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ADDITION OF DICHLOROCARBENE TO FULVENES

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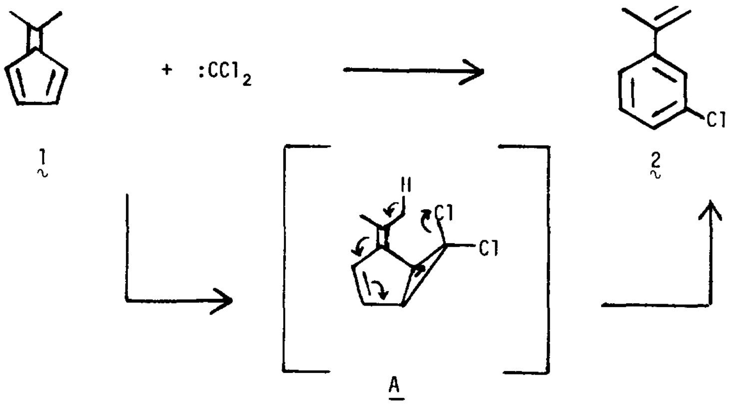
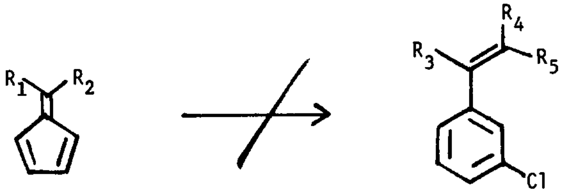
Homofulvenes[3] have been synthesized by photochemical,[4] ionic[5] and carbenoid[6] methods. None of these involved what might be considered the most direct route, *i.e.* the addition of a carbene to an endocyclic double bond of a fulvene. We have studied the addition of dichorocarbene to several fulvenes,[7] and discovered a new rearrangement (presumably of a homofulvene intermediate) which leads to *m*-chlorostyrenes.

When a suspension of sodium trichloracetate (0.08 mole) in a solution which contained 0.04 mole of 6,6-dimethylfulvene (**1**) in 20 ml of tetrachloroethylene and 5 ml of diglyme was heated under reflux for 2 - 6 hours (Procedure A), there was obtained in 25% yield[8] a product identified as *m*-chloro-*α*-methylstyrene (**2**). The structure of **2** was established by elemental analysis,[9] spectroscopic properties[10] and independent synthesis.[11] When the reaction was run at 0° in pentane using potassium *t*-butoxide and chloroform as the carbene source (Procedure B), the same result was obtained. The nmr spectrum of the crude product before distillation showed that it consisted primarily of **2** and unreacted **1**; thus **2** is produced at room temperature or below.



A likely path for the reaction is shown. The presumed intermediate A apparently loses HCl very readily. If this reaction is governed by Woodward - Hoffmann considerations,[12] it is probably the endo-chlorine which is eliminated.[13] One factor which undoubtedly facilitates the reaction is the formation of an aromatic system. It is not known at present whether the proton is lost preferentially from one of the methyl groups in A, or whether it is lost equally from both.

The reaction appears to be general, as illustrated by the following examples:



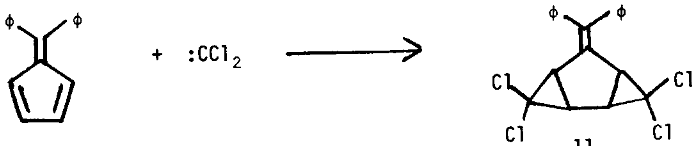
3 (R_1=Me,R_2=ϕ) ⟶ 4 (R_3=ϕ,R_4=R_5=H)[9,14]

5 (R_1=R_2=Et) ⟶ 6 (R_3=Et,R_4=H,R_5=Me)[9,15]

7 (R_1=Me,R_2=Et) ⟶ 8 (R_3=Et,R_4=R_5=H)[9,16] + 9 (R_3=R_5=Me,R_4=H)[9,17]

The structure of 4 was established by independent synthesis; the other structures are assigned on the basis of elemental analysis and spectra (ir, uv, nmr, mass).

It was of interest to examine a fulvene in which aromatization was not possible. When 6,6-diphenylfulvene (10) reacted with dichlorocarbene (Procedure B), the product was the bis-adduct 11, mp 137-138°.[18] The yield was only 13%.[8,9] Attempts to isolate the monoadduct have not yet been successful.



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This study is being continued, to explore the mechanistic details, as well as structural variations in the carbene and fulvene.

