

field shifts of the ethynyl and propynyl hydrogen parallel roughly the order of decreasing carbonium ion stability for systems 3–6. This systematic variation in chemical shift reflects increasing delocalization of positive charge into ethynyl and propynyl groups as the remainder of the system becomes less effective at delocalizing the charge.

The ethynyl- and propynyldicyclopropylcarbonium ions are anomalous. System 2 should be more stable than 5 or 6 but less stable than 3,⁴ yet the downfield shifts of the ethynyl and propynyl hydrogens are smaller than in the other ions. It is tempting to suggest that these ions may have increased stability due to interaction between the cyclopropyl rings and the triple bond.

The absorptions due to hydrogens other than C≡CH or C≡C—CH₃ of the ions also are downfield from the similar absorptions of the parent alcohols. The spectra resemble those reported for the corresponding ions with methyl instead of ethynyl and propynyl groups.^{7,8} The absorptions of each propynyl ion were usually upfield from the absorptions of the corresponding ethynyl ion. This is consistent with the conclusion that C≡C—CH₃ accepts more of the positive charge than C≡CH and is another indication of the importance of charge delocalization into ethynyl and propynyl substituents.

Most of the carbonium ions were generated by addition of sulfur dioxide solutions⁹ of the corresponding alcohols¹⁰ to fluorosulfonic acid.¹¹ To prepare the tripropynyl- (1) and the phenylmethylcarbonium (6) ions, sulfur dioxide solutions of the alcohols were added to solutions of one volume of antimony pentafluoride in about three volumes of fluorosulfonic acid.¹⁴ The solutions were mixed at -78° and n.m.r. spectra were taken at -60°.

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(4) The pK_R⁺ values for the triphenylmethyl-,⁵ tricyclopropyl-,⁶ and tri-*p*-methoxyphenylcarbonium⁵ ions are -6.63, -2.31, and 0.82, respectively.

(5) N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3051 (1955).

(6) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, in press.

(7) G. A. Olah, *ibid.*, **86**, 932 (1964); D. G. Farnum, *ibid.*, **86**, 934 (1964); N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, **85**, 2991 (1963); R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959).

(8) N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *J. Am. Chem. Soc.*, **87**, 3000 (1965); C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998 (1965).

(9) Dichloromethane solutions of some of the alcohols also were added successfully to fluorosulfonic acid.

(10) The only alcohol not prepared previously, 1,1-dicyclopropyl-2-butyne-1-ol, was synthesized by addition of propynyllithium to dicyclopropyl ketone.

(11) Fluorosulfonic acid has been used as a medium for generating carbonium ions.^{8,12,13}

(12) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964); T. S. Sorensen, submitted for publication.

(13) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 2997 (1965).

(14) Fluorosulfonic acid-antimony pentafluoride solutions have been recommended for the preparation of carbonium ions.¹³

Olah for informing us in advance of publication of their work on alkynylcarbonium ions.

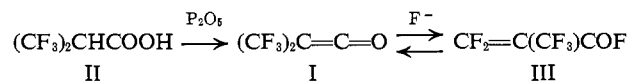
(15) Alfred P. Sloan Foundation Research Fellow.

Herman G. Richey, Jr.,¹⁵ Leonard E. Rennick
Arthur S. Kushner, Jane M. Richey, J. Christopher Philips
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania
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Bis(trifluoromethyl)ketene

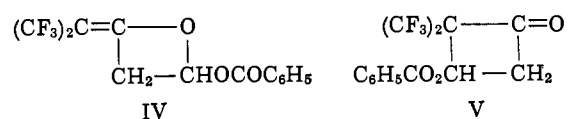
Sir:

Bis(trifluoromethyl)ketene (I), prepared in excellent yield by a simple process, is thermally very stable and has an extensive new chemistry. The synthesis¹ is accomplished by heating a mixture of hexafluoroisobutyric acid (II)² and excess phosphorus pentoxide (molar ratio *ca.* 1:2) up to 250° pot temperature at atmospheric pressure. The ketene is collected in over 90% yield in a -80° trap.



