[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF OHIO UNIVERSITY]

FULVENES. II. REACTIONS WITH HALOGEN

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Introduction. Little work has been done on the reaction of simple fulvenes with the halogens, and experimental conditions are not well defined in the reports. For instance, the product of bromination of diphenylfulvene is given in one paper (1) as a colorless bromide, in another (2) as yellowish tablets, m.p. 123°, and in another (3) as dark blue-violet, m.p. 190–191°. The present paper reports a study of the halogenation behavior of some simple fulvenes, and distinguishes between the products cited above.

EXPERIMENTAL

Fulvenes. The fulvenes used in this work were prepared by the condensation of cyclopentadiene with the proper ketone in the presence of sodium methoxide in absolute ethanol. The liquid fulvenes were purified by vacuum distillation, and the solid fulvenes by recrystallization from petroleum ether.

Reaction of dimethylfulvene with bromine. The addition of bromine, directly or in dilute carbon tetrachloride solution, to dimethylfulvene in carbon tetrachloride solution gave copious fumes of HBr and a green-black resin, even at 0°, from which no well-defined product could be isolated. At $-50°$ a light yellowish oil was obtained on the addition of 4 atoms of bromine per molecule of fulvene. This product darkened and gave the usual resin on warming to room temperature.

The use of milder brominating agents, N-bromosuccinimide, pyridiniumbromide perbromide, and the bromine-dioxane complex under a variety of conditions gave the same eventual result.

Bromination of methylphenylfulvene. The same results were obtained as with dimethylfulvene.

Chlorination of diphenylfulvene; the tetrachloride. Chlorine was bubbled slowly into a dilute solution of diphenylfulvene in carbon tetrachloride at 0°. When the red fulvene color was discharged, the solvent was partly evaporated. Recrystallization of the product from petroleum ether gave light yellow plates, m.p. 150–151°.

Anal. Calc'd for $C_{18}H_{14}Cl_4$: C, 58.09; H, 3.79; Cl, 38.08.
Found: C, 58.48; H, 3.67; Cl, 36.58.

This product is believed to be the 2,3,4,5-tetrachloro addition product, since the disappearance of the typical fulvene color means a change in the fulvene part of the molecule; further, this change does not involve the *exo* double bond since the spectra indicate persistence of the diphenyleneëthylene part of the molecule.

Bromination of diphenylfulvene; addition product. A slight excess of bromine in carbon tetrachloride solution was added dropwise over the period of an hour to a carbon tetrachloride solution of 0.1 mole of diphenylfulvene at 0°. The end of the reaction was signaled by disappearance of the red fulvene color. The product which appeared as a light colored precipitate was recrystallized from benzene and petroleum ether, yielding yellow crystals, m.p. 122–123°.

Anal. Calc'd for $C_{18}H_{14}Br_4$: C, 39.26; H, 2.56; Br, 58.12.
Found: C, 38.95; H, 2.53; Br, 58.52.

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[1] This paper is taken in part from a M.S. thesis presented at Ohio University, August 1953, by Clarence Pidwerbesky. Present address Iowa State University.

This is the 2,3,4,5-tetrabromo addition product (2).

Bromination of diphenylfulvene; substitution product. The theoretical amount of bromine needed to add or substitute four atoms per molecule of fulvene was added directly in a few minutes time to a carbon tetrachloride solution of diphenylfulvene at room temperature, and no effort was made to cool the reaction. The crude product was washed with acetone and recrystallized from dioxane-water. The product was dark blue-violet crystals, m.p. 200-201°.

Anal. Calc'd for $C_{18}H_{10}Br_4$: C, 39.59; H, 1.84; Br, 58.55.
Found: C, 40.06; H, 2.16; Br, 57.22.

This is the 2,3,4,5-tetrabromo substitution product (3).

Analyses. Elementary analyses were made by the Clark Microanalytical Laboratory, Urbana, Illinois.

DISCUSSION

Since it was felt that elementary analyses alone were not sufficient to distinguish surely between substitution and addition products, ultraviolet spectra were run on the products. Diphenylfulvene has a strong absorption peak in the neighborhood of 323 mμ (4), and a smaller peak occurs at about 250 mμ. Since a similar peak occurs in the 250 mμ region for 1,1-bis-(*p*-chlorophenyl)ethylene and for 1,1-bis-(diphenyl)ethylene, the 250 mμ peak is taken to be characteristic of the diphenylethylene moiety of diphenylfulvene and its derivatives in which the exo-double bond is unaffected.

Data on the spectra are shown in Figure 1 and Table I.

The similarity in the spectra of diphenylfulvene and the bromine substituted diphenylfulvene is obvious. The similarity in the spectra of the addition products

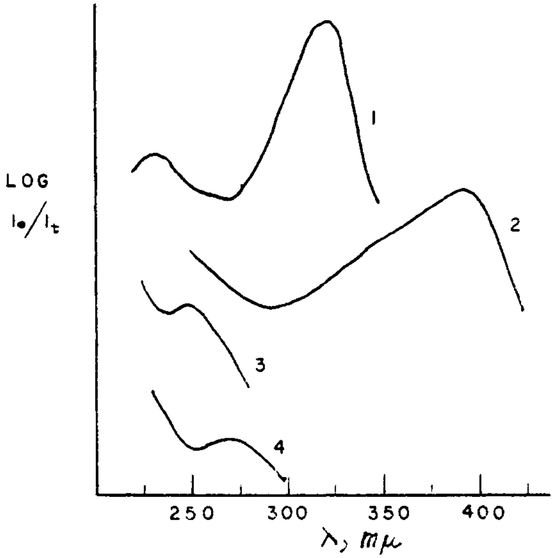

FIG. 1. ULTRAVIOLET SPECTRA OF DIPHENYLFULVENE AND THREE DERIVATIVES. The lines have been displaced vertically for clearness. Curve 1, diphenylfulvene. Curve 2, the tetrabromo substituted product. Curve 3, the tetrabromo addition product. Curve 4, the tetrachloro addition product.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA FOR DIPHENYLFULVENE AND THREE HALOGEN DERIVATIVES

	$\lambda_{max.}$, μ	$\lambda_{min.}$, μ
Diphenylfulvene	323	270
Tetrabromo substitution product	386	310
Tetrabromo addition product	249	243
Tetrachloro addition product	264	250

is clear. The great difference between the spectra of substitution and addition products is equally convincing.

Further evidence lies in the fact that the substitution reaction gave off copious fumes of HBr, while the addition reactions gave none.

The failure to obtain well-defined products from the halogenation of dimethylfulvene and ethylmethylfulvene is probably due to the great reactivity of the allylic hydrogen atoms, since the *exo* double bond is relatively inactive. This relative inertness is probably further compounded in the case of the diphenylfulvene by steric hindrance due to the phenyl groups. Dimethylfulvene has six such allylic hydrogens, and ethylmethylfulvene has five.

The assistance of Dr. Robert Kline in the interpretation of the spectral data is gratefully acknowledged.

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