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AZAPENTATRIAFULVALENIUM IONS. I. SYNTHESIS

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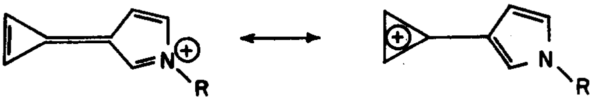
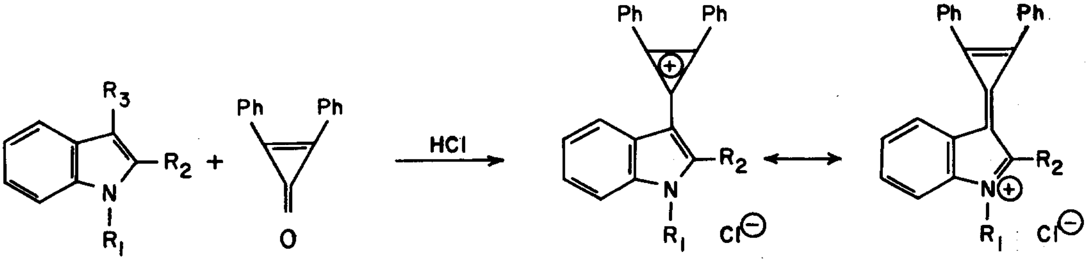
Current interest in heterofulvalenes (3,4) prompts us to report a new and convenient entry into the azapentatriafulvalenium system, I.



I

We have found that cyclopropenones condense rapidly with heterocyclic nitrogen compounds such as indole, substituted indoles and some pyrrole derivatives to produce salts of I in high yields. Typically, a dry ethanolic solution 0.1 M in each of the reactants was cooled to 0° under N_2, dry HCl gas was passed in for a few minutes and, after 3 - 12 hr. at room temperature, the reaction mixture was diluted with a large volume of ether. The crystalline yellow reaction products were isolated as the chlorides, which are somewhat photosensitive and thermally labile, and were recrystallized from $CHCl_3$, CH_3CN, or EtOH:Et_2O. (5) The azapentatriafulvalenium salts



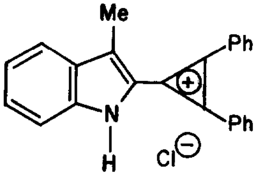
II III

Table 1

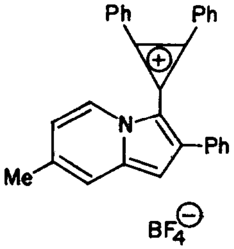
Azapentatriafulvalenium Salts III

	IIIa	IIIb	IIIc	IIId	IIIe	IIIf
Compound	$R_1=R_2=H$	$R_1=H$, $R_2=Me$	$R_1=R_2=Me$	$R_1=H$, $R_2=Ph$	$R_1=Me$, $R_2=Ph$	$R_1=OH$, $R_2=Ph$
% Yield	79	87	84	95	75	84
m.p.	146-47°	163-67°	192-93°	148-55°d	210-20°d	150-90°d
$\nu^{KBr}_{cyclopropene}$	1840	1830	1840	1820	1825	1840

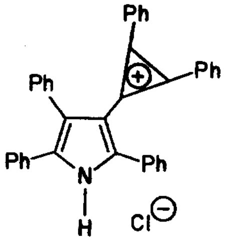
III (6) were prepared from diphenylcyclopropenone and various indoles, II, and are listed in Table 1. In addition, diphenylcyclopropenone condensed with 3-methylindole in the 2-position to yield IV (6) (64%), m.p. 180-85° dec., $\nu^{KBr}_{cyclopropene}$ 1825 cm^{-1}, with 2-phenyl-7-methylindolizine to yield V (3,6) (91%), no definite m.p., $\nu^{KBr}_{cyclopropene}$ 1840 cm^{-1}, and with 2,4,5-triphenylpyrrole to yield VI (6) (88%), m.p. 245° dec., $\nu^{KBr}_{cyclopropene}$ 1825 cm^{-1}. Cycloheptenocyclopropenone condensed with 2-phenylindole, in either ethanolic HCl or HI, to yield VII (6) (62%), which decomposes without melting between 140 - 180°, $\nu^{KBr}_{cyclopropene}$ 1850 cm^{-1}.



