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NOVEL REACTIONS AND MECHANISMS OF IRON CARBONYLS WITH DIHYDROINDENONES AND CYCLOPENTADIENONE DIMERS

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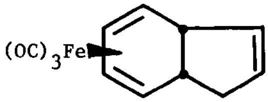
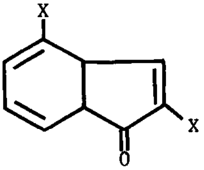
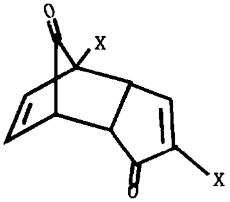
Iron pentacarbonyl reacts with olefins to form the corresponding organometallic compounds,[1] or promotes [1,3]-hydrogen suprafacial shifts.[2] The former reaction is generally favoured if a suitable cis-diene moiety is present in the substrate. To illustrate, dihydroindene readily afforded stable iron carbonyl complex (I) without double bond migration even at elevated temperature.[3] Several 5-vinyl-cyclohexadiene iron carbonyl complexes were also obtained without hydrogen shifts.[4] Birch and his coworkers[5] also reported the isolation of 3a,7a-dihydrobenzofuran tricarbonyliron without isomerization. The complex is usually stable and the bond energy for iron and the diene ligand may sometimes even offset the stabilization energy for an aromatic ring. Thus, the iron carbonyl complexes of 5-cyclohexadienone[6] and 3-6-η-tricyclo$[6.2.2.0^{2.7}]$dodeca-3,5,9,11-tetraene (benzene dimer)[7] were synthesized. We now wish to describe, contrary to the above observations, the first example of the iron pentacarbonyl catalyzed rearrangement of 5-alkenylcyclohexadiene system to benzenoid derivative.



