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REPLACEMENT OF SO_2Ar IN TRICARBONYL-5α-(ARYLSULPHONYL)CYCLOHEXA-1,3-DIENEIRON COMPLEXES: REGIO- AND STEREOCONTROL IN REACTIONS OF DIENYLIRON CATIONS WITH SOME NUCLEOPHILES

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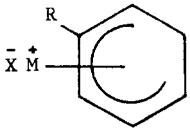
Summary

Regio- and enantiocontrolled bond formation in tricarbonylcyclohexadieneiron complexes is available via the reaction of their derived cations with sodium p-tolylsulphinate followed by nucleophilic displacement of SO_2Ar.

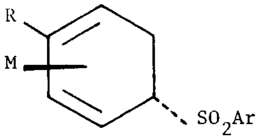
Despite the fact that tricarbonylcyclohexa-1,3-dieneiron complexes are finding increased use in organic synthesis,[1] problems remain regarding efficient control of regiospecificity in nucleophilic addition to their derived cations. In 2-substituted cations most nucleophiles add preferentially to the 5-position and on the α(exo)-face of the mesomeric system. Exceptions include some addition of H^- (or D^-) β(endo) to the 2-Me cation (1b)[2] and reaction of some alkyl lithiums with the 2-Me (1b) or 2-OMe (1c) cation at the 1-position.[3] In the present note we offer an alternative procedure for achieving overall nucleophilic attack on dienyl cations by certain anionoid reagents in which regiospecificity is ensured. The process involves the use of $5\text{-}SO_2Ar$[4] complexes (2) which have previously been noted in connection with synthetic aspects of tricarbonylcyclohexadienyliron anions.[5]



1a R=H

b R=Me

c R=OMe



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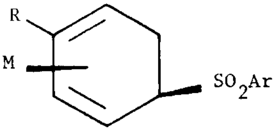

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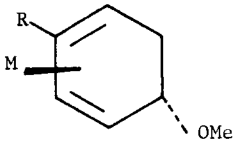
M=$Fe(CO)_3$, X=PF_6

The preparative procedure described[5] for the unsubstituted sulphone complex (2a) is a general one. 2-Substituted cation complexes (1b or 1c) react with sulphinate anion exclusively at C-5 to form the exo-sulphinate in virtually quantitative yields, as stable crystalline solids. The anion generated by base treatment of 5-exo-SO_2Ar (2) complexes[5] by kinetic protonation, at low temperature, produces the corresponding stereoisomeric 5-endo-SO_2Ar isomer (3).

Reaction of either stereoisomer (2a or 3a) with MeOH in the presence of K_2CO_3, or with MeO^-/MeOH, resulted in rapid replacement of the sulphone group to give the known[6] 5-exo-OMe derivative only (4a). The same course of reaction was observed for (2b or 2c). In one experiment, equal amounts of (2a) and (3a) were combined and treated with K_2CO_3/MeOH. Within 5 min. thère was no remaining 5-endo-sulphone while after 15 min. all 5-exo-isomer had been converted (t.l.c. - 10% ethyl acetate in hexane). There was no t.l.c. evidence to suggest that the 5-exo-isomer is converted into the 5-endo during the replacement reaction. Likewise, it has been shown[6] that 5-exo-OMe and 5-endo-OMe complexes are not equilibrated by MeO^-/MeOH. Neither MeOH alone nor K_2CO_3/THF had an effect on (2). However, equilibration of types (2) and (3) may not be observed if the rate of replacement of sulphone in (3) to give (4) is very much faster than the conversion of (2) into (3).



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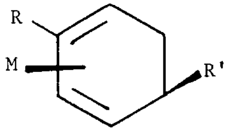

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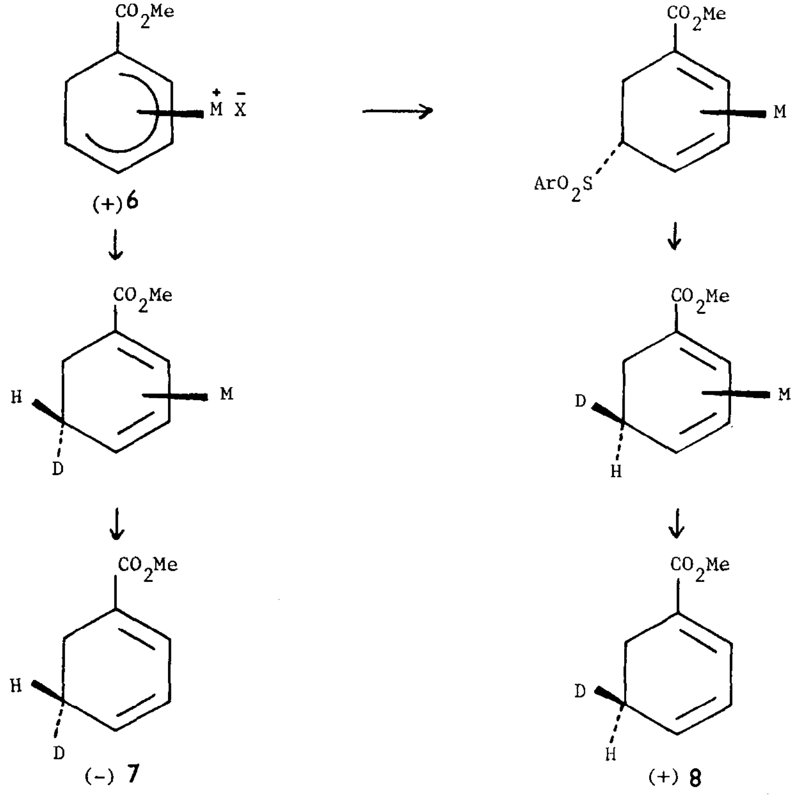
The replacement of SO_2Ar with hydride was examined partly as a means of solving the regiochemical problem in reduction of the 2-Me cation[2] (1b) as well as providing a method of observing the stereochemistry of the displacement using an isotopic label. Treatment of (2a-c) with excess $NaBH_4$ in dry dimethoxyethane at 40°C gave a good yield of the known[1,2] complexes (5a-c; R'=H, R=H, Me or OMe). The result with (1b) shows that the process cannot involve regeneration of the free cation, which is reduced at both the 1- and 5-positions.[2] Direct replacement of SO_2Ar leads to an overall regiospecific reduction of cations of type (1) the specificity depending on that of addition of SO_2Ar. The yield of (5b, R'=H) from (1b) is 75%, compared with the previously reported 14%[2] by direct reduction of the cation.

