yield. Structure of (3) was proved on the basis of the following spectral data: Its ir spectrum (KBr) showed C=O absorption at 1670 cm^{-1}. Its nmr spectrum ($CDCl_3$, 60 MHz) showed absorptions (δ-values) at 7.95(m, 1H, aromatic proton ortho to carbonyl group), 7.19(m, 7H, aromatic), 6.95 (t.d., 1H, $J_{8,9}=J_{9,5}=7$ Hz, $J_{9,1}=2$ Hz, H-9), 6.50(t.d., 1H, $J_{8,9}=J_{8,1}=7$ Hz, $J_{8,5}=2$ Hz, H-8), 4.70(d.d., 1H, $J_{5,9}=7$ Hz, $J_{5,8}=2$ Hz, H-5) and 4.55(d.d., 1H, $J_{1,8}=7$ Hz, $J_{1,9}=2$ Hz, H-1).

Irradiation of 0.0002-0.02 M solution of (3) in acetone under nitrogen atmosphere with a 450-w mercury lamp with pyrex filter for 45 min gave a single product (5)[3], mp 104-105.5°C, in quantitative yield. Compound (5) had the same molecular formula as the starting material and its structure was proved to be 3,4-benzo-4a,9a-dihydrofluorenone through ir and nmr spectra. Ir (KBr): 1710 cm^{-1} (C=O). Nmr ($CDCl_3$, 60 MHz, δ-values): 7.89(m, 1H, aromatic H-8), 7.60-7.02(m, 7H, aromatic), 6.41(d.d., 1H, $J_{2,1}=10$ Hz, $J_{2,9a}=3$ Hz, H-2), 5.86(d.d., 1H, $J_{1,2}=10$ Hz, $J_{1,9a}=3$ Hz, H-1), 4.60

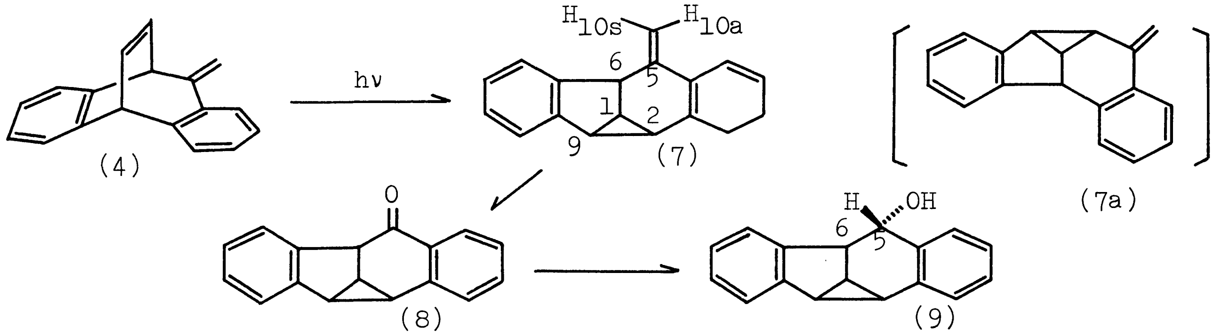
(d, 1H, $J_{4a,9a}=8$ Hz, H-4a), 3.84(d.t., 1H, $J_{9a,4a}=8$ Hz, $J_{9a,1}=J_{9a,2}=3$ Hz, H-9a). Chemical evidence for structure (5) was provided by its ready dehydrogenation in benzene with dichlorodicyano-p-benzoquinone to afford the known 3,4-benzofluorenone (6)[5] as yellow prisms, mp 159-159.5°C [lit.[5] mp 160°C]. Ir 1702 cm^{-1} (C=O).