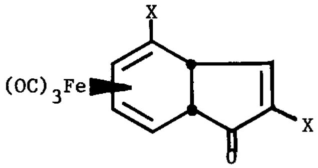
I



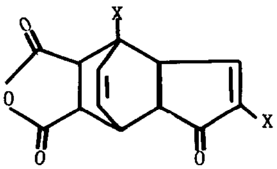
II a X=H
b X=Br



III a X=H
b X=Br



IV a X=H
b X=Br

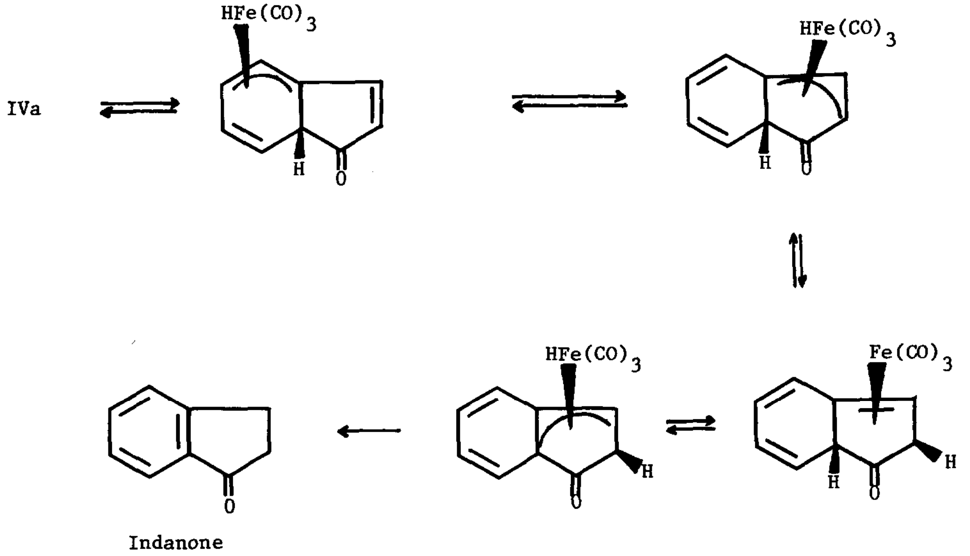


V a X=H
b X=Br

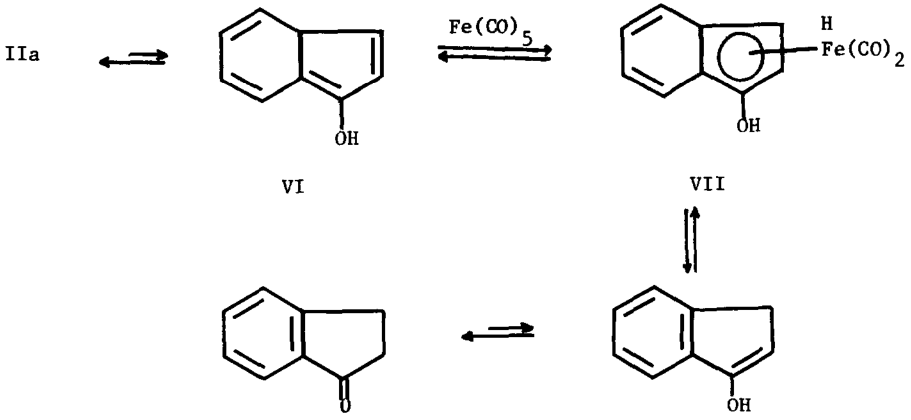
Dihydroindenone (IIa) and 2,4-dibromodihydroindenone (IIb)[8] were obtained by the thermolysis[9] of IIIa and IIIb, respectively, which were prepared according to literature methods.[10] We have established that IIa and IIb are stable in refluxing dioxane or xylenes.

Treatment of IIa with a solution of excess iron pentacarbonyl in refluxing dioxane (18 h) or xylenes (14 h) afforded indanone in 66 or 74% yields, respectively. No corresponding iron carbonyl complex (IVa) was obtained. Similarly, treatment of IIIa with iron pentacarbonyl or diiron enneacarbonyl gave the same product indanone in 44-54% yields under various conditions. There was no direct evidence to show that the decarbonylation process of IIIa did not involve the participation of iron carbonyls. However, the isolation of the adduct Va (74%) from the reaction in the presence of maleic anhydride indicated that the transformation of IIIa to indanone occurred stepwisely via IIa as intermediate which underwent double bond migration.

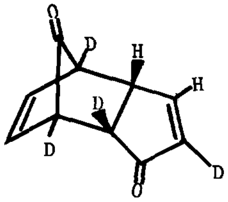
The general mechanism of the migration of double bond catalyzed by iron carbonyls has been proposed via the unstable (olefin)-$Fe(CO)_4$ intermediate.[2] By inspecting the model, the cyclohexadiene moiety of II, however, is planar or at least nearly planar. This should provide a cis-diene system to accommodate iron carbonyls leading to the corresponding organometallic intermediate (IVa). The result that IVa was not isolated from the reaction is striking, which is in contrary to the isolation of the stable dihydroindene iron tricarbonyl complex (I) and related compounds.[3-7] The isolation of the adduct Va as described above may suggest that the rate of formation of diene iron carbonyl complex IVa is slow. In addition, the bridgehead hydrogen in IVa may be activated by the carbonyl group. This may destabilize the complex and lead to subsequent double bond migration to give indanone (Scheme 1). Alternatively, hydroxybenzocyclopentadienyl iron carbonyl complex (VII),[11] which could be formed from enol (VI) and iron carbonyl, may also yield indanone by reductive elimination followed by ketonization (Scheme 2).



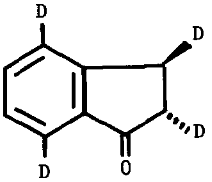
Scheme 1



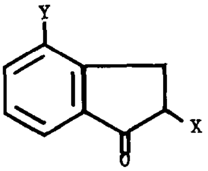
Scheme 2.



VIII



IX



X a X=H, Y=Br
b X=Y=Br

Although the two mechanisms give the same end product, the distribution of migrating hydrogens in the final product should be different. Thus, the deuterium labelled compound (VIII) was prepared from cyclopentanone-2,2,5,5-$\underline{d}_4$[12] according to known methods.[10] On treatment of VIII with iron pentacarbonyl in refluxing xylene afforded indanone-2,3,4,7-$\underline{d}_4$ (IX) in 47% yield. The deuterium distribution in IX was assigned based on nmr and mass spectrometric data. No deuterium scrambling has been observed in IX under the reaction condition. This result favours the rearrangement mode involving two successive 1,3-hydrogen shifts as outlined in Scheme 1. The fact that IX was obtained as the sole product suggests that the hydrogen (or double bond) migration is regiospecific. The mechanistic pathway shown in Scheme 2, however, would lead to more random deuterium distribution and, therefore, is ruled out, even though a more stable intermediate (VII), which is aromatic, may be involved.

