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## PHOTOLYSIS OF CYCLIC ARYLVINYL HALIDES. FORMATION OF 1,2-BENZO-1,3-CYCLOALKADIENYL CATIONS AND THEIR REARRANGEMENTS

Tsugio KITAMURA, Tomonobu MUTA, Toru TAHARA, Shinjiro KOBAYASHI, and Hiroshi TANIGUCHI<sup>\*</sup> Department of Applied Chemistry, Faculty of Engineering, Kyushu University 36, Hakozaki, Fukuoka 812

Photolysis of 1,2-benzo-1,3-cycloalkadien-4-yl bromides and 1,2-benzo-1,3-cycloalkadien-3-yl chlorides showed a remarkable effect of ring size on the rearrangements of the resulting 1,2-benzo-1,3-cycloalkadienyl cations, i.e., 1,2-aryl or alkyl migra-tion across the double bond and 1,2-hydride or methyl migration to the cationic center.

It has been noted recently that photolysis of organic halides generates cationic intermediates.<sup>1)</sup> Vinyl cations have been observed also by photolysis of arylvinyl,<sup>2)</sup> alicyclic and  $alkyl^{3}$  vinyl halides. Generally cyclic vinyl cations are unstable<sup>4)</sup> and their generation is difficult. Especially rigid sixmembered 1,3-dienyl systems are yet unknown.<sup>5)</sup> Then, we conducted the title photolysis in order to know the behavior of cyclic 1,3-dienyl cations. In this paper we report the formation of the 1,3-dienyl cations and a marked effect of ring size on their rearrangements.

First, we describe the photolysis of 1,2-benzo-1,3-alkadien-4-yl systems. Irradiation of 4-bromo-3-phenyl-1,2-benzo-1,3-cycloalkadiene (<u>1</u>) (1 mmol) in methanol (100 ml) containing pyridine (0.1 ml) as a buffer was carried out through quartz by use of a high-pressure Hg lamp (100 W) for 2 h at 5 °C under a  $N_2$  atmosphere. After evaporation of methanol and removal of the pyridinium salt by a short column of alumina, the residue was submitted to column chromatography on alumina. The products were identified by the spectral data and comparison with authentic samples.

In the case of seven-membered ring system <u>1a</u>, 9-methoxy-1,10-propanophenanthrene (<u>2a</u>)<sup>6</sup>) (44%) and 3-phenyl-1,2-benzo-1,3-cycloheptadiene (<u>4a</u>) (46%) were obtained (conversion 54%). <u>4a</u> is derived from hydrogen atom abstraction of vinyl radical <u>5a</u>. <u>2a</u> is methanol-incorporated product via 1,2-benzo-1,3-cycloheptadien-4-yl cation (<u>6a</u>), that is, 1,2-aryl rearrangement across the double bond takes place in the cycloheptadienyl cation <u>6a</u> and produces a stable linear  $\alpha$ -phenylvinyl cation, followed by attack of methanol and stilbene-like photocyclization. In contrast, in the case of six-membered ring system <u>1b</u>, the 1,2-aryl rearrangement across the double bond was not observed. The products were 1-phenylnaphthalene (<u>3b</u>) (68%) and 1-phenyl-3,4-dihydronaphthalene (<u>4b</u>) (4%) in 97% conversion. <u>4b</u> is also hydrogen abstraction product. Although it is possible to consider that <u>3b</u> is derived from <u>4b</u>, it is reasonable to consider the mechanism involving cyclohexadienyl cation <u>6b</u>, followed by 1,2-hydride migration to the cationic center to produce allyl cation <u>8b</u> and deprotonation. This mechanism was supported by photolysis of 4-bromo-5,5-dimethyl-3-phenyl-1,2-benzo-1,3-cyclohexadiene (<u>1c</u>). Similar irradiation of <u>1c</u> in methanol gave 2,3-dimethyl-1-phenylnaphthalene (<u>3c</u>) (62%) accompanied with 1,2-methyl migration to the cationic center.



As described above, photolysis of six- and seven-membered 1,3-dien-1-yl bromides produces the corresponding dienyl cations which have not been reported so far. The bent 1,3-cycloalkadienyl cations  $\underline{6}$  are unstable to undergo rearrangement forming stable cations  $\underline{7}$  or  $\underline{8}$ . In the process of the rearrangement, a remarkable difference of behavior between seven- and six-membered ring systems was observed. The difference is considered to be attributed to the flexibility of the ring. The seven-membered ring has some degree of freedom and the benzo group can interact with the cationic center to cause the ring-contraction, while the benzo group is fixed in the six-membered ring system and cannot interact.<sup>7</sup> Therefore, 1,2-hydride or alkyl migration occurs in the six-membered ring system.

Next, we examined 1,2-benzo-1,3-alkadien-3-yl systems under photolytic conditions. Although reaction of 1,3-alkadien-2-yl derivatives have been carried out under solvolytic conditions,<sup>5)</sup> the six-membered 1,3-dien-2-yl

derivatives do not react to afford the corresponding 1,3-dien-2-yl cations. Similar 4 h-irradiation of 3-chloro-4-methyl-1,2-benzo-1,3-cycloheptadiene (<u>9a</u>) in methanol containing pyridine gave 3-methoxy-4-methyl-1,2-benzo-1,3-cycloheptadiene (<u>10a</u>)<sup>6</sup>) (9%), 3,3-dimethoxy-4-methyl-1,2-benzocycloheptene (<u>11a</u>)<sup>6</sup>) (40%), and 4-methyl-1,2-benzo-1,3-cycloheptadiene (<u>12a</u>) (trace) in 90% conversion. The methanol-incorporated products <u>10a</u> and <u>11a</u> are derived from dienyl cation <u>16a</u> which undergoes nucleophilic substitution by methanol.

