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PHOTO-INDUCED FRIEDEL-CRAFTS TYPE REACTION OF CYCLOHEXENE TO BENZENE RING

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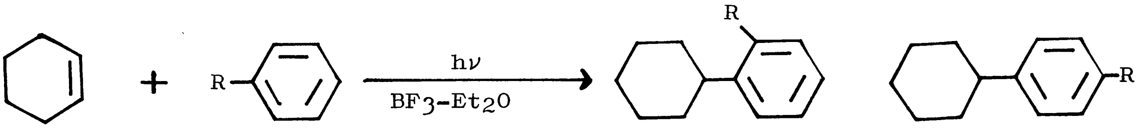
Ultraviolet irradiation of toluene or anisole in the presence of cyclohexene and catalytic amount of BF_3-etherate gave cyclohexyltoluene or cyclohexylanisole. Irradiation of β-(1-cyclohexenyl)-ethylbenzene (V) under the same reaction conditions afforded octahydrophenanthrene VII.

The ionic nature of the photosensitized addition of alcohol to cyclohexene and its derivatives has been settled.[2)] A transoid cyclohexene is one of the most reasonable candidate for the active intermediate which gives rise carbonium ion to capture the alcohol molecule or to give a rearranged product. We will report in this communication the Friedel-Crafts type reaction of cyclohexene,[3)] which gives carbonium ion by the catalysis of BF_3-etherate on the active intermediate derived photochemically.[4)]

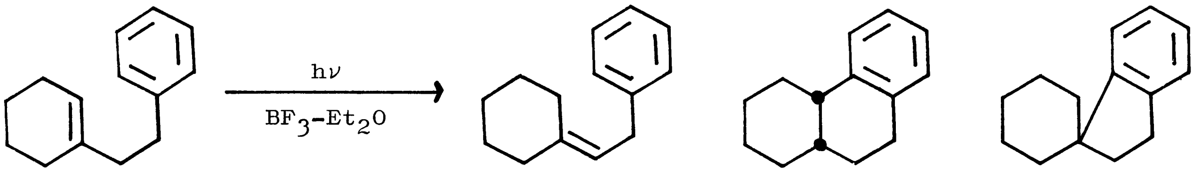
The solution of cyclohexene (0.1 mol/l) in toluene containing a catalytic amount of BF_3-etherate (0.05 mol/l) was placed in a quartz tube and was externally irradiated with a 450 w high pressure mercury lamp for 150 hr under nitrogen. The reaction product,[5)] bp 61-63°C/0.2 mm Hg, consisted of mainly o-cyclohexyltoluene (I) and p-cyclohexyltoluene (II) in the yields of 18 and 22 %, respectively. Vpc analysis of the product containing I and II gave a single peak or a diffused single peak under various conditions. The ratio of the yields of I and II, therefore, was determined from the ratio of dimethyl phthalate and dimethyl terephthalate obtained by permanganate oxidation of the product mixture followed by treatment with diazomethane. The photoreaction between anisole and cyclohexene under the same reaction conditions as above gave the product, bp 77°C/0.4 mm Hg, which consisted of o-cyclohexylanisole (III); nmr(CCl_4) δ=7.34-6.66 (4H, multiplet, aromatic), and p-cyclohexylanisole (IV); nmr(CCl_4) δ=7.23 and 6.93 (4H, AB type, J=9 Hz, aromatic), in the yields of 32 and 28 %, respectively. The reaction mixture kept in the dark afforded only trace amounts of the same products, detected by vpc analysis.



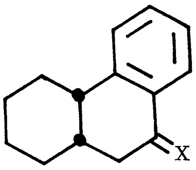
I: R=CH_3 II: R=CH_3

III: R=OCH_3 IV: R=OCH_3

Irradiation of β-(1-cyclohexenyl)ethylbenzene (V) (0.1 mol/l) in benzene containing BF_3-etherate (0.05 mol/l) for 25 hr in the same manner as above gave the product mixture, bp 155-160°C(bath)/22 mm Hg (short column distillation), which contained octahydrophenanthrene VII (70 %) and indane derivative VIII (4 %) together with the rearranged product VI (13 %) of the double bond. The structure of VII including its stereochemistry was deduced by CrO_3/AcOH oxidation of VII to give ketone IX, ir(neat) 1680 cm^{-1}, and further by the comparison of its oxime with authentic cis-oxime X, mp 124°C.$^{6)}$ The structure of VIII was deduced from the spectral data of its CrO_3/AcOH oxidation product XI, ir(neat) 1720 cm^{-1}, nmr(CCl_4) δ=2.56 (2H, singlet, α-methylene to carbonyl). The same reaction mixture kept in tha dark gave 13 % of VII even after prolonged reaction period (75 hr).

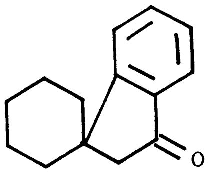


V VI VII VIII



IX: X=O

X: X=NOH



XI

Irradiation of the mixture of cyclohexene and toluene in the absence of acid catalyst caused only the photo-sensitized dimerization of cyclohexene.7) Similarly, irradiation of V without acid catalyst induced only the rearrangement of the double bond to give VI.

Neither cyclopentene nor cyclooctene gave the Friedel-Crafts type adduct with toluene under the same reaction conditions,8) though this type of reaction takes place rather efficiently in the dark by the catalysis of concentrated sulfuric acid. Similarly, the photo-annelation of β-(1-cyclopentenyl)ethylbenzene did not take place under the same reaction conditions. This ring size effect is analogous to that in the attempted photosensitized-addition of methanol to cyclopentene and cyclohexene derivatives.2)

It is noticeable that V has uv-absorption similar to the sum of the absorptions of toluene and methylcyclohexene, indicating that no appreciable π-aryl interaction exists at its ground state, and it is also remarkable that uv-absorption of V does not show any detectable change upon addition of BF_3-etherate, indicating that no appreciable formation of the complex between V and BF_3-etherate before excitation. These findings suggest that the reaction proceeds with the similar mechanism to the ionic addition of methanol to cyclohexene.2) Energy transfer from an excited benzene to cyclohexene moiety produces the unstable species capturing an acid catalyst. The carbonium ion, thus formed, must cause the Friedel-Crafts type alkylation on benzene ring, inter- or intra-molecularly. High selectivity, orienting the entering substituent at the ortho and para positions of toluene and anisole, defines the ionic nature of the present reaction.

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Notes and References

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8) Photocycloaddition between toluene and cyclooctene takes place rather efficiently giving a 1:1 adduct.

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