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SUBSTITUTION EFFECT ON PHOTOISOMERIZATION OF 1-PHENYL-TRICYCLO[4.1.0.$0^{2,7}$]HEPTANE.

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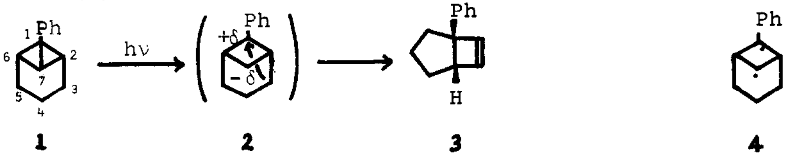
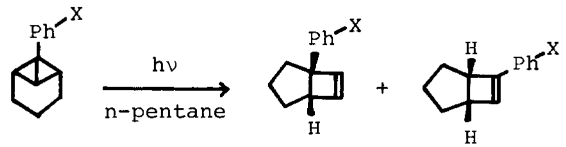
Recently, we reported the novel and selective bond-cleavage in the photoisomerization of 1-phenyltricyclo[4.1.0.$0^{2,7}$]heptane (**1**) (Scheme 1).[1] From the result that C_3 migrated regioselectively to the benzylic position (C_1), we suggested that the nature of the transient species would be ionic (**2**) rather than free radical (**4**).



Scheme 1

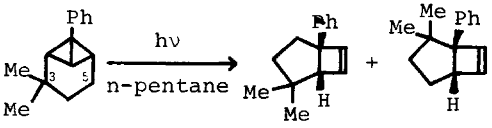
In this study, we report the substitution effect on this isomerization reaction. The results are sumarrized in Scheme 2 and 3, and Table 1. The starting compounds, 1-aryltricyclo[4.1.0.$0^{2,7}$]heptanes (**5**a-d) were prepared from 1-arylcyclohexenes by the procedure previously described.[1] Another starting compound, 1-phenyl-3,3-dimethyltricyclo[4.1.0.$0^{2,7}$]heptane (**8**) was obtained from a mixture of 1-phenyl-3,3-dimethylcyclohexene and 1-phenyl-5,5-dimethylcyclohexene by a similar method.[1] The structural assignment of **5**a-d was carried out by the comparison of their nmr spectra with that of the parent compound (**1**).[1] The structure of **8** was determined on the basis of its nmr spectral data and confirmed further by the nmr analysis of the acid catalyzed-isomerization product (**11**) of **8**.



5a-d **6**a-d **7**a-d

a; X = P-Me
b; X = m-OMe
c; X = P-Cl
d; X = m-CF$_3$

Scheme 2



8 **9** **10**

Scheme 3

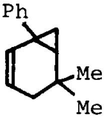


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Table 1 Photoisomerization of 1-Aryltricyclo[4.1.0.0^{2,7}]Heptane

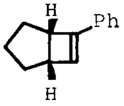
Starting Compound	Products (yield %)	Ratio **6/7**
5a	**6**a(67) + **7**a(0)[a]	1/ 0
1	**3** (54)[a]	1/ 0
5b	**6**b(70) + **7**b(*[b])[a]	1/~0
5c	**6**c(40) + **7**c(19)[a]	1/0.49
5d	**6**d(41) + **7**d(39)[a]	1/0.97
8	**9** (29) + **10**(33)[c]	Ratio **9/10**=47/53

a) This value was obtained by vpc analysis and is based on the unrecovered starting material.

b) trace

c) This value was obtained by nmr analysis and is based on the unrecovered starting material.

