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

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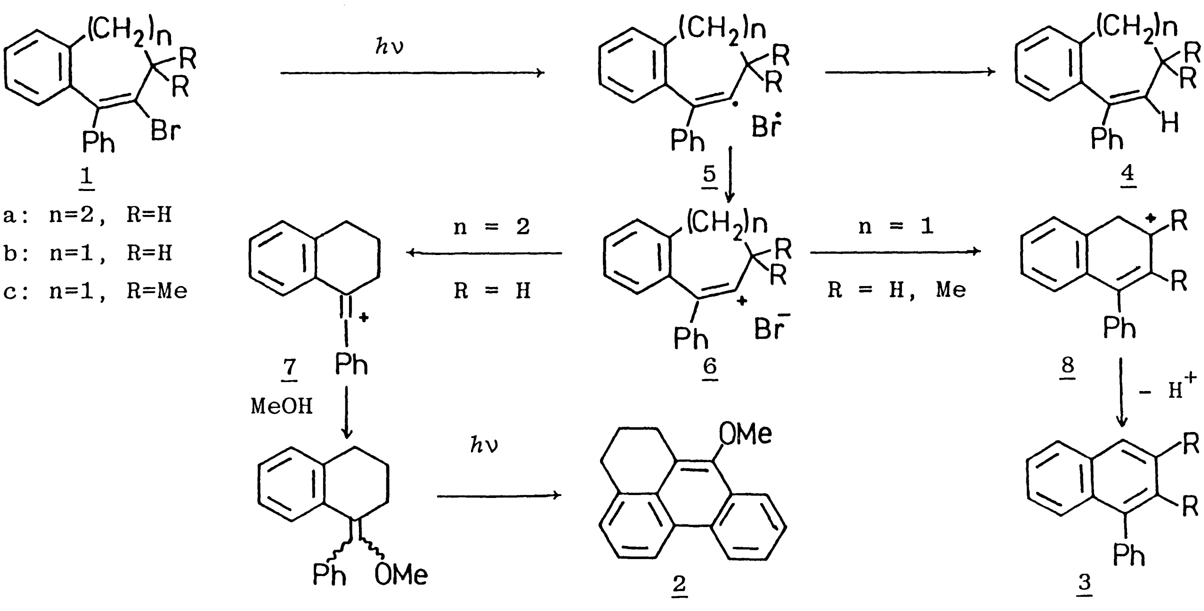
Photolysis of 1,2-benzo-1,3-cycloalkadien-4-yl bromides and 1,2-benzo-1,3-cycloalkadien-3-yl chlorides showed a remarkable effect of ring size on the rearrangements of the resulting 1,2-benzo-1,3-cycloalkadienyl cations, i.e., 1,2-aryl or alkyl migration across the double bond and 1,2-hydride or methyl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

It has been noted recently that photolysis of organic halides generates cationic intermediates.$^{1)}$ Vinyl cations have been observed also by photolysis of arylvinyl,$^{2)}$ alicyclic and alkyl$^{3)}$ vinyl halides. Generally cyclic vinyl cations are unstable$^{4)}$ and their generation is difficult. Especially rigid six-membered 1,3-dienyl systems are yet unknown.$^{5)}$ 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 (1) (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 1a, 9-methoxy-1,10-propanophenanthrene (2a)$^{6)}$ (44%) and 3-phenyl-1,2-benzo-1,3-cycloheptadiene (4a) (46%) were obtained (conversion 54%). 4a is derived from hydrogen atom abstraction of vinyl radical 5a. 2a is methanol-incorporated product via 1,2-benzo-1,3-cycloheptadien-4-yl cation (6a), that is, 1,2-aryl rearrangement across the double bond takes place in the cycloheptadienyl cation 6a and produces a stable linear α-phenylvinyl cation, followed by attack of methanol and stilbene-like photocyclization.

