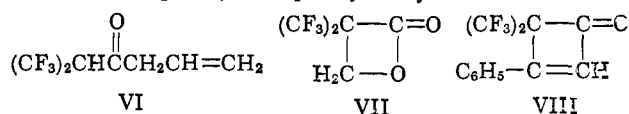


cyclobutenone VIII (b.p. 75° (1 mm.); 5.55  $\mu$  (C=O) infrared absorption) with phenylacetylene at 100°.



Satisfactory analytical data have been obtained for all compounds reported.

Details of the chemistry of bis(trifluoromethyl)-ketene and its perfluorinated relatives will be reported in future publications.

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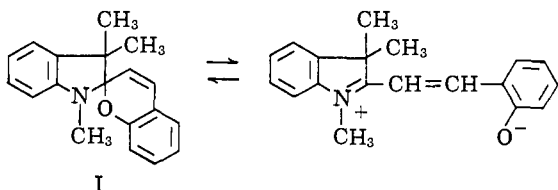
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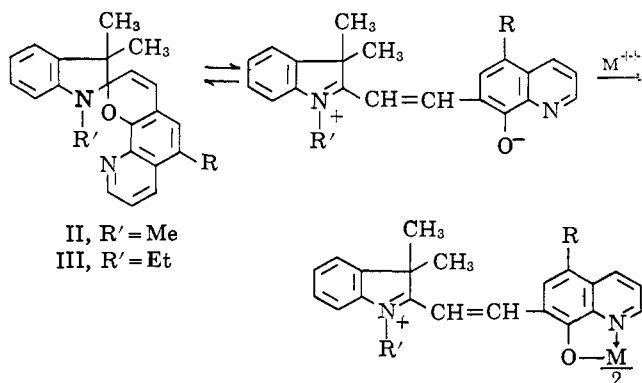
## Photochromic Chelating Agents

Sir:

Spiropyrans formed by the reaction of 1,3,3-trimethyl-2-methyleneindoline with *o*-hydroxyaldehydes are known to be often photochromic in solutions at low temperatures.<sup>1-3</sup> The simplest explanation which has been given by previous authors for the color produced by irradiating a colorless spiropyran such as I with a suitable frequency of light is the opening of the spiropyran to yield a merocyanine-type structure as indicated in the equilibrium below, although more complex mechanistic concepts may well be involved also.<sup>4</sup>



Through the use of 7-formyl-8-quinolinol or its 5-methyl derivative as the aldehyde in the reaction with 1,3,3-trimethyl-2-methyleneindoline we have obtained new spiroyrans (II; R = H, m.p. 193°; R = Me, m.p. 206°; III, R = H, m.p. 167°; R = Me, m.p. 150°; satisfactory analyses for all) that in the merocyanine form are capable of metal chelation like that of the 8-quinolinol from which they are derived (see equations below). These compounds are thus the first known photochromic chelating agents.



- (1) R. Heiligman-Rim, Y. Hirschberg, and E. Fischer, *J. Phys. Chem.*, **66**, 2465 (1962).  
 (2) E. Berman, *ibid.*, **66**, 2275 (1962).  
 (3) T. Bercovici and E. Fischer, *J. Am. Chem. Soc.*, **86**, 5687 (1964).  
 (4) R. S. Becker, *J. Phys. Chem.*, **69**, 1435 (1965).

In solutions in acetone at  $-78^\circ$  II (R = H) is colorless but turns purple on brief irradiation with a mercury arc, showing strong absorption maxima at 556 and 593  $m\mu$ ; reversion to the colorless form is achieved by the action of visible light of high intensity (flood lamp). Similar compounds such as III have similar color changes but the precise results vary considerably with the particular compound used, the solvent, and the temperature. Benzyl alcohol as solvent permits photochromism at relatively high temperatures, up to 20° with some compounds, and other polar solvents are usually satisfactory, but carbon tetrachloride solutions exhibit only an irreversible decomposition by ultraviolet light.

The critical balance between the two forms of these reagents is shown by the fact that solutions in ether or toluene are generally colorless, while those in alcohols or water may be red, purple, or blue. Recrystallization from some solvents gives a white solid, from others a highly colored one. The striking variations in solution colors are no doubt the result of shifts in the equilibrium of zwitterion and uncharged forms of the merocyanine structure,<sup>5</sup> and the variations in the color of the solid probably reflect the changes in thermal equilibrium of spiran (colorless) and merocyanine (colored) forms.<sup>6</sup>

At room temperature the addition of cupric or ferric ions to a colorless solution of II (R = H) gives a red to purple coloration in a few seconds, but at  $-78^\circ$  no color is obtained for many minutes. If the reagent solution at  $-78^\circ$  is first irradiated with ultraviolet light, then the addition of metal ion produces an immediate deepening of the color, an observation consistent with the belief that only the merocyanine form of the compound is capable of chelate formation. At least the spiran form does not have an 8-quinolinol-type chelating center.

The ability of colorless solutions of these photochromic compounds to yield highly colored metal chelates suggests a number of analytical applications.

For comparative purposes we have also prepared the analogous compounds from 5-formyl-8-quinolinol and 1,3,3-trimethyl-2-methyleneindoline; these can exist as merocyanines but not as spiroyrans and hence are highly colored in all solvents and nonphotochromic.

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(5) L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkins, and L. L. Lincoln, *J. Am. Chem. Soc.*, **87**, 2443 (1965).

(6) R. Heiligman-Rim, Y. Hirschberg, and E. Fischer, *J. Chem. Soc.*, 156 (1961).

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## Possible Evidence for a Two-Step Diels-Alder Reaction

Sir:

The question of whether the mechanism of the Diels-Alder reaction involves simultaneous or sequential formation of two new bonds has continued to receive considerable attention.<sup>1,2</sup> Although there seems to be

- (1) (a) M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **85**, 2673 (1963); **87**, 1925, 1933 (1965); (b) D. E. Van Sickle, *ibid.*, **86**, 3091