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DEOXYGENATION OF EPOXIDES BY IRON PENTACARBONYL

Howard Alper* and Daniel Des Roches

Department of Chemistry, University of Ottawa

Ottawa, Ontario, Canada K1N 6N5

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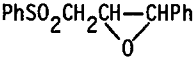
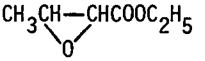
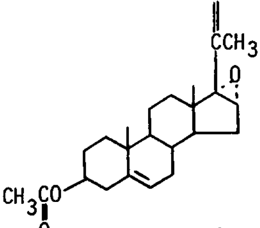
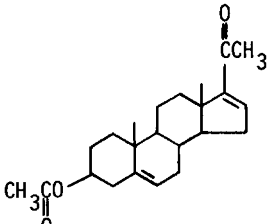
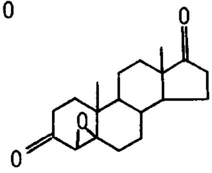
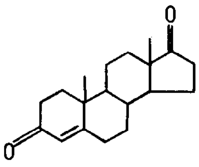
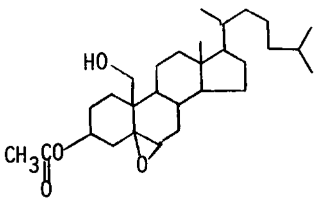
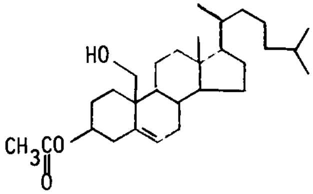
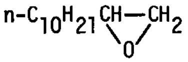
Recent investigations have shown iron pentacarbonyl [$Fe(CO)_5$] to be a useful reagent for effecting a variety of synthetic transformations.[1] Non-polar solvents such as ethers have generally been employed for these reactions. In several cases, it has been demonstrated that reactions which do not take place, or are sluggish in such solvents, can readily occur by the use of dipolar aprotic solvents. For example, treatment of sulfonyl chlorides with $Fe(CO)_5$ in N,N-dimethylacetamide (DMAC) or tetramethylurea (TMU) affords thiosulfonates in good yields (use of dioxane or di-n-butyl ether as the solvent gave low product yields).[2] This communication describes the facile deoxygenation of epoxides by $Fe(CO)_5$ under neutral conditions.

Reaction of *trans*-stilbene oxide (Table 1, entry 1) with an equimolar amount of $Fe(CO)_5$ in TMU for 2.25 hr. at 145°C affords *trans*-stilbene in 56% yield and *cis*-stilbene in 22% yield (DMAC can also be used). Use of refluxing tetrahydrofuran (2.5 hr.) as the reaction medium gave recovered starting material. The reaction in TMU is not catalytic in the metal carbonyl. *trans*-Stilbene does not react at 145° in TMU, either in the presence or absence of $Fe(CO)_5$.

Good yields of olefins were realized by treatment of a variety of epoxides with $Fe(CO)_5$ for 2.0 - 2.5 hr. (Table 1, entries 2-6). Note that particularly high yields resulted if the olefin formed was a conjugated one. The reaction can tolerate a variety of functional groups including ketone, ester, hydroxyl, sulfonyl and olefin.

TABLE 1

YIELDS OF OLEFINS OBTAINED FROM REACTION OF EPOXIDES WITH $Fe(CO)_5$ IN TMU

ENTRY	EPOXIDE	REACTION TIME, hr.	PRODUCT	YIELD[a], %
1	trans-Stilbene oxide	2.25	trans-stilbene	56
			cis-stilbene	22
2	 $\mathrm{PhSO_2CH_2\underbrace{CH{-}CH}_{O}Ph}$	2.0	$PhSO_2CH_2CH=CHPh$	79
3	 $\mathrm{CH_3\underbrace{CH{-}CH}_{O}COOC_2H_5}$	2.0	$CH_3CH=CHCOOC_2H_5$	68
4		2.5		82
5		2.0		95
6		2.5		36[b]
7	 $\mathrm{n\text{-}C_{10}H_{21}\underbrace{CH{-}CH_2}_{O}}$	2.5	$n\text{-}C_{10}H_{21}CH=CH_2$	9
			Internal olefins	33

