Trapping of Kekulé Structures *via* Co-ordination to Iron. Positional Isomerism in Bis-tricarbonyliron Complexes of 3,α-Dimethylstyrene

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Summary *meta*-Substituted α-methylstyrene and pentacarbonyliron afford on irradiation two isomeric bis-tricarbonyliron complexes, in each of which one of the Kekulé structures is trapped.

ONE of the aspects of transition metals that has aroused recent interest among organic chemists is their ability to trap otherwise transient or hypothetical organic species.[1] We now report the isolation and characterization of two isomeric iron carbonyl complexes derived from trapping of the Kekulé-type structures of an appropriately substituted styrene.

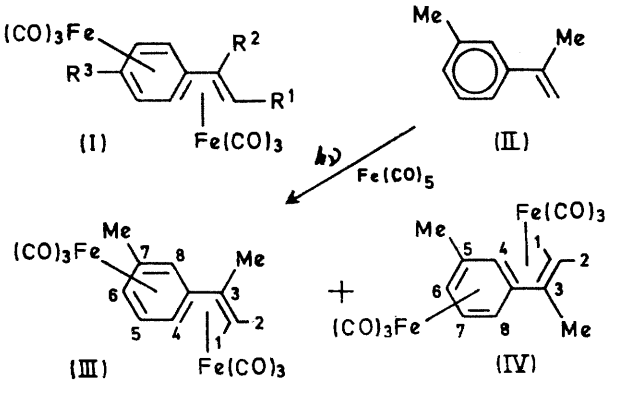
Irradiation of styrenes in the presence of pentacarbonyliron yields, among other products, a novel bis-tricarbonyliron complex (I), in which all six "aromatic" π-electrons are bonded in diene-fashion to iron.[2] We applied this reaction to a *meta*-substituted styrene in the hope of obtaining two complexes analogous to (I). These would constitute positional isomers by virtue of the two distinct environments the substituent can find in the co-ordinated styrene. Indeed, the two isomeric complexes (III) and (IV), bis-tricarbonyliron-3,α-dimethylstyrenes, emerge on work-up from the reaction mixture of 3,α-dimethylstyrene (II) and iron pentacarbonyl†.

The coloured isomers precipitated from petroleum solution were separated manually and recrystallized. Structure (III) was assigned to the orange crystals, m.p. 116° (dec.), and structure (IV) to the purple crystals, m.p. 93° (dec.), on the basis of evidence given below.

^{1}H *N.m.r. spectral parameters*[a] *of* (III) *and* (IV) (CDCl$_3$)

	Chemical Shifts (τ)								Coupling Constants (Hz)				
Position	1	2	3	4	5	6	7	8	J_{12}	J_{45}	J_{56}	J_{67}	J_{78}
(III)	9·79(d)	8·43(d)	7·90(s) (Me)	8·11(d)[b]	6·70(dd)	3·95(d)[b]	7·42(s) (Me$_3$)	6·30(s)[b]	2·4	5·1	6·0	—	—
(IV)	9·68(d)	8·36(d)	7·93(s) (Me)	8·28(s)[b]	8·43(s) (Me)	4·03(d)[b]	3·55(dd)	6·35(d)[b]	2·3	—	—	4·5	6·5

[a] The methods of assigning chemical shifts are described in ref. 2. [b] Broad due to H–C–C–C–H splitting.



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† In contrast, on parallel reaction of 2,α-dimethylstyrene we have isolated only one of the two theoretically possible isomers of this type, the one in which the ring methyl group appears at position 8.

‡ I.r. (hexane): (III), ν_{CO} = 2048, 2036, 1990, 1977, and 1961 cm^{-1}; (IV), ν_{CO} = 2048, 2036, 1984, 1977, and 1965 cm^{-1}. For comparison, see values in ref. 2.

The structures assigned are in agreement with the mass spectral pattern ($M^+_{III} = M^+_{IV} = 412$), and the i.r. spectra show absorptions in the CO region that are typical for a styrene–bis-tricarbonyliron complex.‡ The n.m.r. spectra permit unequivocal assignment of the structures (III) and (IV) to the isomers (Table).

The feature of greatest contrast in the n.m.r. spectra is the shift of approximately 1 p.p.m. of the ring methyl protons from isomer (III) with methyl at position 7 (τ 7·42), to isomer (IV) with methyl at position 5 (τ 8·43). This upfield shift in going from "inner" to "outer" positions of the diene is a well-documented characteristic of cyclic diene–iron tricarbonyl complexes.[3]

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[1] M. D. Rausch, R. F. Kovar, and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1969, **91**, 1259; G. F. Emerson, K. Ehrlich, W. P. Giering, and D. Ehntholt, *Trans. New York Acad. Sci.*, 1968, **30**, 1001, and references therein.

[2] R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Letters*, 1970, 4257.

[3] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332; M. L. Maddox, S. L. Stafford, and H. D. Kaesz, in *Adv. Organometallic Chem.*, 1900, **3**, 1.