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1. National Science Foundation Undergraduate Research Fellow, summer 1969.
2. Honors College Undergraduate, Michigan State University.
3. This trivial name has been used[6] to describe fulvenes in which one endocyclic double bond has been replaced by a cyclopropane ring.
4. D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958); H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967); H. E. Zimmerman, P. Hackett, D. F. Juers and B. Schröder, *J. Am. Chem. Soc.*, **89**, 5973 (1967); H. Hart, J. D. deVrieze, R. M. Lange and A. Sheller, *Chem. Commun.*, 1650 (1968); T. Tabata and H. Hart, *Tetrahedron Lett.*, accompanying paper.
5. W. Schäfer and H. Hellmann, *Angew. Chem.*, **79**, 572 (1967); R. Criegee and H. Grüner, *ibid.*, 447 (1968).
6. M. Rey, U. A. Huber and A. S. Dreiding, *Tetrahedron Lett.*, 3583 (1968).
7. We are unaware of any previous study of this reaction. For recent reviews of fulvene chemistry, see P. Yates in "Advances in Alicyclic Chemistry", edited by H. Hart and G. J. Karabatsos, Academic Press, New York, 1968, Vol. 2, pp. 59-184 and E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968).
8. Some tars are produced, but we do not regard the yields reported here as optimal.
9. All new compounds gave elemental analyses consistent with the assigned structures.
10. Compound **2** had ir bands at 1630 (C=C), 1595, 1485 (arom) and 800, 728 cm^{-1} (*m*-subst). The uv spectrum, with $\lambda_{max}^{Pet.\ ether}$ 244 nm (log ϵ 3.99) was similar to that of *α*-methylstyrene ($\lambda_{max}^{Pet.\ ether}$ 242 nm, log ϵ 4.03). The nmr spectrum (CCl_4) had peaks at τ 7.89 (3H, d, *J* 1.5 Hz, allylic methyl), 4.93, 4.67 (1H each, m, vinyl) and aromatic multiplets at τ 2.75-2.85 (3H) and 2.57-2.69 (1H).
11. *m*-Chloroacetophenone was treated with methylmagnesium bromide, and the resulting tertiary alcohol[9] was dehydrated by reflux over $KHSO_4$. The resulting olefin was identical (ir, nmr) with the product from the carbene reaction.
12. R. Hoffmann and R. B. Woodward, *Accounts of Chemical Research*, **1**, 17 (1968).
13. For a review, see G. B. Gill, *Quart. Rev. London*, **22**, 338 (1968); especially, see pp. 352-354.
14. The yield[8] was 12% using either procedure. Compound **4** was synthesized independently from *m*-chloroacetophenone and phenylmagnesium bromide, followed by dehydration of the resulting tertiary alcohol over $KHSO_4$.
15. The yield[8] (Procedure B) was 35%; the ir spectrum was nearly identical with that of *trans*-3-phenyl-2-pentene, and very different from that of the *cis*-isomer. The nmr spectrum (CCl_4) had bands at τ 9.06 (3H, t, *J* 7.5 Hz, $-CH_2\underline{CH_3}$), 8.65 (3H, d, *J* 6.5 Hz, $=CH\underline{CH_3}$), 7.55 (2 H, q, *J* 7.5 Hz, $-\underline{CH_2}CH_3$), 3.65 (1 H, q, *J* 6.5 Hz, $=\underline{CH}CH_3$), and aromatic multiplets at τ 2.91-2.97 (3H) and 2.78-2.88 (1H).

16. The yield[8] (Procedure A) was 22%. The nmr spectrum (CCl_4) had the familiar triplet-quartet pattern for the ethyl group at τ 8.90 and 7.52 (*J* 7.5 Hz), vinyl protons at τ 4.00 and 3.82 and aromatic multiplets at τ 2.92-2.97 (3H) and 2.79-2.87 (1H).

17. The yield[8] was 14%. The ir spectrum was nearly identical with that of trans-2-phenyl-2-butene, and different from that of the *cis*-isomer. The nmr spectrum (CCl_4) had bands at τ 8.22 (3 H, d, *J* 6.5 Hz, = $CHCH_3$), 8.03 (3H, s, = $C(Ar)CH_3$), 3.23 (1H, q, *J* 6.5 Hz, =$CHCH_3$) and aromatic multiplets at τ 2.91-2.97 (3H) and 2.77-2.85 (1H).

18. The nmr spectrum ($CDCl_3$) of **11** consisted of two doublets at τ 7.62 and 7.45 (*J* 7.0 Hz) for the cyclopropyl protons and a singlet at τ 2.79 (10H, arom). The geometry is not known, but the structure with *anti*-cyclopropane rings seems most likely on steric grounds.