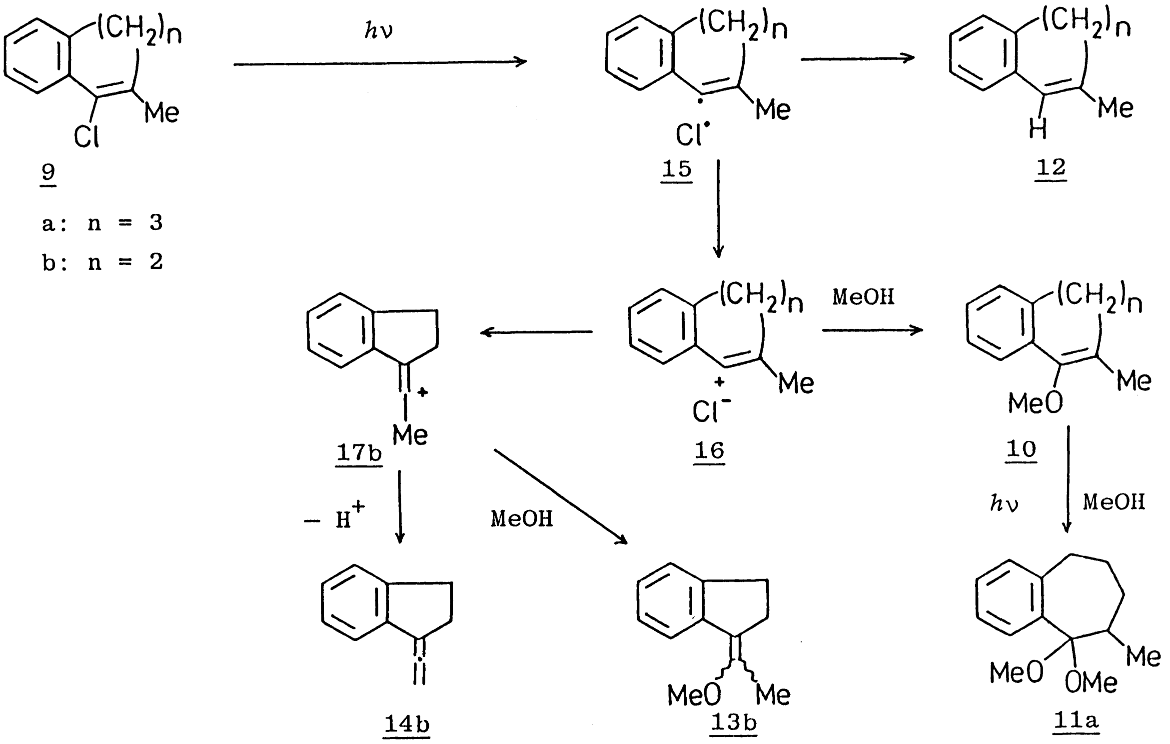
In contrast, in the case of six-membered ring system 1b, the 1,2-aryl rearrangement across the double bond was not observed. The products were 1-phenylnaphthalene (3b) (68%) and 1-phenyl-3,4-dihydronaphthalene (4b) (4%) in 97% conversion. 4b is also hydrogen abstraction product. Although it is possible to consider that 3b is derived from 4b, it is reasonable to consider the mechanism involving cyclohexadienyl cation 6b, followed by 1,2-hydride migration to the cationic center to produce allyl cation 8b and deprotonation. This mechanism was supported by photolysis of 4-bromo-5,5-dimethyl-3-phenyl-1,2-benzo-1,3-cyclohexadiene (1c). Similar irradiation of 1c in methanol gave 2,3-dimethyl-1-phenylnaphthalene (3c) (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 6 are unstable to undergo rearrangement forming stable cations 7 or 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.[7] 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,[5] 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 (9a) in methanol containing pyridine gave 3-methoxy-4-methyl-1,2-benzo-1,3-cycloheptadiene (10a)6) (9%), 3,3-dimethoxy-4-methyl-1,2-benzocycloheptene (11a)6) (40%), and 4-methyl-1,2-benzo-1,3-cycloheptadiene (12a) (trace) in 90% conversion. The methanol-incorporated products 10a and 11a are derived from dienyl cation 16a which undergoes nucleophilic substitution by methanol.

Further, irradiation of 3-chloro-4-methyl-1,2-benzo-1,3-cyclohexadiene (9b) in methanol containing triethylamine8) was carried out for 10 h. The products obtained were 3-methoxy-4-methyl-1,2-benzo-1,3-cyclohexadiene (10b)6) (15%), 1-(1'-methoxyethylidene)indane (13b)6) (11%), 1-vinylideneindane (14b)6) (25%), and 4-methyl-1,2-benzo-1,3-cyclohexadiene (12b) (11%) in 71% conversion. The formation of methanol-incorporated product 10b and ring-contracted products 13b and 14b indicates that 1,2-benzo-1,3-cyclohexadien-3-yl cation (16b) is generated by the photolysis.



A significant difference between the seven- and six-membered cyclic dienyl chlorides 9a and 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 16a. On the other hand, the benzocyclohexadienyl 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 benzocyclohexadienyl cation 16b than in the benzocycloheptadienyl cation 16a. 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 16b, which undergoes 1,2-alkyl shift across the double bond to give the linear α-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) 2a: mp 101-102 °C; NMR (CCl_4) δ = 1.90-2.20 (m, CH_2), 2.95-3.20 (m, $2CH_2$), 3.80 (s, OCH_3), 6.70-7.64 (m, ArH), and 8.06-8.60 (m, ArH); picrate, mp 120.0-121.5 °C. 10a: NMR (CCl_4) δ = 1.72-2.70 (m, $CH_2CH_2CH_2$), 1.89 (s, CH_3), 3.32 (s, OCH_3), and 6.96-7.22 (m, ArH). 11a: NMR (CCl_4) δ = 0.57 (d, J = 7 Hz, CH_3), 1.50-3.03 (m, $CH_2CH_2CH_2$), 2.80 (s, OCH_3), 3.25 (s, OCH_3), and 6.89-7.67 (m, ArH). Acid hydrolysis of 10a and 11a, respectively, gave 7-methyl-2,3-benzocycloheptenone. 10b: NMR (CCl_4) δ = 1.82 (s, CH_3), 2.03-3.00 (m, CH_2CH_2), 3.50 (s, OCH_3), and 6.84-7.15 (m, ArH). 13b: NMR (CCl_4) δ = 1.46 (s, CH_3), 2.60-2.98 (m, CH_2CH_2), 3.40 (s, OCH_3), and 7.00 (bs, ArH); Determination of the stereochemistry (E or Z) was not done. 14b: NMR (CCl_4) δ = 2.83-2.95 (m, CH_2CH_2), 4.85-5.05 (m, $=CH_2$), and 7.00 (bs, ArH); IR 1935 cm^{-1} (C=C=C).

7) The flexibility of the ring was supported by the UV spectra as follows. 1a: λ_{max} (cyclohexane) (ε) 263 (8800) and 232 nm (13900); 1b: λ_{max} (cyclohexane) (ε) 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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