Tetrahedron Letters,Vol.24,No.52,pp 5839-5842,1983 0040-4039/83 $3.00 + .00
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PHOTOCHEMICAL TRANSFORMATIONS. 36. INTRAMOLECULAR ELECTRON TRANSFER FROM PHOTOEXCITED BENZENE RINGS TO CARBON-MERCURY BONDS. STEREOCHEMICAL FATE OF ZWITTERIONIC BIRADICALS LEADING TO WAGNER-MEERWEIN REARRANGED PRODUCTS.[1]

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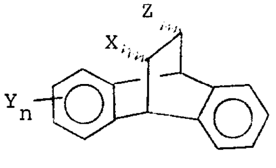
ABSTRACT: Irradiation of *cis*-8-X-mercuri-2,3;5,6-dibenzobicyclo[2.2.2]-octa-2,5-diene-7-ol acetate (X = Cl and OAc) (3) and the *trans*-diastereoisomer (4) (X = Cl) in glacial acetic acid, in acetonitrile, or in a mixture of glacial acetic acid and acetonitrile with 254-nm and 285-nm light gives metallic mercury and Wagner-Meerwein rearranged photosolvolysis or ion-pair return products. The reactions are stereoconvergent. A mechanistic path involving intramolecular electron transfer and an excited-state πp cation biradical is suggested to rationalize the results.

The recent communication by Kochi and coworkers[2] on the irradiation of the charge-transfer complex between hexamethylbenzene and mercuric trifluoroacetate, which results in electron transfer from the arene to mercury, prompts us to report our experiments in which a similar electron transfer may be assumed, but in an intramolecular system, rather than in a charge-transfer complex.

We have recently[1,3] discussed the factors that are apparently involved in the photoactivity of diarobicyclo[2.2.2]octadienyl compounds (1, X = Cl), which undergo photorearrangements to [3.2.1] products 2 (W = Cl) and photosolvolysis to [3.2.1] products 2 (W = OS). In these compounds, electron transfer from a π,π^* activated arene ring to a σ^* orbital of the carbon-nucleofuge bond is required for photoactivity, and this is followed by loss of X^-. With chloride-ion loss, the principal migrating ring is that *syn* to the departing chloride,[1,3] independent of whether the electron-donating ring is *syn* or *anti*.[1] In an extension of the idea that analogous reactions would occur when carbon-X bonds are present which have reduction potentials no less unfavorable than carbon-chlorine bonds, we decided to study similar organomercurials.[4]



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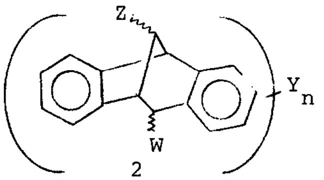

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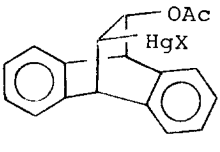

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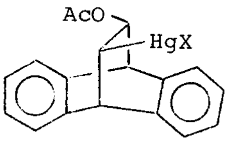

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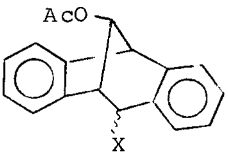

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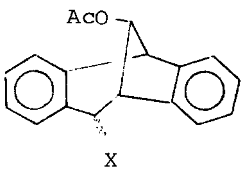