The photoisomerizations of **1**, **5**a and **5**b afforded only 1-arylbicyclo[3.2.0]hept-6-enes (**3**, **6**a and **6**b, respectively). On the other hand, **5**c and **5**d gave 6-aryl-substituted compound **7**c and **7**d, respectively, together with the 1-aryl-substituted compounds (Table 1). The structural assignments of the products **6**a-d (and **9**) and **7**c-d (and **10**) were carried out by the comparison of their nmr spectra with those of the parent compounds, **3** and **12**, respectively.[1]



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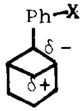
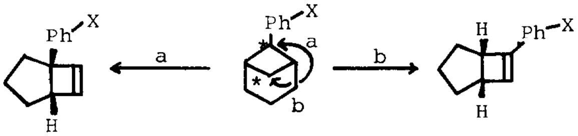
As the nature of the substituent on the phenyl ring is more electron-withdrawing, the ratio of **6/7** becomes smaller. This tendency would be explained by the ionic nature of **2**. In the cleavage of the C_1-C_7 bond, the introduction of the electron-withdrawing group on the phenyl group would decrease the degree of the cationic nature of the benzylic position or increase the probability of the reverse ionic bond cleavage resulting in the formation of **2'**. This nature of the bond cleavage would bring about two competitive Wagner-Meerwein type rearrangements, (a) and (b) (Scheme 4).



2'

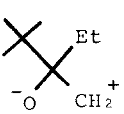


6 **7**

Scheme 4

In order to obtain more information about the nature of the transient ionic species (**2**), following studies were carried out. Since the trapping of the twitterionic intermediate by methanol was reported in the photochemistry of of 1,2-diarylcyclopropanes,[3] **1** was irradiated in a protic solvent (methanol or sodium methoxide-methanol). However any product other than **3** was not obtained. The use of other solvent (iso-propanol, acetonitrile or n-hexane) gave the same result. This observation would suggest that the transient species **2** is so unstable as to rearrange to the product **3** before it is trapped by the solvent.

This speculation seems to be consistent with the result of the photoisomerization of **8**, in which any difference of the migratory apptitude between C_3 (tertiary carbon) and C_5 (secondary carbon) was not observed (Scheme 3). This result would suggest the considerable instability of the transient species **2**, since ethyl group is estimated to possess about three times larger migratory apptitude than t-butyl group in the unstable twitterionic transient species such as **13** formed by the reaction of a ketone with diazomethane.[4]



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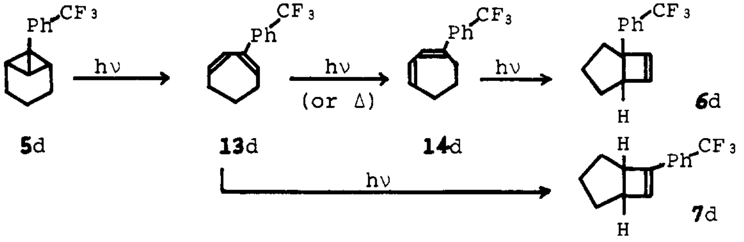
In summary, the transient species **2** would possess ionic nature and would be considerably unstable, at least as unstable as the transient twitterionic species **13**. However it is not necessarily essential that such an ionic species **2** exists as a discrete intermediate, but a polarized concerted process [2σ + 2σ][1] may be operative in this isomerization reaction.

References

1) K. Fujita, T. Nakamura, K. Matsui and T. Shono, Tetrahedron Letters 2441 (1975).

2) The reaction pathway shown in Scheme 5 is not likely as the route to yield **6** and **7**, since the rates of photocyclization of **13**d and **14**d to **6**d and **7**d were smaller than that of the photoisomerization of **5**d to **6**d and **7**d, and the formation of cycloheptenes, **13**d and **14**d, was not detected in the reaction of **5**d.



Scheme 5

3) (a) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinson, C. S. Agron, G. W. Griffin, and G. J. Boudeaux, J. Amer. Chem. Soc., 88, 5675 (1966).
   (b) S. S. Hixon, ibid., 96, 4866, 4872 (1974).

4) H. O. Hause, E. J. Crubbs and W. F. Gannon, J. Amer. Chem. Soc., 82, 4099 (1960).