In a similar fashion, treatment of IIb with excess iron pentacarbonyl in refluxing xylenes (8 h) or dioxane (12 h) interestingly afforded 4-bromoindanone (Xa) in 38 or 36% yields, respectively. Again, the corresponding iron carbonyl complex (IVb) was not obtained. Furthermore, the expected rearrangement product, 2,4-dibromoindanone (Xb) was not detected. Similarly, treatment of IIIb with iron pentacarbonyl in xylene gave Xa in 33% yield. Moreover, the isolation of the adduct Vb from the reaction in the presence of maleic anhydride indicated that the transformation of IIIb to Xa occurred via IIb as intermediate which underwent double bond migration and subsequent debromination. The latter reaction is particularly noteworthy. Related reductive debromination promoted by iron pentacarbonyl has been reported.[13] We have also established that Xb can be smoothly transformed into Xa by treatment with iron pentacarbonyl in refluxing xylenes. We incline to favour a free radical mechanism for this reduction.[14]

In conclusion, we have demonstrated the first instance of the iron pentacarbonyl promoted rearrangement of 5-alkenylcyclohexadiene system to benzenoid derivatives rather than affording the iron carbonyl complex as found in various examples.[3-7] Such contradictory phenomenon was unclear yet and needs further study.

REFERENCES AND NOTES

1. For review, see: R. Pettit and G.F. Emerson, Adv. Organometallic Chem., 1, 1 (1964).
2. (a) E.K. von Gustorf and J.C. Hogan, Tetrahedron Lett., 3191 (1968);
   (b) F.G. Cowherd and J.L. von Rosenberg, J. Amer. Chem. Soc., 91, 2157 (1969);
   (c) K. Cann and J.C. Barborak, Chem. Commun., 190, (1975).
3. E.J. Reardon, Jr. and M. Brookhart, J. Amer. Chem. Soc. 95, 4311 (1973).
4. A Pelter, K.J. Gould, and L.A.P. Kane-Maguire, Chem. Commun. 1029, (1974).
5. A.J. Birch, K.R. Chamberlain, and D.J. Thompson, J.C.S. Perkin I, 1900 (1973).
6. A.J. Birch, P.E. Cross, J. Lewis, D.A. White, and S.B. Wild, J. Chem. Soc. A, 332 (1968).
7. W. Grimme and E. Schneider, Angew. Chem. Int. Ed. Engl. 16, 717 (1977).
8. Satisfactory elemental analyses and spectroscopic data were obtained on all new compounds.
9. (a) J.E. Baldwin, Can. J. Chem. 44, 2051 (1966); (b) E. Baggrolini, E.G. Herzog, S. Iwasaki, R. Shorta, and K. Schaffner, Helv. Chim. Acta, 50, 297 (1967).
10. (a) N.B. Chapman, J.M. Key, K.J. Toyne, J. Org. Chem., 35, 3860 (1970); (b) T.-Y. Luh and L.M. Stock, ibid., 37, 338 (1972).
11. Hydroxycyclopentadienyl-iron complex is a stable compound, see: R. Epton, G. Marr, and G.K. Rogers, J. Organometal. Chem., 110, C42 (1976).
12. W.H. Saunders, Jr., S.D. Bonadies, M. Braunstein, J.K. Borchardt, and R.T. Hargreaves, Tetrahedron, 33, 1577 (1977).
13. (a) H. Alper and E.C.H. Keung, J. Org. Chem., 37, 2566 (1972);
    (b) S.J. Nelson, G. Detre, and M. Tanabe, Tetrahedron Lett., 447 (1973).
14. T.-Y. Luh, C.H. Lai, K.L. Lei, and S.W. Tam, submitted for publication.

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