Tetrahedron Letters No. 29, pp 2441 - 2444, 1975. Pergamon Press. Printed in Great Britain.

PHOTOISOMERIZATION OF 1-PHENYL-TRICYCLO[4.1.0.0^{2,7}]HEPTANE.

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(Received in Japan 23 May 1975; received in UK for publication 3 June 1975)

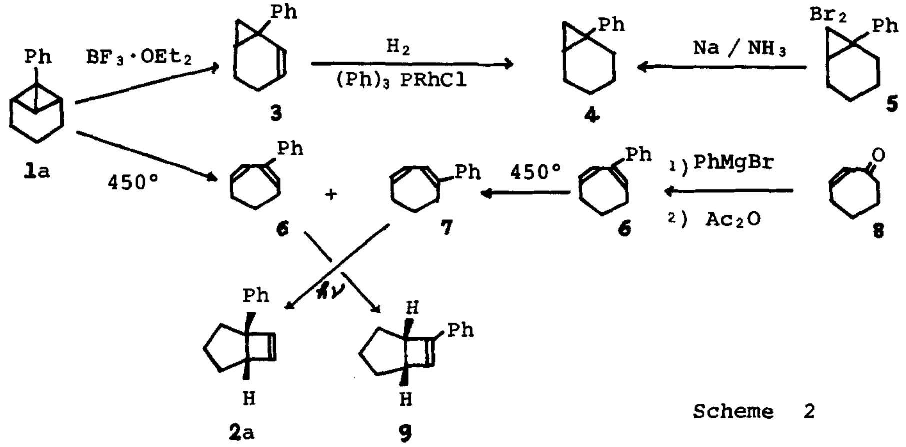
Mechanistic aspects of thermal[1], cationic[2] or metal-promoted[3] isomerization of bicyclobutane ring are well established. On the other hand, photochemical behavior of bicyclobutanes has rarely been investigated[4], although the central bond of the bicyclobutane was expected to conjugate with an appropriate chromophore[5].

In this study, we report a selective preparation and a novel photochemical isomerization of 1-phenyltricyclo[4.1.0.0^{2,7}]heptane (**1**a)[6]. The compound **1**a was obtained as a practically sole product from the reaction of 1-phenyl-7,7-dibromobicyclo[4.1.0]heptane with 1.5 equivalent of methyl-litium in n-pentane (overall yield in Scheme 1; 35%). The structure of **1**a was determined on the basis of its nmr spectral data and also it was confirmed by the conparison of the spectral and gas chromatographic data of the reaction products of 1a with those of the corresponding authentic samples[7] (Scheme 2).

A solution of 1.94g of **1**a in 500ml of n-pentane was irradiated under nitrogen atmosphere with a 15W-low pressure mercury lamp to give a sole product **2**a(50%) (Scheme 1)[8]. The product **2**a was assigned to 1-phenyl-bicyclo[3.2.0]hept-6-ene by the comparison of its spectral data with those of the authentic specimen obtained from the photocyclization of **7** (Scheme 2). The absence of another possible product **9** in the present photoreaction was confirmed by the nmr spectral and gas chromatographic technics[9].

1a;R=H,**1**b;R=D **2**a;R=H,**2**b;R=D

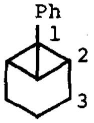
Scheme 1

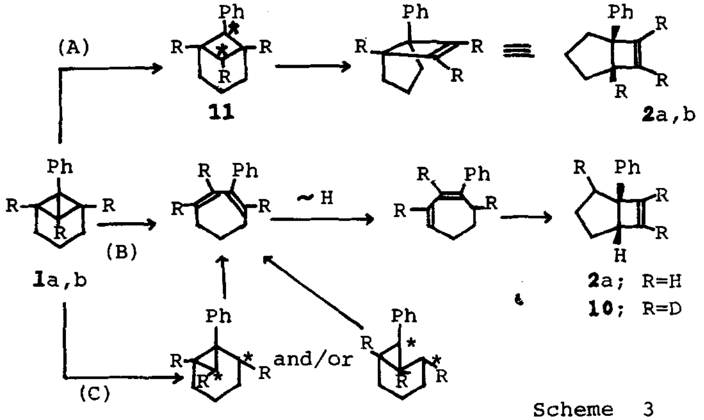


Scheme 2

There are at least three possible pathways to **2a** from **1a** (Scheme 3). The pathways, (B) and (C), including the [1.5]sigmatropic shift of a hydrogen were not suitable since the photoisomerization product from the deuterium compound **1b** was not **10**, product of (B) and (C) pathways, but **2b**. On the other hand, the deuterium position in the product may be rationalized by the pathway (A) which includes conceptually the central bond fission of the bicyclobutane part followed by the migration of C$_3$ to the benzyl moiety.

