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PENTACARBONYLIRON INDUCED REARRANGEMENT OF PHENYL-SUBSTITUTED EPOXIDE UNDER ULTRAVIOLET IRRADIATION

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Phenyl-substituted epoxides rearrange to aldehydes or ketones in the presence of pentacarbonyliron under ultraviolet irradiation. Epoxides which have a phenyl group and an electron-withdrawing substituent at the vicinal positions undergo deoxygenation affording olefins.

Recently, various synthetic transformations using pentacarbonyliron, $Fe(CO)_5$, have been investigated extensively.[1)] Among these transformations, several reports have been concerned with the use of $Fe(CO)_5$ for the reaction of epoxide derivatives. For example, ultraviolet irradiation of vinyl epoxides with $Fe(CO)_5$ has resulted in the formation of tricarbonyliron-lactone complexes,[2)] which has been transformed, in some cases, to β- or δ-lactones by further oxidation reactions.[3)] On the other hand, thermal reaction of various epoxides with $Fe(CO)_5$ in tetramethylurea at high temperature has been reported to undergo deoxygenation to afford the parent olefins.[4)] However, the rearrangement of epoxides to aldehydes or ketones in the reaction with $Fe(CO)_5$ has not been clarified so far. This kind of rearrangement induced by metal carbonyls has appeared: vinyl epoxides react with $[Rh(CO)_2Cl]_2$ at room temperature to afford α,β-unsaturated aldehydes;[5)] phenyl-substituted epoxides rearrange to aldehydes or ketones by $Mo(CO)_6$.[6)] The rearrangement of trans-stilbene oxide to deoxybenzoin and other compounds in the presence of $RhCl(PPh_3)_3$, $RhBr(PPh_3)_3$ or $RhCl(CO)(PPh_3)_2$ have also been reported.[7)]

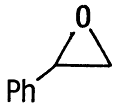
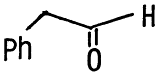
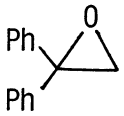
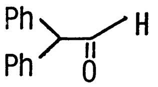
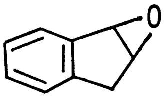
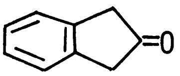
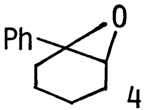
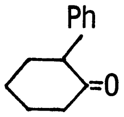
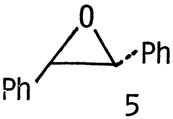
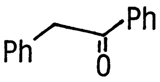
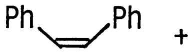
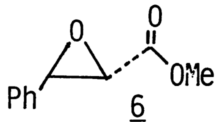
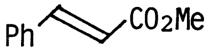
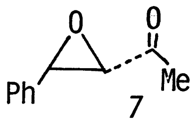
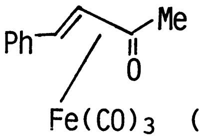
In connection with the synthetic prospect concerning the transformations of epoxide-containing compounds, we would like to present here the reaction of phenyl-substituted epoxides with $Fe(CO)_5$ under ultraviolet irradiation at ambient temperature to result in the formation of aldehydes, ketones or deoxygenated olefins.

Photoirradiation of styrene oxide 1 (Table 1, entry A) with $Fe(CO)_5$ in anhydrous benzene afforded phenylacetaldehyde in a 60% yield.[8)] When 1/10 molar ratio of $Fe(CO)_5$ to 1 was used for this reaction, phenylacetaldehyde and unchanged starting material 1 was obtained in a ratio of 1/12 after irradiation for 3 h.[10)] Therefore, $Fe(CO)_5$ is not catalytic in this reaction. Furthermore the reaction of 1 with $Fe(CO)_5$ in refluxing benzene gave no product and 1 was recovered quantitatively.[11)]

Suitable yields of aldehydes or ketones were realized by photoirradiation of various epoxides with $Fe(CO)_5$ for 3-6 h (Table 1, entries B-D). The reaction of trans-stilbene oxides (5) (Table 1, entry E), however, proceeded very slowly as compared to entries A-D in Table 1, and resulted in the formation of deoxybenzoin in

