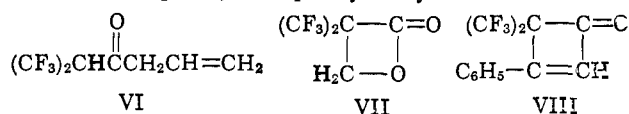


cyclobutenone VIII (b.p. 75° (1 mm.); 5.55  $\mu$  (C=O) infrared absorption) with phenylacetylene at 100°.



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.

D. C. England, C. G. Krespan

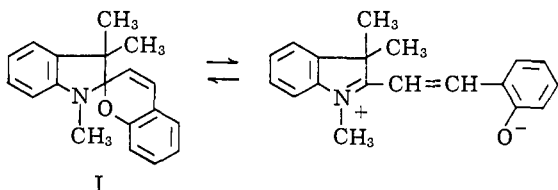
Contribution No. 1058, Central Research Department  
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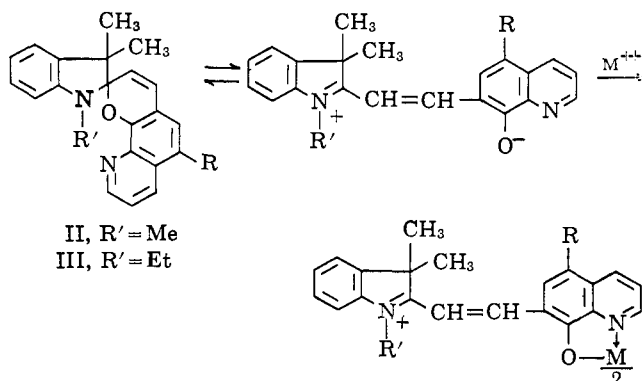
## Photochromic Chelating Agents

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 spiropyrans (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  $-78^\circ$  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 spiropyran 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 spiropyrans and hence are highly colored in all solvents and nonphotochromic.

**Acknowledgment.** This work was supported in part by Grant No. CA-07403 from the Public Health Service.

- (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

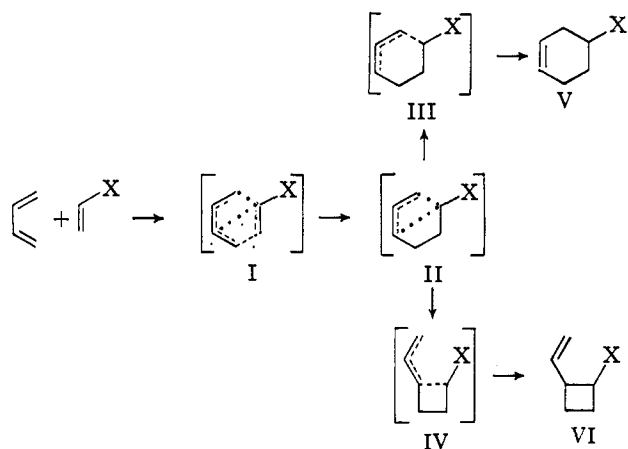
- (1) (a) M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **85**, 2673 (1963); **87**, 1925, 1933 (1965); (b) D. E. Van Sickle, *ibid.*, **86**, 3091

Table I. Reaction of Butadiene with  $\alpha$ -Acetoxyacrylonitrile

Temp., °C.		Cyclohexane	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> CN	CH <sub>3</sub> NO <sub>2</sub>
126.6 ± 0.3	$k \times 10^6$ l. mole <sup>-1</sup> sec. <sup>-1</sup>	1.7	2.2	3.5	...
	Rel. $k$	1.0	1.3	2.1	...
	VIII:IX	82:18	91:9	91:9	90:10
152.2 ± 0.3	$k \times 10^6$ l. mole <sup>-1</sup> sec. <sup>-1</sup>	6.6	10	11	17
	Rel. $k$	1.0	1.5	1.7	2.6
	VIII:IX	81:19	85:15	91:9	91:9
174.9 ± 0.3	$k \times 10^6$ l. mole <sup>-1</sup> sec. <sup>-1</sup>	23	37	40	72
	Rel. $k$	1.0	1.6	1.7	3.1
	VIII:IX	77:23	80:20	85:15	88:12
189.9 ± 0.3	$k \times 10^6$ l. mole <sup>-1</sup> sec. <sup>-1</sup>	55	96	...	180
	Rel. $k$	1.0	1.7	...	3.3
	VIII:IX	83:17	82:18	...	86:14

some agreement<sup>1a,1b,3</sup> that at the transition state of certain systems formation of one bond may be more complete than formation of the second bond, as suggested by Woodward and Katz,<sup>4</sup> there is disagreement as to whether clear-cut evidence exists for an intermediate and a subsequent, lower-energy barrier prior to product formation<sup>2,3</sup> (*i.e.*, a two-step mechanism).

