Preliminary communication

RATES OF REACTION OF PENTANE-2,4-DIONE WITH SOME SUBSTITUTED TRICARBONYLCYCLOHEXADIENYL IRON CATIONS

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Summary

The rates of reaction of pentane-2,4-dione with a range of η^5-tricarbonyl-cyclohexadienyliron cation salts substituted by Me, OMe or CO_2Me have been measured under pseudo-first-order conditions. Rates are found to be affected not only by the nature of the substituent but by its position: e.g. a 2-OMe group causes retardation and a 3-OMe group a slight acceleration.


The stabilisation of cations of the Wheland type by the tricarbonyliron group permits their controlled use in organic synthesis [1]. The fundamental reactivity is independent of whether the groups attached to the cyclohexadienyl nucleus are electron donating or releasing in nature and anionoid reagents are capable of forming new C—X bonds (X = C, N, O, S, P etc.) at a terminus of the η^5-fragment [2]. The nature and position of the substituent influences the regio-chemistry of this type of process and the control exerted by a variety of substituents has been delineated [3]. This communication relates to the quantitative evaluation of the reactivity of such cations as influenced by substituents attached to the ring, and the results permit for the first time predictions of reactivity in this series [4].

The study examines the effects on reactivity of (a) the type of substituent (OMe, CO_2Me) and (b) change in the position of a given group (e.g. 2-OMe, 3-OMe). Certain salts desirable for the work are either unavailable in suitably pure form, e.g. $2\text{-}CO_2Me$ [5], or are too unstable, e.g. 1-OMe. Structures 1—11 show those cations employed. The method used to obtain the relative reactivities is based on earlier studies of Kane-Maguire [6] and consists of measuring pseudo-first-order rate constants for the reaction between the cation salts and pentane-2,4-dione (in large molar excess) at $40° \pm 0.1°$ in either CH_3CN or CH_3NO_2.
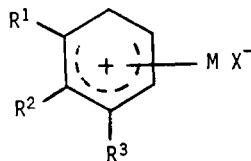
The $k_{obs.}$ was obtained by following quantitatively the disappearance of the

Structures		Abbreviated name used in Table 1
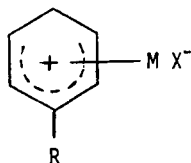
Symmetrical

(1) R = H   Unsub.

(2) R = Me   3-Me

(3) R = MeO   3-Meo

Unsymmetrical

(4) R^1 = Me, R^2 = R^3 = H   1-Me

(5) R^1 = R^3 = H, R^2 = Me   2-Me

(6) R^1 = R^3 = H, R^2 = MeO   2-MeO

(7) R^1 = CO_2Me, R^2 = R^3 = H   1-CO_2Me

(8) R^1 = CO_2Me, R^2 = Me, R^3 = H   1-CO_2Me-2-Me

(9) R^1 = CO_2Me, R^2 = MeO, R^3 = H   1-CO_2Me-2-MeO

(10) R^1 = H, R^2 = R^3 = -$(CH_2)_4$ Bicyclic

(11) R^1 = H, R^2 = R^3 = Me   2,3-DiMe

M = Fe(CO)$_3$

X = PF$_6$ (or BF$_4$ where noted in the Table)

IR stretching frequency at 2100 cm^{-1} corresponding to the initial cation.

To compare rate values between all the complexes in this series requires an awareness of the fact that unsymmetrical 1- or 2-substituted cations have one preferred site of reaction, whereas the unsubstituted or symmetrically substituted cases react with equal probability at two positions. Table 1 has been constructed accordingly. It also gives details of relative rates in two experimentally useful solvents.

Substitution by saturated Me or $(CH_2)_4$ in all cases reduces the rate, by a lesser degree in the 3- (entries c and d) than the 1- (entry f) or 2-positions (Entries g and h). The 1-Me is attached at the opposite end of the cation, so the effects cannot be just steric ones. The fact that the bicyclic and 2,3-Me$_2$ derivatives are of the same order as the mono-substituted series shows that the effects with such substituents are not directly additive. The effects of adjacent substituents (Me$_2$, $(CH_2)_4$) may be partly due to steric interactions which differ from the cation to the product. The effect of 2-Me on the 1-CO_2Me complex shows that it is also inhibitory in this di-substituted case (entries k/l and m/n).

