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PHOTOINDUCED ANTI-MARKOVNIKOV ADDITION OF METHANOL TO ALKYLINDENES

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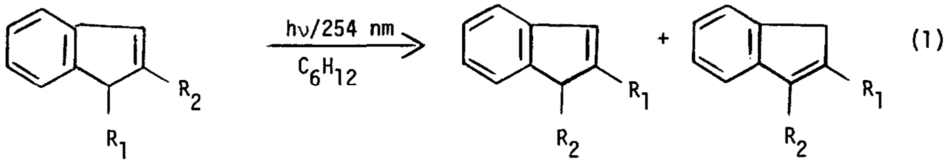
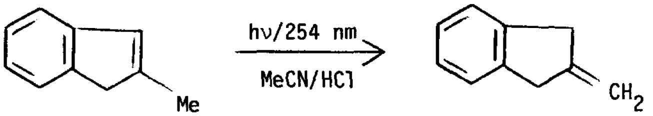
Summary: Irradiation of acidic methanol solutions of several alkylindenes leads to anti-Markovnikov addition of the solvent to the double bond with previously reported photoisomerizations virtually eliminated.

We have recently reported on two photoisomerization reactions of alkylindenes, i.e. phototransposition (interchange of C_1 and C_2; cf. eq. 1)[1,2] and acid-catalyzed photoisomerization (of 2-alkylindenes to 2-alkylideneindanes; cf. eq. 2).[1,3] The two reactions are competitive, so that the presence of acid quenches transposition while catalyzing the double-bond migration. We now present our observations on a third mode of reaction: acid-catalyzed anti-Markovnikov addition of methanol.



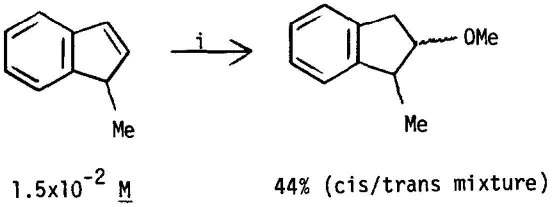
(1)



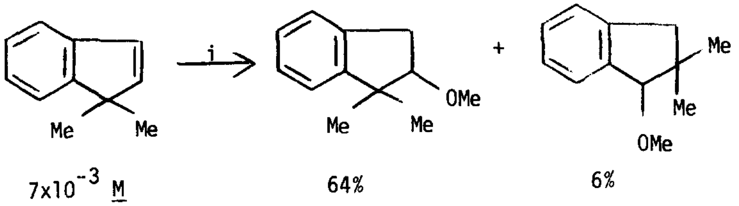
(2)

Several examples are presented in equations 3-5 (yields are by vpc and are based on reacted starting material; the ethers were identified by analysis of their nmr spectra and, for equations 3 and 5, by spectral comparison with independently synthesized samples).

Equations 4 and 5 demonstrate that phototransposition can be a small but observable side reaction under these conditions, as is the endocyclic to exocyclic olefin migration equation 5); however, both processes are dominated by the solvent addition reaction. We have examined the potential scope of this reaction by irradiating 2-methylindene in several other alcohols. Only transposition and olefin migration were observed when 0.25 M HCl was used in ethanol, i-propyl alcohol or t-butyl alcohol. However, we have observed[1] that H_2SO_4 is less effective in bringing about the competitive olefin migration, and the use of this acid (0.20 M) did lead to an 83% conversion of the indene to 2-ethoxy-2-methylindane (eq. 6) (there was no observable addition of i-propyl alcohol under comparable conditions).



(3)



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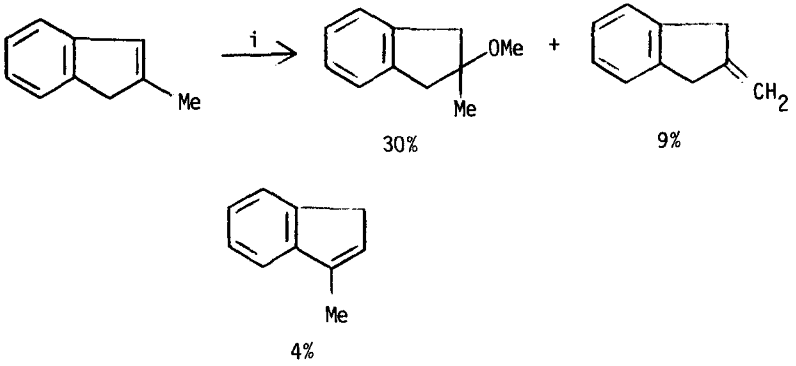
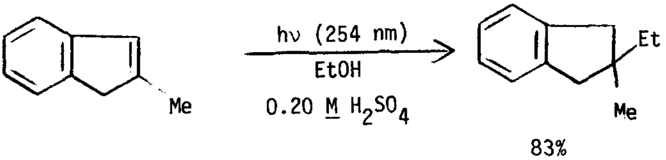