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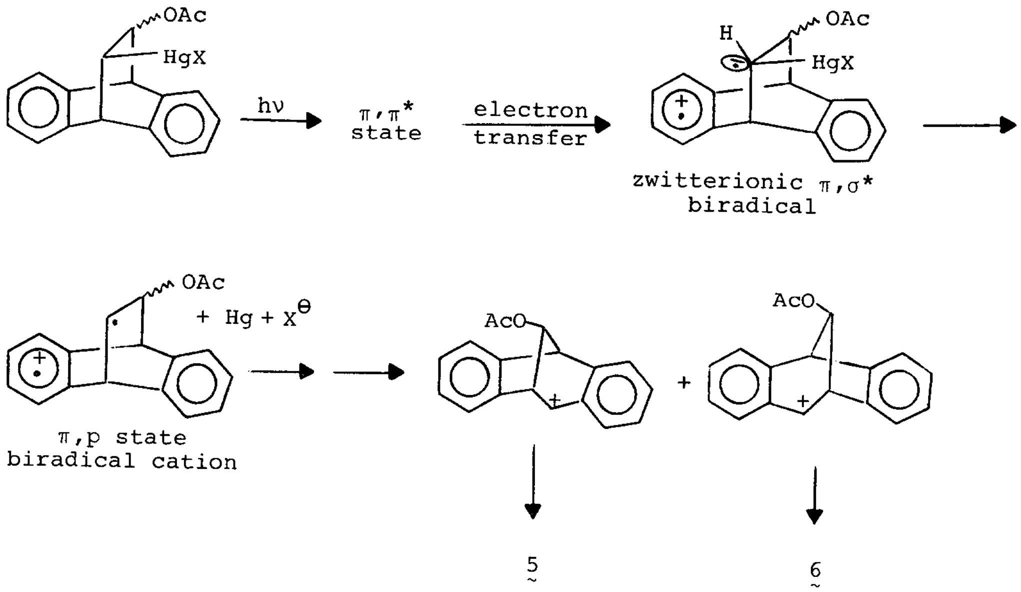
When compound 3 (X = OAc)[5] was irradiated in acetic acid solution,[6a,b] it was rapidly transformed to an approximately 60:40 mixture of 5 and 6 (X = OAc, largely exo), accompanied by the formation of metallic mercury. The corresponding chloromercurial (3, X = Cl)[5] irradiated in acetic acid containing acetonitrile to solubilize the mercurials, gave, in addition to a 60:40 mixture of 5-OAc and 6-OAc, smaller amounts of 5-Cl and 6-Cl in about the same ratio, the chloride products undoubtedly the result of ion-pair return. Ion-pair return was also observed when 3-OAc was irradiated in acetonitrile, which led not only to solvolysis products (acetamides 5 and 6, X = NHAc), but also to a 60:40 mixture of 5-OAc and 6-OAc.

Irradiation of the trans compound 4-Cl[5] in acetic acid-acetonitrile with 254-nm light led to a mixture of diacetates and acetoxy chlorides 5 and 6 quite similar to that from 3-Cl, although containing about 30% chlorides (rather than about 20% from the cis compound).

Two points are to be noted from these experiments. First, intramolecular electron transfer from a photoexcited benzene ring to a carbon-mercury bond occurs readily and is followed by (or accompanied by) formation of a carbocationic species, metallic mercury, and X$^-$, consistent with ideas recently proposed.[1,3] Second, unlike the chlorides, where predominant ring migration is syn,[1,3] loss of mercury and acetate (or chloride) from 3 or 4 gives a cation which has no memory of the stereochemistry of the initial carbon-mercury bond. It has been proposed, as a result of recent work,[1] that the predominant syn migration with chloride loss, is the result of a concerted Wagner-Meerwein migration from the π,σ^* zwitterionic biradical,[8] and that nonstereospecific migration is the result of loss of nucleofuge to give a biradical cation[9] prior to the Wagner-Meerwein shift. The two processes are clearly competitive, and their relative importance may well depend upon the exergonicity of the electron-transfer step, which measures, in a way, the excess energy available for loss of nucleofuge. Scheme I summarizes the process which rationalizes the results with the mercurials.