TABLE 1

YIELDS OF ALDEHYDES, KETONES AND OTHER PRODUCTS OBTAINED FROM REACTIONS OF EPOXIDES WITH $Fe(CO)_5$ UNDER ULTRAVIOLET IRRADIATION[a)]

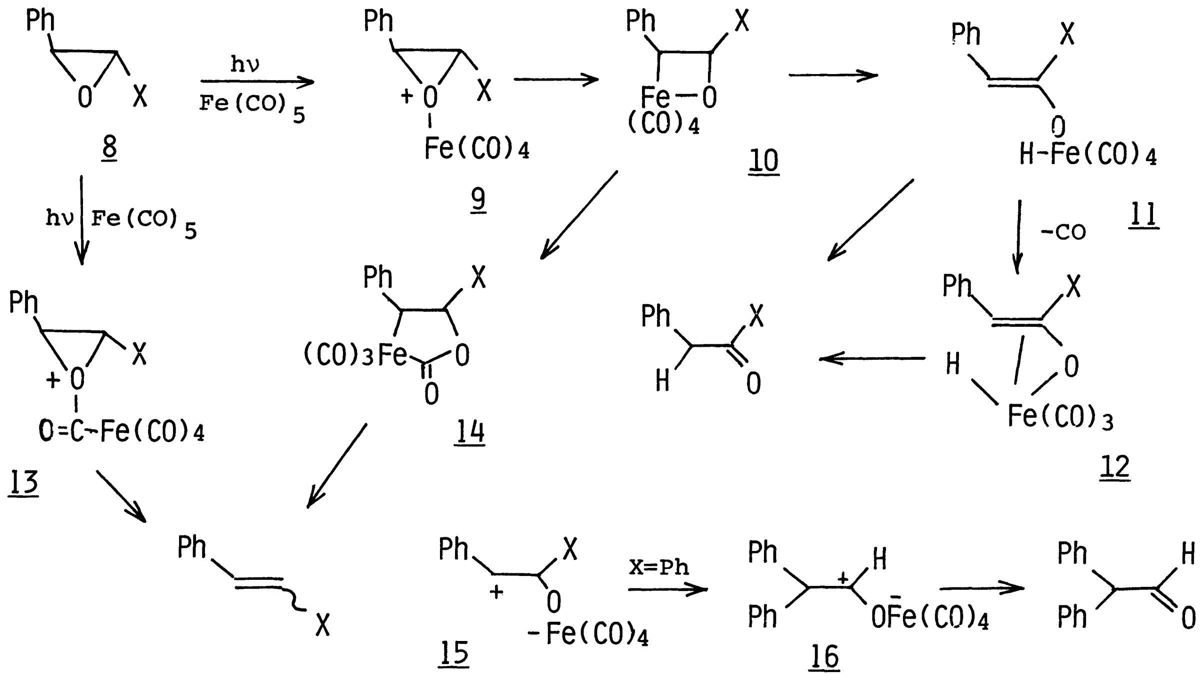
ENTRY	EPOXIDE	MOLAR RATIO OF $Fe(CO)_5$	IRRADIATION TIME (h)	PRODUCTS (YIELDS) (%)
A	 1	1.5	3	 (68)
B	 2	1.5	3	 (79)
C	 3	1.5	3	 (85)
D	 4	2.0	6	 (78)
E	 5	2.0	24	 +  + 5 (23) (4) (63)
F	 6	2.0	24	 + 6 (12) (4)
G	 7	2.0	24	 (19) + 7 (40)

a) All products are known compounds and were identified by comparison of melting points or boiling points and spectral data (IR, NMR) with those of authentic materials.

23% yield. The deoxygenation to afford cis-stilbene occured as well, leaving 63% of unchanged starting material 5 after irradiation for 24 h. Trans-stilbene photoisomerized to cis-stilbene in the presence of $Fe(CO)_5$, therefore the stereochemical aspect of the deoxygenation is obscure.