It is presumed that the acetone sensitized photoconversion (3) to (5) involves an initial triplet state since the irradiation even in dilute acetone solution (2 x 10^{-4} M) unequivocally demonstrates that photosensitization is observed. Interestingly, despite the fact that the triplet sensitized photolysis of β,γ-unsaturated ketone generally proceeds by [1,2]-acyl migration,[6] the present ketone (3) proceeds exclusively by [1,3]-shift of acyl group.[7]

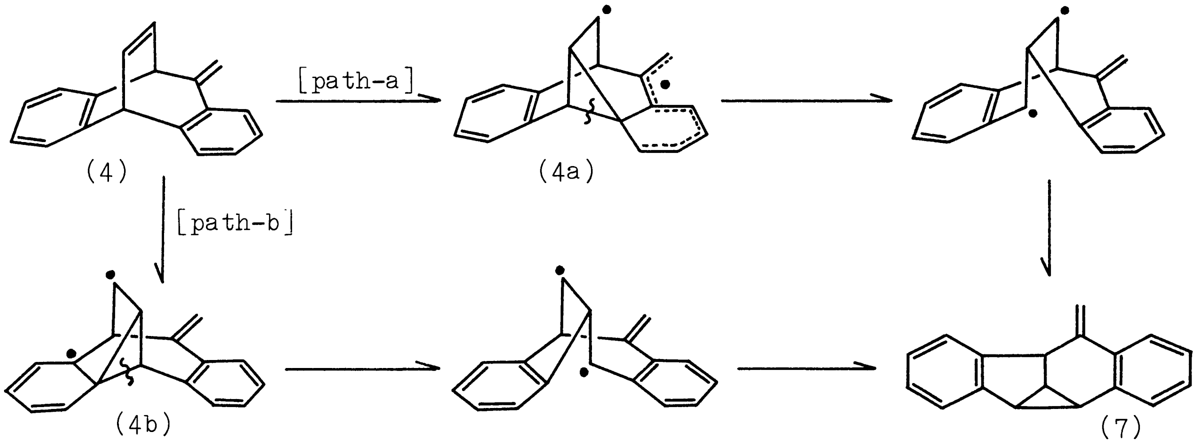
The direct irradiation of (3) in tetrahydrofuran with a 450-w mercury lamp through pyrex was examined and was found to give rise to a same photoproduct (5). Although the effect of added piperylene as a possible triplet quencher on this photoreaction was examined, no effective quenching was observed over a concentration range of 0.5 to 5 M.[8]

The corresponding hydrocarbon (4)[3] possessing an exomethylene group was obtained in 85 % yield by reaction of methylenetriphenylphosphorane with ketone (3) followed by chromatography over silica gel. Colorless oil, ir (film): 882 cm^{-1} (exomethylene), nmr ($CDCl_3$, 60 MHz, δ-values): 4.29(2H, d.d., 6.5, 2 Hz, bridgehead), 5.13, 5.44(2H, methylene, s. each), 6.46, 6.77(2H, olefin, t.d. each, 6.5, 2 Hz) and 7.0-7.8(8H, m, aromatic).