(5)

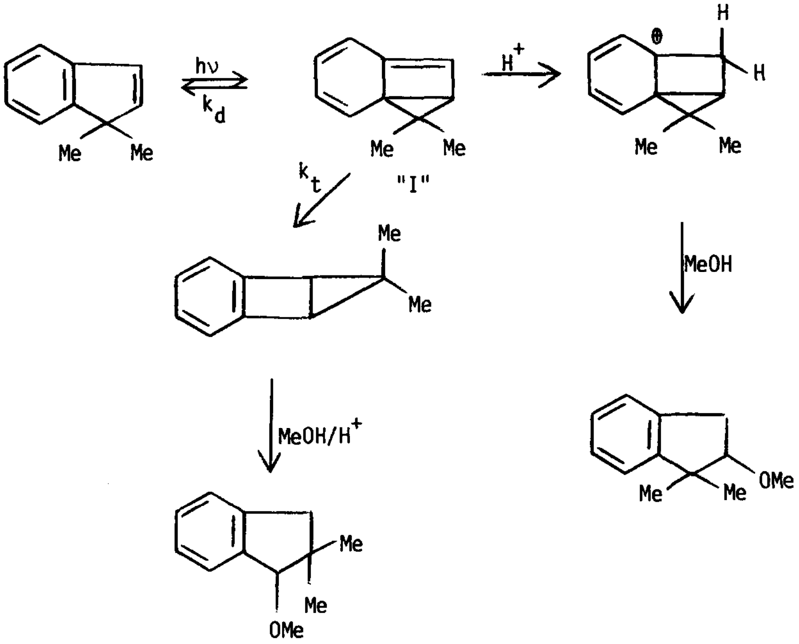
i, hν(254 nm), MeOH, 0.25 M HCl



(6)

Others have observed anti-Markovnikov photoaddition to indenes, but via the use of electron acceptor sensitizers (e.g. 1-cyanonaphthalene) which create the indene radicalcation.[4] Our reaction appears to be more closely related to the other indene (excited singlet state derived) photoisomerizations mentioned above and, for example, no significant conversion to an ether was noted for indene itself nor for 1,3-dimethylindene. Both substrates are also unreactive in the phototransposition and olefin isomerization reactions.[1,3] We believe that the acids are intercepting the initially formed bicyclic intermediate, "I", which otherwise leads to the indene isomerizations.[3] The cation thus generated is then trapped by the solvent (illustrated for 1,1-dimethylindene in the Scheme). (The final rearomatization and ether formation is shown as proceeding in concert, but initial opening to a 2-indyl cation is also possible).

Scheme



Photolyses done at low temperature lend support to this picture. When 1,1-dimethylindene is photolyzed at -40°C in neutral media, with HCl (to 0.25 M) added 1-2 seconds later in the dark, the product is entirely the 1-methoxyindane (i.e. k_t and k_d are rapid at this temperature and none of the "I" has survived). When the photolysis at -40°C is done in the presence of the 0.25 M HCl, the product is entirely the 2-methoxyindane (capture of "I" by the acid is complete).

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References and Footnotes

1. F. J. Palensky and H. Morrison, *J. Am. Chem. Soc.,* 99, 3507 (1977); D. Giacherio and H. Morrison, *ibid,* 100, 7109 (1978); H. Morrison, D. Giacherio and F. J. Palensky, *J. Org. Chem.,* 47, 1051 (1982).
2. See also, A. Padwa, S. Goldstein, R. Loza and M. Pulwer, *J. Org. Chem.,* 46, 1858 (1981) and preceding papers in this series.
3. H. Morrison and D. Giacherio, *J. Chem. Soc. Chem. Comm.,* 1080 (1980); H. Morrison and D. Giacherio, *J. Org. Chem.,* 47, 1058 (1982).
4. M. Yasuda, C. Pac and H. Sakurai, *Bull. Chem. Soc. Japan,* 53, 502 (1980).

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