Formation of 6-Chlorofulvene from Cyclopentadiene and Dichlorocarbene

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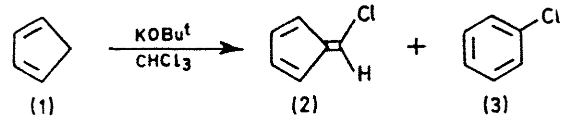
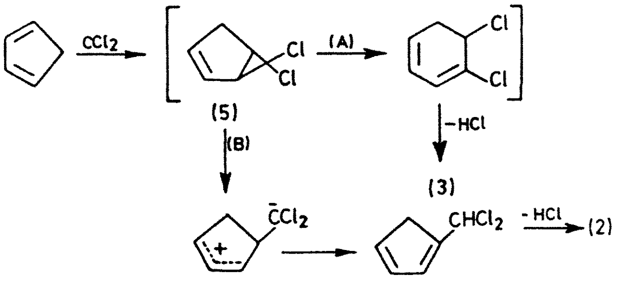
Summary Cyclopentadiene reacts with potassium t-butoxide and chloroform, giving 6-chlorofulvene as a product.

IN an attempt to prepare the diadduct of dichlorocarbene with cyclopentadiene (**1**), we discovered an unusual reaction leading to the formation of 6-chlorofulvene (**2**), which may prove useful since (a) no simple 6-halogeno-fulvene derivatives appear to have yet been reported;[1,2]† (b) such derivatives are of interest with regard to the effect of halogen on the C(5)–C(6) π bond strength; and (c) a number of attempts to add dichlorocarbene to cyclopentadiene have been reported to be either unsuccessful[3] or to yield only chlorobenzene (**3**).[4]



Dropwise addition of chloroform to a stirred mixture of potassium t-butoxide, cyclopentadiene (**1**), and pentane at −20° followed by work-up and distillation gave an orange oil which exhibited three peaks on g.l.c.; the first (4%) component has not been identified, the second (1—2%) was chlorobenzene (**3**) and the third (10%) condensed as an air-sensitive yellow oil,‡ shown to be 6-chlorofulvene (**2**) by n.m.r. [τ 3·22 (s, 1H), 3·42—3·70 (m, 3H), and 3·82—4·0 (m, 1H)], u.v. [λ_{max} 261 (log ϵ 4·4), 268 (4·2), 277 (4·2), and 371 (2·5) nm], and i.r. spectra (ν_{max} 3080, 1645, 1610, 1600, 1358, 1080, and 822 cm^{-1}).§ This was confirmed by chemical correlation; it reacted with piperidine instantaneously at room temperature, producing the known[5] 6-piperidinofulvene (**4**). Thus (**2**) is considerably more reactive than either the 6-dimethylamino-[6] or 6-tosyloxy-[7] derivatives, which apparently require several h to undergo displacement with piperidine under similar conditions.



The formation of chlorobenzene in this reaction suggests that monoadduct (**5**) (path A) may be an intermediate; peripheral bond cleavage in (**5**) could also lead to (**2**) (path B). Other possible mechanisms involve initial reaction of cyclopentadienyl-anion with dichlorocarbene or CHCl$_3$.[8] Whatever the precise path, however, this reaction may open up convenient routes to a number of new substituted fulvenes, either by reaction of cyclopentadiene with different haloforms or by nucleophilic substitution upon the very reactive chloro-derivative (**2**). We are currently examining these possibilities.

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† A complex 6-chlorofulvene with a fused lactone ring has been prepared (ref. 2a). Two reports of the synthesis of perchloro-6-methylfulvene (ref. 2b, c) were later shown to be in error (ref. 2d).

‡ Percentages given are absolute yields based on cyclopentadiene.

§ For a discussion of fulvene spectra, see ref. 1a.

We are grateful for financial support from the National Science Foundation, the National Institutes of Health, and the donors of the Petroleum Research Fund administered by the American Chemical Society.

(*Received, January 4th,* 1971; *Com.* 012.)

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