On the Stereochemistry and Mechanism of the Iron Carbonyl Promoted Ring-opening of 2-Phenylmethylenecyclopropane

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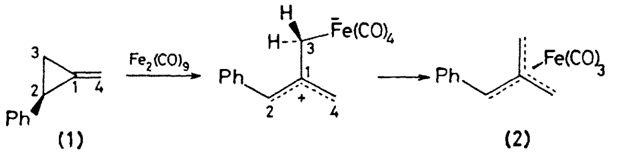
Summary The iron carbonyl promoted ring-opening of 2-phenylmethylene[3-$^2H_1$]cyclopropane is found to be stereospecific and disrotatory, a result that rules out a previously proposed zwitterionic mechanism but which is consistent with the frontier molecular orbital predictions for a pericyclic process

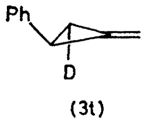
In the previous communication we pointed out that the iron carbonyl promoted ring-opening of cyclobutenes and methylenecyclopropanes may be reactions whose stereochemistries are predictable by the application of frontier molecular orbital theory and the rules of conservation of orbital symmetry.[1] We report here some experimental results designed to elucidate the stereochemistry and mechanism of one such reaction, the iron carbonyl promoted ring-opening of 2-phenylmethylenecyclopropane.

Reaction of 2-phenylmethylenecyclopropane (**1**) with di-iron nonacarbonyl in benzene at room temperature for 18 h afforded tricarbonyl(phenyltrimethylenemethane)iron[2] (**2**) and tricarbonyl(1-phenylbutadiene)iron in a ratio of *ca.* 1·3 : 1.† If iron pentacarbonyl and trimethylamine oxide[3] were used instead of di-iron nonacarbonyl, (**2**) was still formed in good yield but the phenylbutadiene complex could no longer be detected.

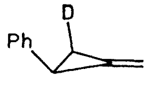
Billups *et al.*[4] have suggested a mechanism for the di-iron nonacarbonyl induced ring-opening of 2,2-dimethyl(allylidene)cyclopropane which, if applied to the iron carbonyl promoted ring-opening of methylenecyclopropanes in general, would have a number of attractive features. The proposed scheme for the ring-opening of (**1**) is illustrated in Scheme 1. This mechanism nicely explains the apparent substituent effect whereby the trimethylenemethane complex is the major product when the initial methylenecyclopropane bears alkyl,[4] phenyl,[2] or vinyl[5] substituents but is not formed at all from unsubstituted[2] or ester substituted[6] methylenecyclopropanes. It is also made especially attractive by its similarity to the established mechanism for the Ag^{I} and Pd^{II} catalysed reactions of small ring hydrocarbons.[7,8]



SCHEME 1



(3t)



(3c)

The crucial, experimentally testable feature of the mechanism illustrated in Scheme 1 is that the zwitterionic intermediate possesses a plane of symmetry which renders the two hydrogen atoms attached to C-3 equivalent. The mechanism would therefore require that the *cis* and *trans* isomers of 2-phenylmethylene[3-$^{2}H_{1}$]cyclopropane, (**3c**) and (**3t**) respectively, give identical mixtures of products which are isomeric with regard to the labelling. Accordingly we set out to synthesize (**3c**) and (**3t**) and to subject them to the reactions with di-iron nonacarbonyl and iron pentacarbonyl–trimethylamine oxide.‡

The ^{1}H n.m.r. spectra of the tricarbonyl(phenyltrimethylenemethane)iron products arising from reaction of (**1**), (**3t**), and (**3c**) are shown in the Figure. The assignment of the protons in spectrum (A) follows that reported by Ehrlich and Emerson.[9] We have confirmed these assignments by the use of nuclear Overhauser enhancement and $^{13}C\{^{1}H\}$ n.m.r. techniques. Examination of spectra (B) and (C) in the Figure shows that the products from reaction of (**3t**) and (**3c**) with di-iron nonacarbonyl are not identical. The same results were obtained when iron pentacarbonyl–trimethylamine oxide was used in place of di-iron nonacarbonyl. Clearly, then, the mechanism outlined in Scheme 1 cannot be correct.

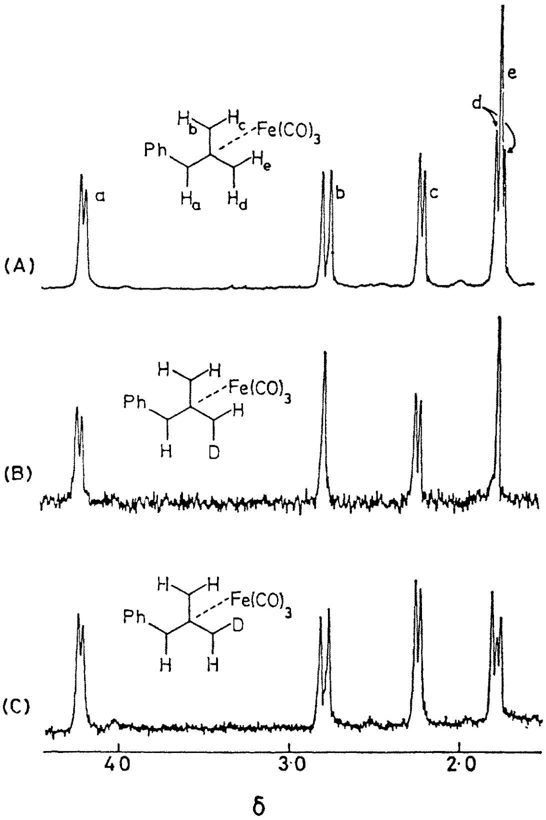


FIGURE. 90 MHz ^{1}H n.m.r. spectra (CS_2) of phenyltrimethylenemethane complexes derived from (**1**) (A), (**3t**) (B), and (**3c**) (C).

