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Heptafulvene Complexes of Iron Carbonyl

By B. F. G. JOHNSON, J. LEWIS,* P. MCARDLE, and G. L. P. RANDALL

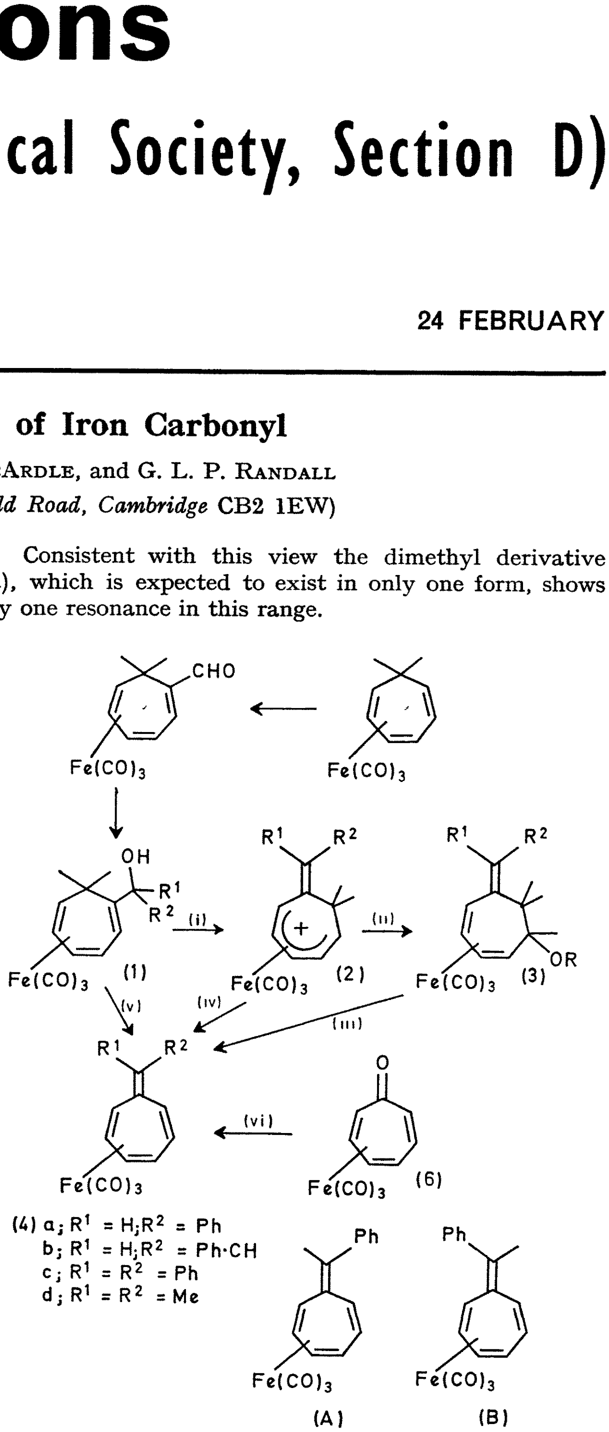
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary Iron tricarbonyl complexes of several substituted heptafulvenes have been prepared and characterised.

IN a previous communication[1] we reported that salts of the type (**2**), which may be produced in a three-stage synthesis from tricarbonylcycloheptatrieneiron (see Scheme), readily undergo nucleophilic addition of OR^- ($R = H$ or Me) to produce the substituted derivatives (**3**). We have now found that these complexes readily eliminate ROH to produce iron tricarbonyl derivatives of substituted heptafulvenes (**4**). This discovery led us to devise other more synthetically useful routes to these complexes utilizing the more readily available substances (**1**) and (**2**) (see Scheme). In considering the various isomeric forms possible for (**4**) (see below) it appeared necessary to produce the dimethyl derivative (**4d**). Here we were able to employ an alternative preparative route from tricarbonyltroponeiron (**6**). Treatment of (**6**) with isopropylmagnesium bromide led to the alcohol $C_{10}H_{14}O_4$ which on dehydration yielded the expected dimethyl derivative (**4d**). We attempted to synthesize the *parent* heptafulvene complex (**4**; $R^1 = R^2 = H$) *via* dehydration of $(C_8H_7CH_2OH)$–$Fe(CO)_3$ but only a dimeric complex $C_{16}H_{16}Fe_2(CO)_6$ was obtained.

Complexes (**4a**) and (**4b**) formed yellow crystals, and complexes (**4c**) and (**4d**) distillable yellow oils. All give the correct parent peak in the mass spectra and show three sharp bands (ν_{CO}) in the i.r. spectra (hexane) which are similar in appearance to those normally observed for diene–irontricarbonyl derivatives.

The n.m.r. spectra of the complexes are in agreement with the assigned structures, showing, for example in the case of the phenylheptafulvene complex (**4a**), signals at τ 2·8 (multiplet, 5H), 3·5 (doublet, 1H), 4·1—4·8 (multiplet, 4H), 6·0 (doublet of doublets, 1H), and 7·1 (triplet, 1H). The appearance of two signals at τ 6·0 is consistent with the presence of two isomeric forms of the complex (A and B). Consistent with this view the dimethyl derivative (**4d**), which is expected to exist in only one form, shows only one resonance in this range.



SCHEME. (i) Proton addition. (ii) Nucleophilic addition of OR^- ($R = H$ or Me). (iii) Elimination of ROH. (iv) Reaction with Et_3N. (v) Dehydration. (vi) Reaction with isopropylmagnesium bromide to give (**4d**).

Valence isomers of structure (**4**), *e.g.* tricarbonylphenylbicyclo[4,2,0]octatrieneiron and tricarbonylphenylcyclooctatetraeneiron (synthesised for comparison) can be eliminated on the basis of the n.m.r. spectra.

The unco-ordinated heptafulvene and its related substituted derivatives are not particularly stable species although in general the stability of such substances is known to increase as electron-withdrawing substituents are introduced on to the 8-carbon atom. The thermal stability of the complexes produced in this work again demonstrates the effectiveness of the iron tricarbonyl group as a stabilising unit. Pettit and his co-workers[3] have shown in their elegant studies of tricarbonylcyclobutadieneiron that the chemistry of the stabilised organo-group (*albeit* modified on co-ordination) may be readily studied. We are at present examining in detail the chemistry of both the heptafulvene complexes (**4**) and the heptafulvenes themselves (produced *in situ* from the complexes). Preliminary experiments have confirmed the feasibility of such studies.

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[1] B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *Chem. Comm.*, 1969, 1273.

[2] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1967, **89**, 2491.

[3] J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 3254.