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STEREOSELECTIVE PHOTOSOLVOLYSES OF <u>ipso</u>-ACETOXYNITRO-ADDUCTS OF <u>p</u>-XYLENE

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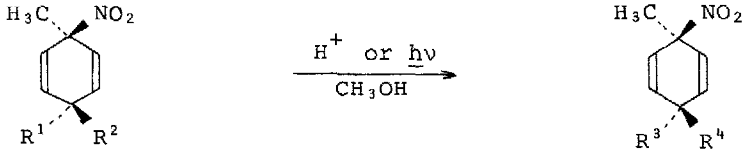
Summary: Diastereoisomers of 1,4-dimethyl-4-nitro-2,5-cyclohexadienyl acetate exchanged acetoxyls for alkoxyls on irradiation in alcohols to give the diastereoisomers of alkyl 1,4-dimethyl-4-nitro-2,5-cyclohexadienyl ethers in isomer ratios of 70:30, whereas the irradiation in pentane yielded p-xylene.

Nitrations at a substituted position (ipso-position) of aromatic hydrocarbons have been studied extensively.[1] Fischer and Ramsay have found acid-catalyzed solvolytic replacements of acetoxyls with methoxyls in the ipso-acetoxynitro adducts of p-xylene (**1a** and **1b**) to give ipso-methoxynitro adducts



1a $R^1 = CH_3$, $R^2 = OCOCH_3$

1b $R^1 = OCOCH_3$, $R^2 = CH_3$

2a $R^3 = OCH_3$, $R^4 = CH_3$

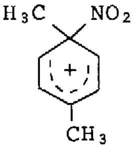
2b $R^3 = CH_3$, $R^4 = OCH_3$

(**2a** and **2b**).[2,3] In this paper we would like to report similar solvolyses induced by photolyses, which showed striking stereoselectivities in marked contrast to the nonstereoselective acid-catalyzed solvolyses.[2]

The acetoxydienes **1a** and **1b** were prepared according to the literature.[2] A cis-configuration in respect to the 1- and 4-methyl groups has tentatively been assigned to **1a** and a trans-one to **1b**.[2] Irradiation of **1a** (100 mg) in 10 ml of methanol under nitrogen at 20 °C with an external 100 W high pressure mercury lamp equipped with a Pyrex filter yielded an oil including 70% of **2a** and 30% of **2b** as revealed by NMR. The combined yield of **2a** and **2b** based on the converted **1a** was almost quantitative through a conversion of about 95%. Similar irradiation of **1b** gave 30% of **2a** and 70% of **2b**. The IR and NMR spectra of the products coincided with those of the authentic **2a** or **2b** which were prepared by the solvolysis of the acetoxydiene catalyzed by sulfuric acid.[2] The configurations of the methoxydienes **2a** and **2b** have recently been determined; that is, **2a** has a trans-configuration and **2b** has a cis-one.[4] The cis/trans ratios of the photoproducts were kept constant throughout the reaction proceedings. In fact **2a** and **2b** underwent no mutual exchange when irradiated in methanol. The acetoxydienes recovered from the reaction mixtures contained no mutually exchanged isomers, either. The photolyses of the methoxydienes in acetic acid caused no conversion to the acetoxydienes.

Benzyl acetates with methoxyl groups at the meta-position are known to exchange acetoxyls for methoxyls on irradiation in methanol.[5,6] No stereoselectivity has been found in this system; the photolysis of a chiral benzyl acetate, for example , resulted in racemization.[6]

The photosolvolyses of the benzyl acetates were considered to involve the intermediates of benzyl cation type.[6] Similarly, the cyclohexadienyl cation (**3**)



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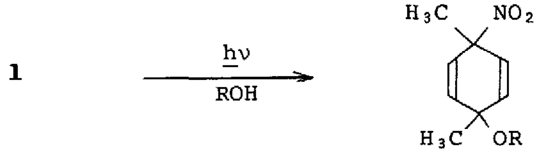
was proposed as an intermediate for the acid-catalyzed solvolysis of the acetoxydiene.[2] This planar cation cannot account for the stereoselective reaction. The photosolvolysis of the acetoxydiene suggests a synchronous mechanism.

Irradiations of **1a** in ethanol, propanol and allyl alcohol yielded ethyl, propyl and allyl ethers of 1,4-dimethyl-4-nitro-2,5-cyclohexadienol (**4**, **5** and **6**), respectively, in isomer ratios of 70:30; **1b** underwent similar photosolvolyses affording the same alkoxydienes with reversed isomer ratios. The major photo-



4 R = CH_2CH_3

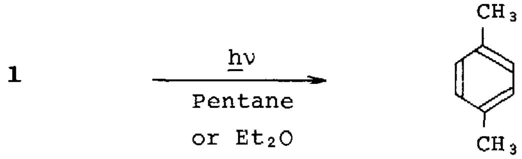
5 R = $CH_2CH_2CH_3$

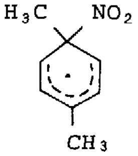
6 R = $CH_2CH=CH_2$

products from **1a** (**2a**, **4a**, **5a** and **6a**) were eluted from aluminum columns faster than the corresponding minor products (**2b**, **4b**, **5b** and **6b**), suggesting a common configuration in **a**-isomers and the compliment in **b**-isomers.

The alkoxydienes **4**, **5** and **6** were also prepared from **1** by the acid-catalyzed solvolyses by sulfuric acid in the corresponding alcohols. Like the reaction in methanol,[2] no stereoselectivity was observed in these acid-catalyzed reactions.

Irradiations of the acetoxydienes in pentane or ethyl ether yielded p-xylene. It has been known that the carboxylic esters of aliphatic alcohols are





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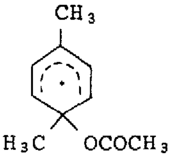

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reduced to alkanes on irradiation in a hexamethylphosphoramide-water system.[7] Similarly photolysis of 3,5-dimethoxybenzyl acetate in hexane has given rise to a homolytic cleavage of the benzyl-acetate bond.[8] The photoreactions of the acetoxydienes in the aprotic solvents might be initiated by a similar homolytic cleavage of C^1-O bond to yield the cyclohexadienyl radical (**7**) which would subsequently lose a nitro radical to resume the benzene system. Otherwise, as encountered in aliphatic nitro compounds,[9] the photolysis might induce a cleavage of the C-N bond to give another cyclohexadienyl radical (**8**) as a precursor of p-xylene.

REFERENCES

1. R. B. Moodie and K. Schofield, Accounts Chem. Res., 9, 287 (1976).
2. A. Fischer and J. N. Ramsay, Can. J. Chem., 52, 3960 (1974).
3. **1a**, **1b**, **2a** and **2b** correspond to the compounds '**1a**', '**1b**', '**3a**' and '**3b**', respectively, in the ref. 2.
4. H. Shosenji, A. Nagayoshi, T. Takemoto and K. Yamada, J. Chem. Soc. Chem. Comm., in press.
5. H. E. Zimmerman and V. R. Sandel, J. Amer. Chem. Soc., 85, 915 (1963).
6. D. A. Jaeger, J. Amer. Chem. Soc., 97, 902 (1975).
7. H. Deshaes, J.-P. Pete, C. Portella and D. Scholler, J. Chem. Soc. Chem. Comm., 439 (1975).
8. D. A. Jaeger, J. Amer. Chem. Soc., 96, 6216 (1974).
9. H. A. Morrison, "The Chemistry of the Nitro and Nitroso Groups", Wiley, N. Y. (1969) p. 165.

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