

The Addition of Dichlorocarbene to Ferrocenylethylenes

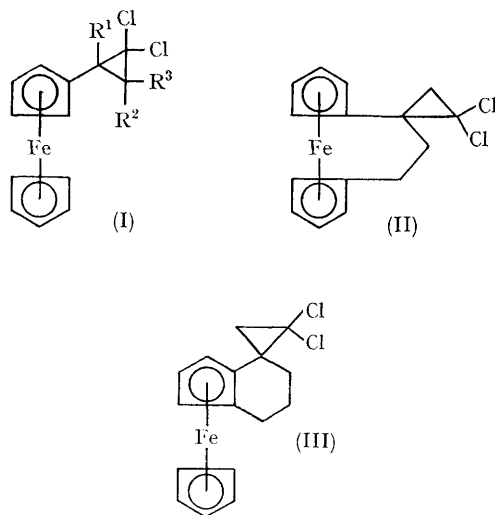
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As part of wider investigations on the reactions of electron-deficient species with metallocenes, an area which has not been explored in great detail,¹ we report the reactions of dichlorocarbene with several ferrocenylethylenes.

The ferrocenylethylenes² were prepared by addition of the ferrocenyl carbonyl compound to the appropriate Wittig reagent. The phosphorane was generated from the phosphonium salt by the use of dimethylsulphinyl anion in dimethyl sulphoxide.³ This method is superior to the other syntheses described in the literature.

The decomposition of sodium trihalogenoacetates in 1,2-dimethoxyethane,⁴ a reaction known to produce dihalogenocarbenes under neutral conditions, was carried out in the presence of the ferrocenylethylenes. The major product isolated from the dichlorocarbene reaction⁵ was the dichlorocyclopropane⁶ obtained from the addition of the carbene to the olefinic double bond.² The structures have been assigned on the basis of satisfactory elemental analysis and spectral properties. The yields and physical properties are summarised in the Table.



It is significant that the replacement of one of the β -hydrogens of the double bond by an ethoxycarbonyl group leads to a considerable decrease in

TABLE

| Olefin | m.p. | Dichlorocarbene adduct | | | Yield (%) ^c |
|--|--------------|-------------------------------|---------------------------|------------------|------------------------|
| | | Cyclopropyl ring ⁷ | i.r. (cm. ⁻¹) | C-Cl | |
| (Ia) R ¹ =R ² =R ³ =H | 80.5—82° | 1055, 1038 | 760 ^a | 760 ^a | 37 |
| (Ib) R ³ =H; R ¹ =R ² =Me | 103.5—104.5° | — | 760 ^a | 760 ^a | 20 |
| (Ic) R ² =R ³ =H; R ¹ =Me | 95.5—97° | 1075, 1040, 1030 | 760 ^a | 760 ^a | 47 |
| (Id) R ¹ =R ² =H; R ³ =CO ₂ Et | 105.5—106.5° | 1085 | 810 ^a | 810 ^a | poor |
| (Ie) R ¹ =R ² =R ³ =Me | | no reaction | | | |
| (II) | 87—88° | 1055 | 765 ^b | 765 ^b | 66 |
| (III) | 140—142° | 1045 | 790 ^b | 790 ^b | 66 |

Infrared spectra were measured in either (a) KBr or (b) Nujol.

^cYields are based on the amount of olefin used.

the yield of adduct even in the presence of a large excess of sodium trichloroacetate, while the replacement of all three hydrogens with methyl groups gave no isolable quantity of product. As yet no adducts have been obtained from difluorocarbene generated from the decomposition of sodium chlorodifluoroacetate in dimethoxyethane.

The addition of dichlorocarbene to the exocyclic methylene compounds leads to the synthesis, in good yield, of the novel spiro-compounds (II and III).

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¹ (a) For leading references see M. Rosenblum, "Chemistry of the Iron Group Metallocenes. Part 1", Interscience, 1965; (b) M. N. Appelbaum, R. W. Fish, and M. Rosenblum, *J. Org. Chem.*, 1964, **29**, 2452; (c) P. L. Pauson, M. A. Sandhu, and W. E. Watts, *J. Chem. Soc. (C)*, 1966, 251.

² Satisfactory analytical and/or mass-spectral data have been obtained for all new compounds reported.

³ E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 866.

⁴ (a) W. M. Wagner, *Proc. Chem. Soc.*, 1959, 229; (b) J. M. Birchall, G. E. Cross, and R. N. Haszeldine, *ibid.*, 1960, 81.

⁵ The nature of the minor products obtained in the reactions will be discussed at a later date.

⁶ Products were isolated by chromatography on alumina.

⁷ H. E. Simmons, E. P. Blanchard, and H. D. Hertzler, *J. Org. Chem.*, 1966, **31**, 295.