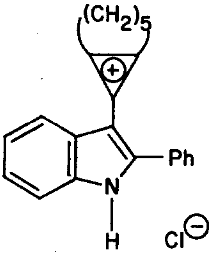
IV



V



VI

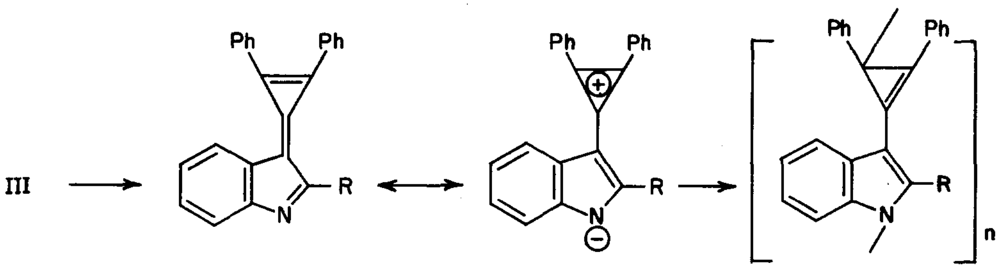


VII

The reactions described presumably involve electrophilic substitution on the most reactive position of the heterocyclic ring by the 1-hydroxy-2,3-diphenyl- or the 1-hydroxy-2,3-cycloheptenocyclopropenium cation, produced in situ from the cyclopropenone and HCl. (7) Apparently equilibrium protonation of the indole or pyrrole does not occur to a sufficient extent to suppress the reaction. (8)

All these compounds had spectral properties consistent with the proposed structures. The ir spectra all showed a medium intensity peak at 1825 - 1850 cm^{-1} characteristic of the 2,3-disubstituted cyclopropene ring.(9) The nmr and uv spectral data are discussed in the companion communication.

Attempts to produce azapentatriafulvalenes, **VIII**, by treatment of the azapentatriafulvalenium salts III with a variety of bases of low nucleophilicity (triethylamine, pyridine, carbonate, t-butoxide, etc.) in aprotic solvents produced, at best, only fleeting colors attributable to the deprotonated species **VIII**.(10) No monomeric products, **VIII**, were isolable. A polymeric material, **IX**, retaining the disubstituted cyclopropene absorption at about 1810 cm^{-1} could usually be isolated when IIIa, IIIb, or IIId was treated with a suitable base in aprotic media. Suspension of this polymer in alcoholic HCl resulted in efficient reconversion into the corresponding monomeric salt. Presumably electron release from the cyclopropenylidene ring in **VIII enhances the** nucleophilicity of the indole nitrogen, thus encouraging polymerization by an ionic mechanism to give **IX**. Depolymerization could occur by protonation of the terminal nitrogen in strongly acidic solution with reformation of the electron deficient species III.



IX

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REFERENCES

1. On leave from Hobart and William Smith Colleges, Geneva, New York, 1967 - 1968.

2. Alfred P. Sloan Foundation Fellow, 1967 - 1969.

3. T. Eicher and A. Hansen, *Tetrahedron Letters*, 4321 (1967).

4. R. Gompper and R. Weiss, *Angew. Chem.*, **80**, 277 (1968).

5. Solvents of crystallization, particularly $CHCl_3$ and CH_3CN, were tenaciously retained. HCl was also retained in the crystals and often could not be completely removed even by pumping at 10^{-6} mmHg in the presence of KOH.

6. Satisfactory elemental analyses were obtained for all compounds reported: IIIb, IIIc, IIId, and IV were analyzed as the chlorides, IIIa and V as the fluoborates, IIIe, IIIf, and VI as the perchlorates, and VII as the iodide.

7. R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson and J. Posner, *J. Am. Chem. Soc.*, **87**, 1326 (1965).

8. Since the basicity of diphenylcyclopropenone (pK = -2.6) (7) is comparable to that of indole (pK = -2.70) or 2-methylindole (pK = -4.28) (E. M. Arnett, *Prog. Phys. Org. Chem.*, **1**, 223 (1963)) and the ethanolic HCl solutions were approximately 2 *M*, most of the indole will be unprotonated in solution whereas sufficient diphenylcyclopropenone may be protonated to promote reaction.

9. A. Krebs, *Angew. Chem.*, **77**, 10 (1965).

10. Pentatriafulvalenes are generally highly colored materials (W. M. Jones and R. S. Pyron, *J. Am. Chem. Soc.*, **87**, 1608 (1965)). Azasubstitution produces a bathochromic shift in fulvenes (J. H. M. Hill, *J. Org. Chem.*, **32**, 3214 (1967)) and pentatriafulvalenes. (4)