Generally, there are three different bonds to be cleaved in the bicyclobutane part of **1a**. However, a novel and selective central bond cleavage was observed in the present photoisomerization. This mode of bond cleavage would be attributable to the high p character[10] of the central bond which is expected to conjugate with the phenyl ring. The step of the selective





Scheme 3

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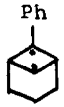

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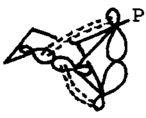

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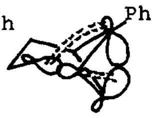

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migration of C_3 to the benzyl moiety would be explicable by assuming the nature of the transient species **11** to be ionic (**12**) rather than free radical (**13**)[11]. If **13** is the reactive species of rearrangement, **9** should be obtained at least one of the photoisomerization products[12]. On the contrary, it seems to be reasonable that the ionic character of **12** brings about the selective formation of the product **2**a through the well-known Wagner-Meerwein type rearrangement. However it is not necessarily essential that such an ionic species **12** excists as a discrete intermediate. Thus, a polarized concerted process, $[\sigma 2s+\sigma 2s]$ (**14**) or $[\sigma 2a+\sigma 2a]$ (**15**), may be responsible to the selective formation of 2a[13].

References

1) For example, K.B.Wiberg and G.Szeimies, Tetrahedron Lett., 1235 (1968)

2) For example, W.R.Moor and B.J.King, J.Org.Chem., 36, 1882 (1972)

3) For example, L.A.Paquette and G.Zon, J.Amer.Chem.Soc., 96, 224 (1974)

4) (a) J.M.Lavanish, Diss.Abstr., B 27 (8), 2652 (1967), (b) P.M.Pagni and C.R.Watson, Tetrahedron Lett., 59 (1973)

5) For example, S.Masamune, J.Amer.Chem.Soc., 86, 735 (1964)

6) Spectral data of **1**a. nmr (CCl_4, τ); 2.47-3.25 (5H, m), 7.07 (2H, broad singlet), 8.26 (1H, t, J=3.2Hz) and 8.54 (6H, m), ir (neat, cm^{-1}); 1135, 760, 740 and 690, mass (m/e); 170.

7) The compound **1**a was isomerized quantitatively to **3** in the presence of a trace amount of $BF_3(OEt_2)$ followed by the selective hydrogenation of **3** to **4**. The authentic **4** was prepared by the known procedure; S.Fujita, Y.Hayashi and H.Nazaki, Bull.Chem.Soc.Japan, 44, 1970 (1971). The compound **1**a was pysolyzed at 450° to afford the mixture of phenylcycloheptadienes (**6** and **7**) (yield; 85%) which was the same to the thermally equilibrated (450°) mixture (**6** and **7**) obtained from the authentic compound **6**.

8) Spectral data of **2**a. nmr (CCl_4, τ); 2.64-3.04 (5H, m), 3.84 (1H, d, J=2.8Hz), 4.01 (1H, d, J=2.8Hz), 6.85-6.98 (1H, m) and 7.98-8.63 (6H, m), ir (neat, cm^{-1}); 1495, 1450, 740, and 695, mass (m/e); 170

9) Spectral data of **9** prepared from the photocyclolization of **6**. nmr (CCl_4, τ);

2.79 (5H, m), 3.92 (1H, m), 6.46-6.94 (2H, m) and 7.75-8.85 (6H, m), ir (neat, cm^{-1}); 1490, 1450, 760 and 690, mass (m/e); 170

10) For example, M.D.Newton and J.M.Schulman, J.Amer.Chem.Soc., 94, 767 (1972)

11) The meaning of this particular term "free radical" is similar to that described in the reference 12.

12) (a) H.Kristinsson and G.W.Griffin, Tetrahedron Lett., 3259 (1966), (b) J.N.Pitts, Jr. and I.Norman, J.Amer.Chem.Soc., 76, 4815 (1954). The Photoisomerization of 1-phenyl-2,3-dimethylcyclopropane[a] or acetylcyclopropane[b] was reported to give 1-phenyl-2-methyl-but-1-ene or pent-2-en-4-one, respectively. These reactions were considered to occur through the 1,3-diradical species, where the hydrogen migrated to the unconjugated radical center to form the olefinic compound conjugated with phenyl or acetyl group. If the rearrangement similar to those above described were operative in the present photoreaction, **9** should be obtained as a major product.

13) The ionic character of **12** was confirmed on the basis of the substitiuent effect on the ratio **2a**/**9** in the photoisomerizations of 1-m- or p-substituted phenyltricyclo[4.1.0.$0^{2,7}$]heptane. K.Fujita, T.Nakamura, K.Matsui, K.Kida and T.Shono, Abstract of the 32nd Annual Meeting of Chemical Society of Japan, III, 1193 and 1194 (April, 1975).