# Vapour Phase Generation of Dichlorocarbene; Ring Expansion of Cyclic Compounds Accompanied by Formation of Fulvene Derivatives[1]

By R. E. BUSBY, M. IQBAL, R. J. LANGSTON, J. PARRICK, and C. J. G. SHAW*
(*Department of Chemistry, Brunel University, Kingston Lane, Uxbridge, Middlesex*)

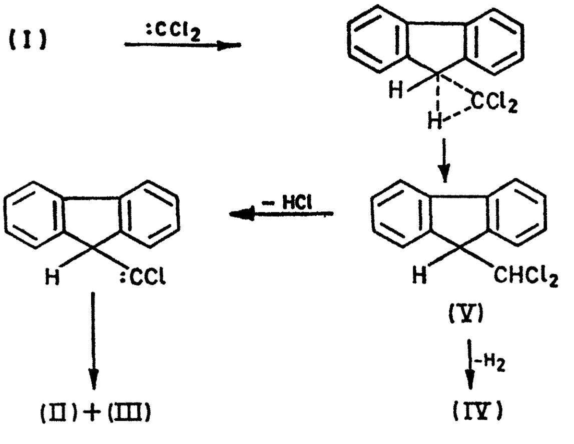
*Summary* Cyclopentadiene, indene, and fluorene react with dichlorocarbene at 550°, giving fulvene derivatives in addition to ring-expanded products.

THE reactions of five-membered cyclic olefins with dihalogenocarbenes generally produce ring-expanded products. Very recently however, D'Amore and Bergman,[2] by the addition of chloroform to a mixture of potassium t-butoxide, cyclopentadiene, and pentane at −20°, obtained 6-chlorofulvene (10%) as an air-sensitive yellow oil, in addition to a small yield (1—2%) of chlorobenzene.

We have studied the reactions of these and other cyclic compounds with dichlorocarbene generated from chloroform in the vapour phase. Using the same experimental procedure as described in previous communications,[3,4] cyclopentadiene (or dicyclopentadiene) reacted with dichlorocarbene at 550° to give chlorobenzene in 98% yield, together with a small amount (<1%) of 6,6-dichlorofulvene,† an unstable yellow oil separated by preparative g.l.c. [7 ft × 3/8 in glass column, Carbowax 20M (20%) on Diatomite C (60—80 mesh), 120°]. 6-Chlorofulvene was not formed under these conditions.

The reaction of indene with dichlorocarbene at 550° yielded 2-chloronaphthalene (72%), and 1-dichloromethyleneindene (5%),† a moderately stable yellow oil separated by preparative g.l.c. [OV17 (10%) on Diatomite C (60—80 mesh), 175°].

When fluorene (I) was treated with dichlorocarbene under these conditions, preparative g.l.c. [Apiezon L (20%) on Diatomite C (60—80 mesh), 220°] enabled 9-chlorophenanthrene (II) (19%), 9-chloromethylenefluorene[5] (III) (8%),† and 9-dichloromethylenefluorene[6] (IV) (20%)† to be separated; the latter two were both stable yellow solids. These same three products were also obtained from the pyrolysis of 9-dichloromethylfluorene (V), suggesting the intermediacy of the latter compound in the reaction of fluorene with dichlorocarbene: (V) losing either hydrogen to give (IV), or HCl to give (II) and (III).



It is clear that in passing from cyclopentadiene to indene and fluorene, the fulvene derivatives form an increasing proportion of the total yield, the latter decreasing in this

---

† Structures confirmed by elemental analysis, i.r., n.m.r., and mass spectra.

sequence. The reason for this is not entirely clear, but from a number of possible factors, two may be selected.

(a) If the reaction is under thermodynamic control the energy difference between the ring-expanded and fulvene products is likely to decrease in the substrate sequence: cyclopentadiene, indene, fluorene. Thus, the relative proportion of ring-expanded and fulvene products would approach a more even value along this sequence.

(b) For cyclopentadiene and indene, dichlorocarbene attack can occur by addition or by insertion at the allylic position, but for fluorene, only the latter type of attack may be possible, and this would presumably favour the formation of (III) and (IV) at the expense of the ring-expanded (II). This factor may be particularly relevant to the large decrease in total yield when fluorene was the substrate.

We thank the S.R.C. for financial support, and Professor C. W. Rees for helpful comments.

(*Received, July 16th,* 1971; *Com.* 1223.)

---

[1] Presented in part at the Symposium on Reactive Intermediates in Organic Chemistry, Edinburgh, April 1970.

[2] M. D'Amore and R. G. Bergman, *Chem. Comm.*, 1971, 461.

[3] F. S. Baker, R. E. Busby, M. Iqbal, J. Parrick, and C. J. G. Shaw, *Chem. and Ind.*, 1969, 1344.

[4] R. E. Busby, M. Iqbal, J. Parrick, and C. J. G. Shaw, *Chem. Comm.*, 1969, 1344.

[5] E. J. Greenhow, A. S. Harris, and E. N. White, *J. Chem. Soc.*, 1954, 3116.

[6] R. Rabinowitz and R. Marcus, *J. Amer. Chem. Soc.*, 1962, **84**, 1312; U.S.P. 3,225,106/1965.