Further, irradiation of 3-chloro-4-methyl-1,2-benzo-1,3-cyclohexadiene  $(\underline{9b})$  in methanol containing triethylamine<sup>8</sup> was carried out for 10 h. The products obtained were 3-methoxy-4-methyl-1,2-benzo-1,3-cyclohexadiene  $(\underline{10b})^{6}$  (15%), 1-(1'-methoxyethylidene)indane  $(\underline{13b})^{6}$  (11%), 1-vinylideneindane  $(\underline{14b})^{6}$  (25%), and 4-methyl-1,2-benzo-1,3-cyclohexadiene  $(\underline{12b})$  (11%) in 71% conversion. The formation of methanol-incorporated product  $\underline{10b}$  and ring-contracted products  $\underline{13b}$  and  $\underline{14b}$  indicates that 1,2-benzo-1,3-cyclohexadien-3-yl cation ( $\underline{16b}$ ) is generated by the photolysis.



A significant difference between the seven- and six-membered cyclic dienyl chlorides  $\underline{9a}$  and  $\underline{9b}$  are occurrence of 1,2-alkyl shift across the double bond. The benzocycloheptadienyl system is flexible and the phenyl group can interact with the vacant p orbital of dienyl cation <u>16a</u>. On the other hand, the benzo-cyclohexadienyl system is rigid and coplanar, so that the phenyl group cannot interact with the vacant orbital. In addition, the deviation from a stable linear geometry of an sp-hybridized carbon becomes larger in the benzocyclo-

hexadienyl cation <u>16b</u> than in the benzocycloheptadienyl cation <u>16a</u>. Therefore, lack of stabilization by the neighboring phenyl group and large deviation from a stable linear geometry give rise to the instability of the benzocyclohexadienyl cation <u>16b</u>, which undergoes 1,2-alkyl shift across the double bond to give the linear  $\alpha$ -methylvinyl cation 17b.

In summary, 1,2-benzo-1,3-cycloalkadienyl cations can be generated by the corresponding cycloalkadienyl halides and show 1,2-aryl or alkyl migration across the double bond and 1,2-alkyl or hydride shift to the carionic center. These rearrangements are governed by the ring system concerning the stability of the resulting cyclic dienyl cation and the participation of phenyl group.

## References

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- 6)  $\underline{2a}$ : mp 101-102 °C; NMR (CCl<sub>4</sub>)  $\delta = 1.90-2.20$  (m, CH<sub>2</sub>), 2.95-3.20 (m, 2CH<sub>2</sub>), 3.80 (s, OCH<sub>3</sub>), 6.70-7.64 (m, ArH), and 8.06-8.60 (m, ArH); picrate, mp 120.0-121.5 °C. <u>10a</u>: NMR (CCl<sub>4</sub>)  $\delta = 1.72-2.70$  (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.89 (s, CH<sub>3</sub>), 3.32 (s, OCH<sub>3</sub>), and 6.96-7.22 (m, ArH). <u>11a</u>: NMR (CCl<sub>4</sub>)  $\delta = 0.57$  (d, J = 7 Hz, CH<sub>3</sub>), 1.50-3.03 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.80 (s, OCH<sub>3</sub>), 3.25 (s, OCH<sub>3</sub>), and 6.89-7.67 (m, ArH). Acid hydrolysis of <u>10a</u> and <u>11a</u>, respectively, gave 7-methyl-2,3-benzocycloheptenone. <u>10b</u>: NMR (CCl<sub>4</sub>)  $\delta = 1.82$  (s, CH<sub>3</sub>), 2.03-3.00 (m, CH<sub>2</sub>CH<sub>2</sub>), 3.50 (s, OCH<sub>3</sub>), and 6.84-7.15 (m, ArH). <u>13b</u>: NMR (CCl<sub>4</sub>)  $\delta = 1.46$  (s, CH<sub>3</sub>), 2.60-2.98 (m, CH<sub>2</sub>CH<sub>2</sub>), 3.40 (s, OCH<sub>3</sub>), and 7.00 (bs, ArH); Determination of the stereochemistry (E or Z) was not done. <u>14b</u>: NMR (CCl<sub>4</sub>)  $\delta = 2.83-2.95$  (m, CH<sub>2</sub>CH<sub>2</sub>), 4.85-5.05 (m, =CH<sub>2</sub>), and 7.00 (bs, ArH); IR 1935 cm<sup>-1</sup> (C=C=C).
- 7) The flexibility of the ring was supported by the UV spectra as follows. <u>1a</u>:  $\lambda_{max}$  (cyclohexane) ( $\varepsilon$ ) 263 (8800) and 232 nm (13900); <u>1b</u>:  $\lambda_{max}$  (cyclohexane) ( $\varepsilon$ ) 279 (12900), 271 (12200), and 224 nm (17400).
- 8) Instead of pyridine, triethylamine was used to prevent further photoaddition of methanol.

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