TABLE I

SYMMETRICAL CATIONS				UNSYMMETRICAL CATIONS			
Entry	Salt	Solvent	k_{rel}	Entry	Salt	Solvent	k_{rel}
a	UNSUB	CH_3CN	1.00	f	1-Me	CH_3NO_2	0.37
b	UNSUB	CH_3NO_2	1.00	g	2-Me	CH_3CN	0.38
c	3-Me	CH_3CN	0.81	h	2-Me	CH_3NO_2	0.35
d	3-Me	CH_3NO_2	0.65	i	2-MeO	CH_3CN	0.09
e	3-MeO	CH_3NO_2	1.40	j	2-MeO	CH_3NO_2	0.16
				k	1-CO_2Me	CH_3CN	12.10
				l	1-CO_2Me	CH_3NO_2	10.40
				m	1-CO_2Me-2-Me	CH_3CN	6.56
				n	1-CO_2Me-2-Me	CH_3NO_2	7.22
				o	1-CO_2Me-2-OMe	CH_3CN	1.61
				p	Bicyclic (BF_4)	CH_3CN	0.75
				q	Bicyclic (PF_6)	CH_3CN	0.75
				r	Bicyclic (PF_6)	CH_3NO_2	0.67
				s	2,3-DiMe	CH_3NO_2	0.41

The highly inhibitory effect of the 2-OMe group [7], shown both with un-substituted (entries i/j) and 1-CO_2Me (entry o), but the slight accelerating effect of the 3-OMe group (entry e), indicates the importance of position in this case. This may well be due to the dual character of OMe, which shows a mesomeric electron-release and an inductive electron-attraction. Whether the former, which would have an inhibitory effect on reactivity of a cation, can be exercised depends on the orbitals of the cation to which it is attached, while the latter, with an accelerating effect, could be exercised directly. The mesomeric effect due to p-orbitals on the oxygen would be expected to dominate if it can inter-vene at all. The evidence, including regio-selectivity [8], is that the mesomeric effect of 2-OMe is involved dominantly in the 1-position and effectively but to a lesser extent in the 5-position, whereas 3-OMe exercises an inductive effect leading to acceleration at the terminus.

The 1-CO_2Me cation shows a greatly enhanced rate (entries k/l), which is partly offset by 2-Me (entries g/h) and even more so by 2-OMe (entry o).

The results are, however, clearly not independent of the nature of the nucleophile. The highly delocalised and rather unreactive anion from pentane-2,4-dione reacts slowly enough to permit the measurements recorded. A local-ised anion such as that in t-butyllithium reacts to a marked extent at the 1- as well as the 5-position of the 2-OMe cation [9]. The relative rates given here are therefore indicative of trends, but different nucleophiles, for both steric and electronic reasons, may provide different experimental sequences. In the gen-eral case both the nature of the metal and of the organic system (e.g. Os instead of Fe [10], a seven-rather than a six-membered ring [11]) must affect the issue since the position of attack of anions (2- or 3- rather than the terminus) can vary, with a change in the nature of the product. This remains to be exam-ined. In the present case the reaction of the central position of the cation does not occur, probably because of the unfavourable, 1,4-diene—tricarbonyliron complex which would result, and the 2-position is not involved since the product would be a σ,π-allyl complex which is formed with Os not Fe [10].

Charge density calculations for the unsubstituted tricarbonylcylcohexadien-

yliron cation 1 show [12], in the ground state, C-2,4 > C-3 > C-1, 5, but similar calculations [13] for OMe or CO_2Me tricarbonylcycloheptatrienyl-chromium complexes were not useful in prediction of site of nucleophilic attack.

The indications provided in this communication of substituent effects in the tricarbonylcyclohexadienyliron cation series supplement previous synthetic work. A full report will provide a wider study together with details of the preparations of the cations listed.

References

1   A.J. Birch, B.M.R. Bandara, K. Chamberlain, B. Chauncy, P. Dahler, A.I. Day, I.D. Jenkins, L.F. Kelly, T.-C. Khor, G. Kretschmer, A.J. Liepa, A.S. Narula, W.D. Raverty, E. Rizzardo, C. Sell, G.R. Stephenson, D.J. Thompson and D.H. Williamson, Tetrahedron, in press.
2   L.F. Kelly, A.S. Narula and A.J. Birch, Tetrahedron Lett., 21 (1980) 871 and ref. therein.
3   A.J. Birch, Ann. New York Acad. Sci., 333 (1980) 107.
4   Comparisons of the reactivity of the 2-MeO cation 6 with the unsubstitured cation 1 have been reported, see reference 6.
5   A.J. Birch and D.H. Williamson, J.Chem. Soc. Perkin I, (1973) 1892.
6   L.A.P. Kane-Maguire, J. Chem. Soc. (A), (1971) 1602.
7   L.A.P. Kane-Maguire and C.A. Mansfield, J.Chem. Soc. Dalton, (1976) 2187, 2192.
8   A.J. Birch, K. Chamberlain, M. Haas and D.J. Thompson, J.Chem. Soc. Perkin I, (1973) 1882.
9   B.M.R. Bandara, A.J. Birch and T.-C. Khor, Tetrahedron Lett., 21 (1980) 3625.
10 A.L. Burrows, B.F.G. Johnson, J. Lewis and D.G. Parker, J. Organometal. Chem., 194 (1980) C11.
11 R. Edwards, J.A.S. Howell, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1974) 2105.
12 D.W. Clack, M. Monshi and L.A.P. Kane-Maguire, J. Organometal. Chem., 107 (1976) C40.
13 D.W. Clack, M. Monshi and L.A.P. Kane-Maguire, J. Organometal. Chem., 120 (1976) C25.