On the other hand, the phenyl-substituted epoxides 6 and 7 (Table 1, entries F and G), both of which have an electron-withdrawing substituent such as methoxycarbonyl or acetyl group, did not undergo rearrangement. In this case, the reaction proceeded very slowly and the only detected reaction is the deoxygenation to lead to trans-methyl cinnamate or trans-4-phenyl-3-buten-2-one coordinated with Fe(CO)$_3$,12) leaving unchanged starting material.

A thermally induced reaction of Fe(CO)$_5$ with epoxides in tetramethylurea at 145 °C has been reported to cause only deoxygenation via an ionic intermediate.4a) In this reaction, trans-stilbene oxide is also deoxygenated. Ionic intermediates appear to be involved in several other reactions induced by Fe(CO)$_5$.1) Similar to the above reactions, tentatively proposed mechanistic pathways of reactions carried out under mild conditions are outlined in the scheme below, using general formula 8. Initial photolysis of Fe(CO)$_5$ and the subsequent ligand complexation of 8 would afford complex 9. Carbon-oxygen bond cleavage of 9 and the subsequent complexation would afford 10. This intermediate 10 may also be derived from the direct insertion of Fe(CO)$_4$ to the C-O bond of epoxide ring.4a) The acid-catalized rearrangement of trans-stilbene oxide 5 has been shown to afford diphenylacetaldehyde,13) therefore if the free carbocation intermediate such as 15, instead of 10, is involved, diphenylacetaldehyde would be expected for the reaction of 5 (Table 1, entry E). This is not the case here, therefore the coordinated intermediate 10 seems to be prefered in the present reactions. By analogy to other postulated ligand migration processes,14) hydride migration in the intermediate 10 may afford 11.15) If the decomplexation of Fe(CO)$_4$ from 11 is accomplished to afford aldehydes or ketones, the catalytic cycle can be realized, however this is not the case here. Another plausible intermediate for the formation of aldehydes or ketones would be 12, which may be derived from 11. The deoxygenation pathway may be the rearrangement of 10 to 14 and the subsequent decomplexation. Another possible pathway may be the bonding of the epoxide-oxygen with a carbonyl carbon of the metal carbonyl to give 13.4a) The intermediate 13 may collapse directly, or via 14, to the olefin, carbon dioxide and iron carbonyl species. The epoxide such as 6 or 7, which have an



electron-withdrawing carbonyl function, underwent deoxygenation. If the intermediate 10 is involved, the hydride migration in 10 seems to be retarded by the electron-withdrawing substituent (X=CO_2Me or COMe), then 10 may rearrange to 14 leading to olefins. Furthermore the reactions of 5, 6 and 7 proceeded very slowly and underwent deoxygenation. Judging from this fact, the steric hindrance of the carbonyl-ligands of $Fe(CO)_4$ with the substituents on both sides of the epoxide ring may exist in the complexation step. In this case, the addition of epoxide-oxygen to the carbonyl moiety of $Fe(CO)_4$ affording 13 may be sterically preferable to the formation of 9.

Consequently the steric requirement as well as the electronic effect of the substituent seems to affect the pathways of the present reactions. Further study concerning the details of the present reactions are now underway.

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8) The following general procedure was applied. A solution of epoxide (1 mmol) and an adequate amount of $Fe(CO)_5$ in 20 cm^3 of anhydrous benzene was irradiated using RPR-350 nm lamps9) under a nitrogen atmosphere during a period indicated in Table 1. The reaction was monitored by TLC on silica gel. After solvent removal in vacuo, the residue was washed with hexane or carbon tetrachloride to remove insoluble materials. The product, if it is single, was distilled or chromatographed on silica gel for further purification. If it was a mixture, it was separated by preparative TLC on silica gel.
9) Rayonet RPR-100 photoreactor, Pyrex filter.
10) Photoirradiation of 1, without $Fe(CO)_5$, in the similar condition did not cause the reaction.
11) The light and $Fe(CO)_5$ are indispensable for the present transformation.
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