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ADDITION OF DICHLOROCARBENE TO 6,6-DIPHENYLFULVENE

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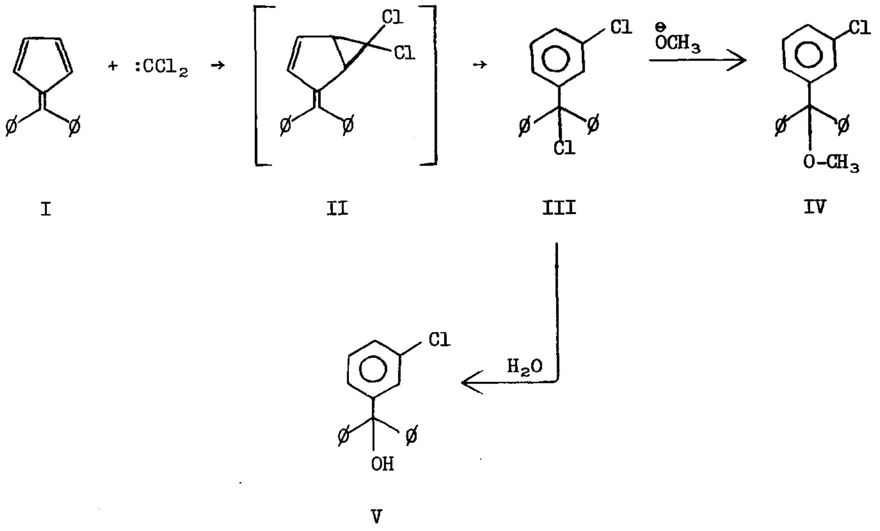
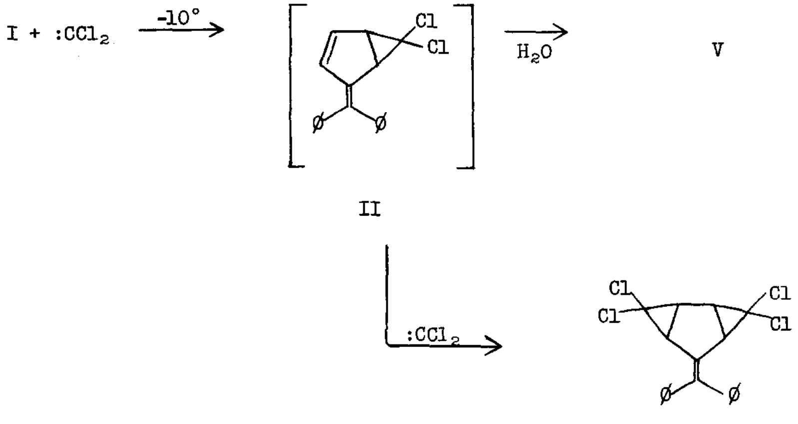
In view of the recent publication of the work of Hart and co-workers[2] on the addition of dichlorocarbene to 6,6-diphenylfulvene, we wish to report the results of our work on this system. Our work was carried out without knowledge of the work of Professor Hart's group and was initiated before publication of his findings.

The reaction of 6,6-diphenylfulvene (I) with dichlorocarbene (from ethyl trichloroacetate and sodium methoxide in dry olefin free petroleum ether at room temperature) gave in a total yield of 70% a mixture of m-chlorophenyldiphenylcarbinol (V) and methyl m-chlorophenyldiphenylcarbinyl ether (IV).



The carbinol was identified by comparison of its infrared and NMR spectra with those of the carbinol synthesized by the method of Marvel.[3] The ether was identified by its NMR spectrum (14 proton multiplet centered at 7.25 δ, 3 proton singlet at 2.95 δ), its infrared spectrum and elemental analysis.[4] We used a 5:1 ratio of carbene to fulvene.[5]

When the reaction was run at -10°C with a 5:1 carbene:fulvene ratio and the carbene generated from chloroform and potassium t-butoxide, we obtained, after washing the reaction mixture with water, the carbinol V[6] and compound VI, which we believe to have the structure shown. The yield of VI was 57%. No hydroxyl peaks were present in the reaction mixture before treatment with water and all the fulvene was consumed in the reaction.



VI

Compound VI melted at 138-139° and the mp was raised to 148-149° by recrystallization from methanol-ether. Infrared spectra of the high and low melting compounds were almost identical. The NMR spectrum of VI is essentially that reported by Hart et al for their compound 11. Elemental analysis of VI was correct for $C_{20}H_{14}Cl_4$.[7] The UV spectrum in petroleum ether showed λ max 232 mμ, ε 10,100 and λ max 275 mμ, ε 10,800. Compound VI was recovered unchanged in 98% yield from reaction with excess potassium permanganate in refluxing acetone. Reaction of VI with refluxing silver nitrate-water-dioxane gave a small amount of ketonic material, as yet unidentified.[8] We are continuing experiments with VI to attempt to prove its structure by double bond cleavage and identification of benzophenone.

The rearrangement of 6,6-dichlorobicyclo [3.1.0] hexyl systems such as found in the unisolated mono-adduct II has been previously reported.[9] The absence of any "di-adduct" VI at room temperature can be explained on the basis of the rapid rearrangement of II to the chloride III and IV at these temperatures. We believe that carbinol V results from hydrolysis of III on alumina during work-up of the reaction. At -10°C the mono-adduct survives long enough for the addition of a second mole of dichlorocarbene to occur.

When we used sodium trichloroacetate in reflexing tetrachloroethylene-diglyme mixtures to generate dichlorocarbene in the presence of 6,6-diphenylfulvene, we obtained dark colored reaction mixtures containing several products (judged from TLC of the reaction mixtures). We were not successful in isolating any pure products from this reaction.

Work on this system is being continued, using benzofulvenes as well as aryl substituted 6,6-diphenylfulvenes.

References

1. To whom inquiries should be addressed.

2. H. Hart, R. L. Holloway, C. Landry and T. Tabata, Tetrahedron Letters, 1969, (56), 4933.

3. C. S. Marvel, C. Dietz and C. M. Himel, J. Org. Chem., 7, 392 (1942).

4. Calc. for $C_{20}H_{17}ClO$: C, 77.6%; H, 5.5%; Cl, 11.7%.

   Found for IV: C, 77.14%; H, 5.48%; Cl, 11.73%.

5. Carbene:fulvene ratios are based on the amounts of carbene precursors present at the start of the reaction.

6. Identified by R_f values and comparison of its infrared spectrum with the spectrum of the independently prepared carbinol (ref. 3).

7. Calc. for $C_{20}H_{17}Cl_4$: C, 60.6%; H, 3.5%; Cl, 35.8%.

   Found for VI: C, 60.88%; H, 3.51%; Cl, 35.63%.

8. In addition to rapid uncatalyzed rearrangement of 6,6-dichlorobicyclo [3.1.0] hexyl systems (ref. 7), silver ion catalyzed rearrangements of such systems have been reported [for example, E. Bergmann, J. Org. Chem., 28, 2210 (1963).] If the postulated structure for VI is correct, two such rearrangements would lead to a substituted tropylium compound.

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