A feature significant both to the mechanism and the utilisation of the reduction process concerns the stereochemistry of reductive removal of SO_2Ar from the complexes as revealed by using $NaBD_4$ as the reagent. Treatment of exo-sulphone (2b) with $NaBD_4$ gave the endo-labelled[2] complex (5b, R'=D) by an apparent SN2-type of process. Initial interaction between the reducing agent and $Fe(CO)_3$ is a possibility.[7] Introduction of D on the metal occupied face has hitherto been accomplished as a major reaction by the use of deutero-acid, a process difficult to stop at a D_1-stage.

In the case of a resolved cation salt the opportunity is now available to produce both antipodes of a chiral molecule using as starting material only one enantiomer of a complex. For example, resolved ester (6)[8] with $NaBD_4$ then Me_3NO[9] gave the enantiospecifically labelled compound (7) which had an optical rotation value of (-) 1.5°.[10] Reaction of the same salt (6) with $NaSO_2Ar$, followed by reductive replacement of the sulphone group by $NaBD_4$,[11] then decomplexation gave (8), the enantiomer of (7), (α) = (+) 1.4°.[10] Absolute configurations are as shown.[8,12]



(+)6

(-) 7

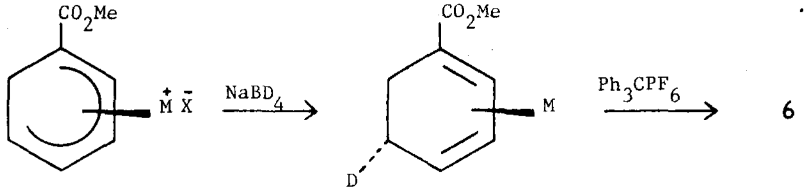
(+) 8

We thank the ARGS for support.

References

1. A.J. Pearson, "Comprehensive Organometallic Chemistry", G. Wilkinson (ed.), Pergamon Press, Exeter, 1982, Vol. 8, 939.
2. A.J. Birch and G.R. Stephenson, J. Organomet. Chem., 218 (1981), 91.
3. B.M.R. Bandara, A.J. Birch and T.C. Khor, Tetrahedron Lett., 21 (1980), 3625.

4. Throughout this paper Ar denotes the 4-tolyl group. This choice is rather abitrary, although the characteristic aromatic splitting pattern and methyl group visibility in the ^1H NMR are convenient for identification purposes.
5. A.J. Birch and L.F. Kelly, J. Org. Chem., in the press. Extension of the present sequence to include replacement of SO_2Ar with carbon nucleophiles is under way, a limitation being the acidity of the proton adjacent to the sulphone group which is removed by, for example, alkyl lithium reagents.
6. K. Hine, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Chem. Comm., (1975), 81.
7. J.A. Gladysz, Aldrichimica Acta, 12 (1979), 13.
8. B.M.R. Bandara, A.J. Birch and L.F. Kelly, J. Org. Chem., 49 (1984), 2496.
9. The oxidation procedure involved heating the complex in benzene at 60-70°C during 2 h in the presence of Me_3NO (sublimed; 8 equivalents). See Y. Shvo and E. Hazum, J. Chem. Soc. Chem. Comm., (1974), 336.
10. $[\alpha]_{589}$ measured: C = 0.25, $CHCl_3$.
11. Tricarbonyl-1β-deutero-1α-carbomethoxycyclohexa-1,3-dieneiron ($[\alpha]_{589}$ = (-) 52°, C = 1, $CHCl_3$) was also formed and was separated by chromatography over silica-gel using 5% ethyl acetate in hexane.
12. The expected exo-direction of addition of D^- to cation salt (6) was confirmed by the sequence:



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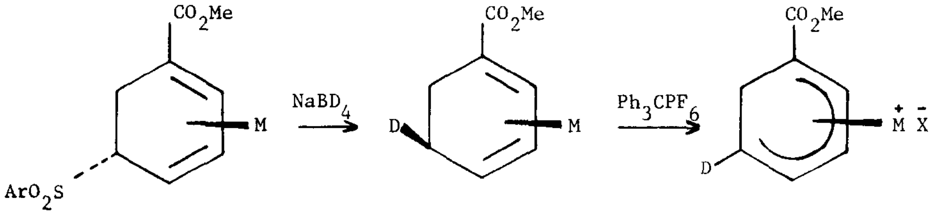
Similarly, treatment with trityl cation in CH_2Cl_2 of the endo-deutero complex, obtained by D^- displacement of SO_2Ar, gave the 5-D dienyl cation as indicated by ^1H NMR (δ 5.05, H-5, absent).



These results, in conjunction with the established[8,13] absolute configuration of (6), confirm the stereochemistries shown in structures (7) and (8).

13. A.J. Birch and B.M.R. Bandara, Tetrahedron Lett., 21 (1980), 2981.

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