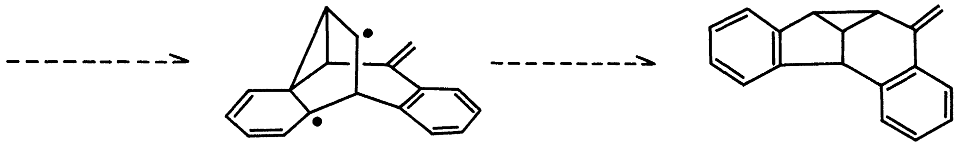
Direct irradiation of a 0.3 % solution of the hydrocarbon (4) in tetrahydrofuran resulted in rapid consumption of (4) [after 4 hr] with formation of an isomeric product, mp 124°C, colorless plates from ether, in almost qunatitative yield. The spectroscopic data indicate structure (7) for the photoproduct. The ir spectrum of (7) (KBr) exhibits strong absorption at 885 cm^{-1} attributable to an exocyclic methylene group. Compound (7) displays nmr signals ($CDCl_3$, 100 MHz, δ-values) at 2.33(1H, t, 6.8 Hz, H-9), 2.57(1H, t.d., 6.8, 5.9 Hz, H-1), 2.75(1H, d.d., 6.8, 5.9 Hz, H-2), 4.26(1H, d, 6.8 Hz, H-6), 5.16(1H, d, 0.2 Hz, H-10s), 5.25(1H, d, 0.2 Hz, H-10a) and 6.9-7.4(8H, m, aromatic). NOE measurements were carried out to determine the site of methylene group. A small but distinct increase (4.4 %) and decrease (6.4 %) in the integrated intensities of the H-10s and H-10a signals, respectively, caused by saturation of the H-6 signal indicate that the methylene group is located on C-5. The alternative possibility (7a) can be ruled out by these observations. A final structure proof was obtained by chemical degradation. Treatment of (7) with osmium tetroxide followed by potassium periodate gave a 60 % yield of the ketone (8),[3] mp 181-182°C, ν 1680 cm^{-1} (C=O), δ(in $CDCl_3$), 2.56(1H, t, 7.9 Hz), 2.90(1H, t.d., 7.9, 7.0 Hz), 3.17(1H, t, 7.9 Hz), 4.25(1H, d. 7.0 Hz), 6.9-7.7(8H, m.). Reduction of (8) with lithium aluminum hydride in tetrahydrofuran readily gave rise to the alcohol (9),[3] mp 208-209°C (from dichloromethane). Its nmr spectrum showed a doublet of doublets at δ 4.00 (J=6.3, 4.2 Hz) due to a bridgehead hydrogen (H-6) and a doublet at 5.50(J=4.2 Hz) due to a hydrogen attached to carbon atom bearing hydroxyl group, along with the cyclopropyl hydrogens at 2.20-2.99(m, 3H) and the aromatic hydrogens at 6.9-7.4(m, 8H). Irradiation at δ 4.00 (H-6) collapsed the doublet at δ 5.50 attributed to H-5 into a singlet and the doublet of doublets at δ 4.00 becomes a doublet by irradiating at δ 5.50. Thus ascertaining the relationship between the benzylic and the methylene groups as proposed in the structure shown (7).

Although the sensitized photolysis of (4) in acetone also afforded photoisomer (7) in 50 % yield, sensitized photoisomerization took place much slower [18 hr] than the direct reaction. The remaining 50 % was a mixture of starting material plus resinous product. In contrast with the photolysis of 6,7-benzobicyclo[3.2.2]-nona-3,6,8-triene (2),[2] the present compound (4) containing two annelated benzene rings isomerizes preferentially by way of a singlet excited state.



A priori, two alternative bonding processes are possible for the formation of (7) as initial excited-state reaction, vinyl-styryl [path-a] and vinyl-benzo bridging [path-b]. In the photoisomerizations, both the singlet and triplet processes, the preferred vinyl-styryl bridging [path-a] can be understood on the following bases. 1st, retention of maximum electron delocalization during isomerization,[9] (4a), may be anticipated in path-a. 2nd, the singlet excitation energy of styrene [long wave length absorption maximum at 291 nm[10a]] is lower than that of benzene [long wave length absorption maximum at 254 nm[10b]]. 3rd, the triplet excitaiion, before bridging, is more preferred in the styryl moiety [E_T (styrene)=61.8 kcal[11]] than that of benzo portion [E_T (benzene)=84.2 kcal[11]]. Finally, path-b can be excluded since the intermediate (4c) involved in the potentially available vinyl-benzo bonding process of (4) does not lead to the actual photoproduct (7) but to the isomer (7a) which could not be detected in the photolysis.

(4)



(4c) (7a)

It is interesting to note that the photolysis of (4) is the highly regiospecific di-π-methane rearrangement which proceeds by way of both singlet and triplet excited states.

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8) The lack of quenching by piperylene denotes that singlet (3) can lead to (5). The triplet intermediate, however, could not be ruled out since the rate of intramolecular rearrangement of a triplet intermadiate is possibly more rapid than diffusion control.

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