SCHEME I



In recent papers,[10,11] Morrison and his coworkers described the photochemistry of exo-2-benzonorbornenyl chloride and methanesulfonate, of endo-2-benzonorbornenyl chloride, and of the endo- and exo-2-benzobicyclo-[2.2.2]octenyl chlorides in various alcohols. They noted that the products of the photosolvolyses were quite different from those of ground-state solvolyses. They proposed reaction sequences leading to "hot" carbocations, "neither appreciably stabilized by the aryl group nor extensively solvated"[10] and "perhaps partially pyramidal"[11] as intermediates in the photoreactions. We cannot guess as to whether the lifetimes of such species would be long enough to account for the considerable discrepancy in ionic-product distribution between the exo and endo systems or between the chloride and methanesulfonate of the norbornenyl system. It is of interest that the dual mechanism proposed by us, in which the choice of reaction path is dependent upon the nature of the electron donor, of the electron acceptor, of the migrating group and of the stereochemistry of the system, is consistent with the greater syn migration observed by Morrison and coworkers for the methanesulfonate over that for the chloride. Further, their observed ratios of olefin to solvolysis product for the two leaving groups as well as for exo vs. endo norbornenyl systems, is consistent with known effects of base strength[12] and stereochemistry,[13] upon elimination vs. substitution in fates of ion pairs. We would, therefore, recommend consideration of our proposal for the Morrison cases as well.[14]

ACKNOWLEDGMENT: The authors are indebted to the National Science Foundation (Grant CHE80-11933) for support of this work.

REFERENCES AND FOOTNOTES

(1) Previous paper in series: Cristol, S.J.; Seapy, D.G.; Aeling, E.O. *J. Am. Chem. Soc.*, accepted for publication.

(2) Lau, W.; Huffman, J.C.; Kochi, J.K. *J. Am. Chem. Soc.*, **1982**, *104*, 5515.

(3) Cristol, S.J.; Opitz, R.J.; Bindel, T.H.; Dickenson, W.A. *J. Am. Chem. Soc.*, **1980**, *102*, 7977.

(4) The first reduction potential (E_1) of isopropylmercuric chloride is reported to be -1.31 v in 50% aqueous ethanol. Hush, N.S.; Oldham, K.B. *J. Electroanal. Chem.*, **1963**, *6*, 34.

(5) Jensen, F.R.; Miller, J.J.; Cristol, S.J.; Beckley, R.S. *J. Org. Chem.*, **1972**, *37*, 4341.

(6) (a) Carbon-mercury bonds are reported[7] to be transparent above 260 nm and have only low extinction coefficients at 254 nm. We observed no differences in irradiations conducted in Rayonet Srinivasan-Griffin photochemical reactors with either Rayonet RPR2537Å through quartz and RPR3000Å lamps through Pyrex; the latter lamps have considerable intensity at 285 nm where 3 and 4 have absorption tails; (b) the UV spectra of 3 and 4 are quite similar to those of other 1 (Y = H) species, and give no evidence for charge-transfer interactions.

(7) Hirata, T.; Sujishi, S.; Gunning, H.E. *J. Am. Chem. Soc.*, **1960**, *82*, 5045.

(8) Cristol, S.J.; Strom, R.M.; *J. Am. Chem. Soc.*, **1980**, *102*, 5577.

(9) Cristol, S.J.; Dickenson, W.A.; Stanko, M.K. *J. Am. Chem. Soc.*, **1983**, *105*, 1218.

(10) Morrison, H.; Miller, A.; Bigot, B. *J. Am. Chem. Soc.*, **1983**, *105*, 2398.

(11) Morrison, H.; Miller, A.; Pandey, B.; Pandey, G.; Severance, D.; Strommer, R.; Bigot, B. *Pure Applied Chem.*, **1982**, *54*, 1723.

(12) Goering, H.L.; Humski, K. *J. Am. Chem. Soc.*, **1968**, *90*, 6213; Goering, H.L.; Clevenger, J.V. *Ibid.*, **1972**, *94*, 1010.

(13) Skell, P.S.; Hall, W.L. *J. Am. Chem. Soc.*, **1963**, *85*, 2851.

(14) A referee has suggested that the mercurial reaction may be that of a triplet state, while the chloride reacts *via* the singlet state. We have observed that the formation of 5 and 6-OAc from 3-OAc is not quenched by 0.1 *M* piperylene, and that the irradiation of 3-OAc in 50:50 (vol.) acetone:acetic acid at 300 nm does not lead to 5 or 6 (or to their triplet reaction products), or to significant amounts of metallic mercury, although it is *slowly* photoreactive (products unidentified).

(Received in USA 12 September 1983)