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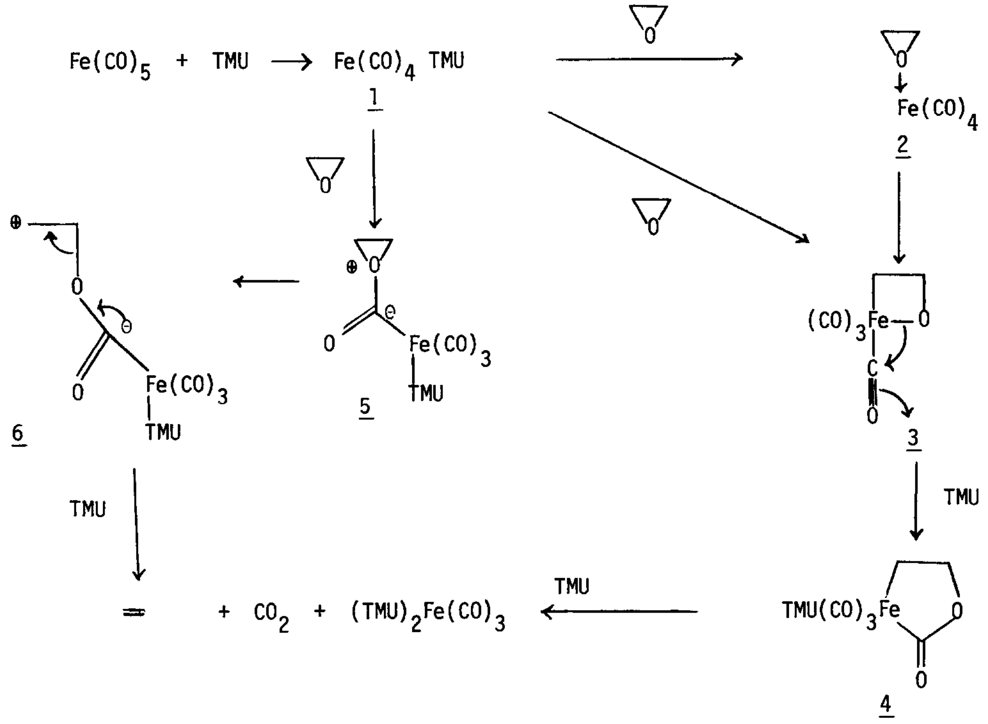
[a] Products were identified by comparison of m.p. or b.p., and spectral data with authentic samples. [b] An unidentified by-product was also formed.

Monosubstituted epoxides such as 1,2-epoxydodecane (Table 1, entry 7) are also deoxygenated by $Fe(CO)_5$ but isomerization of the resultant olefin occurs as well. Very rapid isomerzation of 1-decene and 5-methyl-1-hexene to mixtures of internal olefins occurred in the presence of a catalytic quantity of $Fe(CO)_5$ (TMU, 1 hr., 145°). No isomerization was observed in the absence of $Fe(CO)_5$. The disubstituted olefins, 2,4-dimethyl-1-pentene and 2,4,4-trimethyl-1-hexene, were inert to $Fe(CO)_5$ in TMU, and therefore could be obtained from the corresponding epoxides without undergoing further reaction. The isomerization of certain olefins by iron carbonyls has been reported previously[3].

Possible pathways for the deoxygenation reaction are outlined in Scheme 1. What likely occurs first is displacement of a carbon monoxide ligand of $Fe(CO)_5$ by the solvent to give (tetramethylurea)iron tetracarbonyl (1), a much more reactive species than $Fe(CO)_5$ itself.

Scheme 1



Reaction of 1 with an epoxide may afford 2, which, on subsequent insertion into a C-O bond of the epoxide, affords 3. The latter may also be generated by direct insertion from 1. By analogy to other ligand migration processes,[4,5] donor solvent induced migration of the Fe-O sigma bond to one of the terminal carbonyl carbons attached to Fe would give the ferrolactone 4. Collapse of the latter affords the olefin. The formation of 3 from 1 and/or 2 may proceed *via* a radical intermediate, consistent with the non-stereospecificity of the reaction.

It is conceivable that, instead of TMU displacement from 1 by the epoxide, attack by the epoxide oxygen at a terminal carbonyl carbon of 1 occurs to give 5. Carbon-oxygen bond cleavage of the latter (6), followed by elimination of CO_2, would afford the olefin. For entries 3-5 (Table 1), the carbon atom involved in C-O bond cleavage (5 → 6) cannot bear an electron-withdrawing group.

The following general procedure was used. An equimolar mixture of the epoxide and $Fe(CO)_5$ in TMU (10-15 ml.) was stirred at 145° for 2.0-2.5 hr. (N_2 atmosphere). The solution was cooled to room temperature and then poured into water. The product, if solid, was filtered and recrystallized or chromatographed on silica gel or Florisil. If liquid, the olefin was extracted with ether, washed 4-5 times with water, dried ($MgSO_4$), and evaporated. Further purification, if required, was effected by column chromatography.

In summary, $Fe(CO)_5$ can effeciently deoxygenate a wide variety of epoxides to olefins. There are, of course, other reported methods for effecting this transformation.[6] However, in many cases, the reaction is of limited scope (i.e., few functional groups can be tolerated)[6a,b], and expensive reagents are required in certain instances (WCl_6-RLi).[6c]

Acknowledgements

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