Comparison of spectra (B) and (C) with the assignments of spectrum (A) reveals that the ring-opening has occurred in a disrotatory sense. Within the error limits of our

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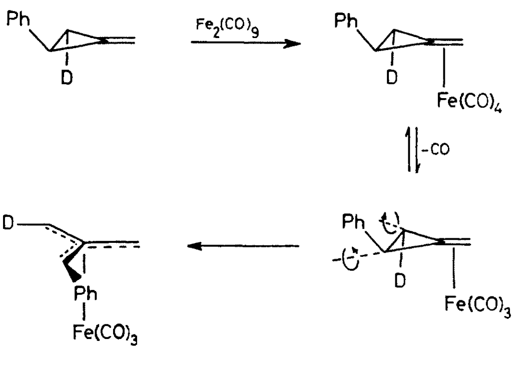
† The product distribution appears to be time dependent. Under the conditions reported by Noyori *et al.* (see ref. 2) one obtains very little of the phenylbutadiene complex but a considerable amount of unchanged methylenecyclopropane remains. The quoted product ratio is obtained after complete consumption of the methylenecyclopropane.

‡ The syntheses of (**3c**) and (**3t**) will be reported in a forthcoming full paper. In the 90 MHz ^{1}H n.m.r. spectrum ($CDCl_3$) unlabelled 2-phenylmethylenecyclopropane shows multiplets at δ 7·2 (5H), 5·55 (2H), 2·4—2·7 (1H), 1·5—1·9 (1H), and 1·0—1·3 (1H). The integral ratios of the peaks at δ 5·55, 2·4—2·7, 1·5—1·9, and 1·0—1·3 are 2·18 ± 0·11 : (1·00) : 0·18 ± 0·03 : 0·92 ± 0·08 for (**3t**) and 1·96 ± 0·12 : (1·00) : 1·08 ± 0·08 : 0·50 ± 0·10 for (**3c**).



SCHEME 2

integration the reaction is stereospecific.§ We suggest that a mechanism consistent with these observations, with the established mechanism for the iron carbonyl induced ring-opening of strained cyclobutenes,[10] and with the calculations reported in the previous communication is as in Scheme 2.

It is interesting to note that if one assumes initial co-ordination of the iron tetracarbonyl unit on the side away from the bulky phenyl group,¶ the breaking σ bond must bend up away from the metal, as predicted by frontier molecular orbital theory.

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§ From the observed amounts of (**1**), (**3c**), and (**3t**) in each of the labelled phenylmethylene-cyclopropanes one can calculate that the integral ratio of peaks a:b:c:d:e should be (1·00):1·09 ± 0·15:1·09 ± 0·15:0·18 ± 0·06:0·92 ± 0·10 for spectrum (B) and (1·00):0·98 ± 0·20:0·98 ± 0·20:1·08 ± 0·20:0·50 ± 0·20 for spectrum (C) if the reaction was completely stereospecific. We observe (1·00):1·00 ± 0·03:1·00 ± 0·03:0·22 ± 0·04:0·84 ± 0·05 and (1·00):1·00 ± 0·12:1·09 ± 0·10:1·23 ± 0·13:0·20 ± 0·18, respectively. The larger uncertainties in the data for spectrum (C) are due primarily to the higher proportion of (**1**) contaminating the reactant (**3c**). Integration of peaks d and e is performed in C_6D_6 which allows better separation of the resonances.

¶ The crystal structure of η^2-*cis*-2,3-bis(methoxycarbonyl)methylenecyclopropane]tetracarbonyliron has been published.[11] In this case it is found that the iron co-ordinates to the same side as the ester substituents, although it is known that ester functions cause intramolecular 'delivery' of an $Fe(CO)_4$ unit in cyclohexa-1,3-dienes.[11] Normally bonding of the iron occurs on the side opposite a bulky substituent (see V. N. Piottukh-Peletskii, R. N. Berezina, A. I. Rezvukhim, and V. G. Shubin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1973, 2083).

[1] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.
[2] R. Noyori, T. Nishimura, and H. Takaya, *Chem. Comm.*, 1969, 89.
[3] Y. Shvo and E. Hazum, *J. Chem. Soc. Chem. Comm.*, 1975, 829.
[4] W. E. Billups, L.-P. Lin, and B. A. Baker, *J. Organometallic Chem.*, 1973, **61**, C55.
[5] W. E. Billups, L.-P. Lin, and O. A. Gansow, *Angew. Chem. Internat. Edn.*, 1972, **11**, 637.
[6] T. H. Whitesides and R. W. Slaven, *J. Organometallic Chem.*, 1974, **67**, 99.
[7] J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Comm.*, 1971, 40.
[8] K. C. Bishop, *Chem. Rev.*, 1976, **76**, 461 and references therein.
[9] K. Ehrlich and G. F. Emerson, *J. Amer. Chem. Soc.*, 1972, **94**, 2464.
[10] W. Slegeir, R. Case, J. S. McKennis, and R. Pettit, *J. Amer. Chem. Soc.*, 1974, **96**, 287.
[11] T. H. Whitesides, R. W. Slaven and J. C. Calabrese, *Inorg. Chem.*, 1974, **13**, 1895.