Bis(trifluoromethyl)ketene (I, b.p. 5°; 4.54 μ (C=C=O) infrared absorption) and perfluoromethacrylyl fluoride (III, b.p. 52°; 5.40 (C=O) and 5.80 μ (C=C) infrared absorptions) are in equilibrium in the vapor phase over anionic catalysts such as sodium fluoride.³

Bis(trifluoromethyl)ketene also reacts with uncharged nucleophiles. Illustrative is the formation of adducts with olefins with an ease roughly paralleling the nucleophilicity of the olefin. Cycloaddition to both the C=C and C=O groups of ketene I can occur as shown by formation of adducts IV (m.p. 99–100°; 5.72 (C=O) and 5.82 μ (C=C) infrared absorptions) and V (m.p. 45–46°; 5.50 (ketone) and 5.74 μ (ester carbonyl) infrared absorptions) with vinyl benzoate at 100°, formed in 34 and 42% yields, respectively.



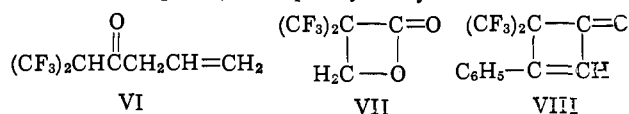
Simple alkenes also add to ketene I to form cyclobutanones and linear adducts. A condensed phase is necessary, so lower alkenes require higher pressures. A mixture, b.p. 63–70° (100 mm.), obtained from propylene at 150° and 800 atm., was separated by gas chromatography into about 70% of a cyclobutanone (5.50 μ (C=O) infrared absorption) and 30% linear ketone VI (5.72 (C=O) and 6.15 μ (C=C) infrared absorptions). Ketene I gives the β-lactone VII (b.p. 95°; 5.35 μ (C=O) infrared absorption) with trioxane using zinc chloride as catalyst in ether at 150° and the

(1) We are grateful to Dr. S. Andreades of this laboratory for helpful discussions leading to this route. Bis(trifluoromethyl)ketene and its isomer, perfluoromethacrylyl fluoride, have also been prepared independently by less attractive routes by I. L. Knunyants *et al.*, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1265, 1432, (1963).

(2) I. L. Knunyants, L. German, and B. Dyatkin, *Bull. Acad. Sci. USSR Div. Chem. Sci.*, 1391 (1956).

(3) Anionic catalysis of fluoroolefin reactions is well documented. See, for example, W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

cyclobutenone VIII (b.p. 75° (1 mm.); 5.55 μ (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.

D. C. England, C. G. Krespan

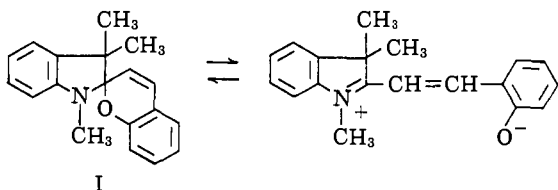
Contribution No. 1058, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Co.
Wilmington, Delaware

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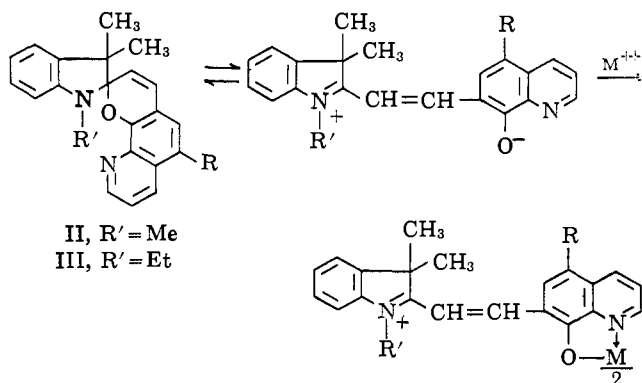
Photochromic Chelating Agents

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.¹⁻³ The simplest explanation which has been given by previous authors for the color produced by irradiating a colorless spirocyclic compound such as I with a suitable frequency of light is the opening of the spirocyclic ring to yield a merocyanine-type structure as indicated in the equilibrium below, although more complex mechanistic concepts may well be involved also.⁴



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 spirocyclic compounds (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.



II, R' = Me
III, R' = Et

- (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° 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,⁵ and the variations in the color of the solid probably reflect the changes in thermal equilibrium of spiran (colorless) and merocyanine (colored) forms.⁶

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° no color is obtained for many minutes. If the reagent solution at -78° 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 spirocyclic compounds 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).

J. P. Phillips, A. Mueller, F. Przystal

Department of Chemistry, University of Louisville
Louisville, Kentucky

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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.^{1,2} 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