The best evidence for a two-step Diels-Alder mechanism involving a true intermediate would be isolation or unquestionable detection of the intermediate. In lieu of this and of establishment of, *e.g.*, an unambiguous relationship<sup>3</sup> between the stereospecific Cope rearrangements of Diels-Alder adducts<sup>4,5</sup> and the retrograde Diels-Alder reaction, it would appear that the next best evidence would be that for a diene-dienophile reaction (a) involving a common transition state such as I<sup>4,6</sup> and (b) leading simultaneously to the normal Diels-Alder adduct V and the vinylcyclobutane



VI.<sup>7</sup> The addition of tetracyanoethylene to 1,1-dimethylbutadiene forms the corresponding cyclohexene and vinylcyclobutane in about 30:70 ratio in cyclohexane,<sup>8</sup> thus satisfying condition (b), but the marked

(1964); (c) S. Seltzer, *Tetrahedron Letters*, **11**, 457 (1962); *J. Am. Chem. Soc.*, **85**, 1360 (1963); (d) J. B. Lambert and J. D. Roberts, *Tetrahedron Letters*, **20**, 1457 (1965); (e) C. Ganter, U. Scheidegger, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 2771 (1965).

(2) For an excellent recent review of the Diels-Alder reaction see R. Huisgen, R. Grashy, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishing Co., New York, N. Y., 1964, pp. 878-929.

(3) See, for example, discussion by J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).

(4) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

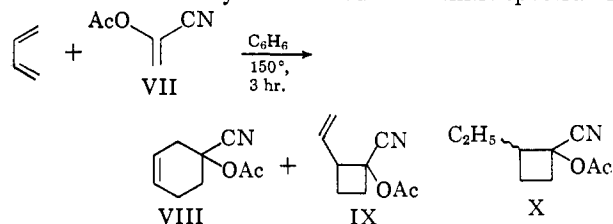
(5) R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2198 (1961).

(6) In formulas I-IV, following the suggestion of Woodward and Katz,<sup>4</sup> solid lines represent  $\sigma$  bonds, broken lines symbolize partial bonds, and dotted lines designate "secondary attractive forces," semantics notwithstanding.<sup>3</sup>

(7) See ref. 2, p. 927.

dependence of the course of the reaction on solvent (polar media favor the cyclobutane) suggests that a common transition state is improbable<sup>8</sup> and condition (a) is thus unsatisfied. We now present evidence for a reaction which we suggest might fulfill both of these conditions.

Butadiene adds to 1-cyanovinyl acetate ( $\alpha$ -acetoxyacrylonitrile, VII) in benzene at 150° after 3 hr. to form the cyclohexene VIII, b.p. 109.5-110° (5 mm.), and the vinylcyclobutane IX, b.p. 98.6-99° (5 mm.), in a ratio of 7:1 and 72% over-all yield based on unrecovered VII (58% conversion). The structure of IX was confirmed by its infrared and n.m.r. spectra and



by hydrogenation (platinum-ethanol) to the corresponding ethyl derivative (X) followed by hydrolysis to 2-ethylcyclobutanone (three protons near  $\tau$  7.0,  $\alpha$ -to the carbonyl; semicarbazone m.p. 154-155°, also having three protons near  $\tau$  7.0). Two isomers of IX were formed (two acetate methyl groups *ca.* 1 c.p.s. apart at  $\tau$  7.29, ratio *ca.* 55:45), but these could not be separated by g.l.p.c. The ethyl derivatives (X), however, were separable (b.p. 85 and 91° at 4 mm.); each isomer was converted to the semicarbazone of 2-ethylcyclobutanone, confirming the position of substitution of the ethyl groups of X and hence the vinyl groups of the two isomers of IX.<sup>9</sup>

A preliminary study of the effect of solvents and of temperature on the relative rates and the isomer distribution was carried out by heating samples 1 *M* in butadiene, 0.1 *M* in VII, and 0.1 *M* in *p*-BrC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> (internal standard) in various solvents for an appropriate time.<sup>10</sup> Approximate bimolecular rate constants for the formation of (VIII + IX) were calculated assuming pseudo-first-order kinetics for VII. Re-

(8) C. A. Stewart, Jr., *J. Am. Chem. Soc.*, **84**, 117 (1962).

(9) Satisfactory microanalyses and spectral data were obtained for all compounds. Infrared interpretations were by Dr. W. J. Potts and R. A. Nyquist, and n.m.r. interpretations by Dr. J. P. Heeschen of the Dow Chemical Physics Research Laboratory.

(10) One hour at 189°, 3 hr. at 175°, 8 hr. at 152°, and 64 hr. at 126°. Each series of determinations at the same temperature was made simultaneously to minimize relative errors. Duplicates were run in most cases. Analyses were made by g.l.p.c.; both the initial and final solutions were analyzed for all volatile reactants and products. The amount of VII lost to decomposition was estimated from a material balance on this component.

actions in nitromethane were accompanied by considerable decomposition of VII to undetermined, nonvolatile products, but yields were high (80–95%) in the other solvents. The decomposition reaction was assumed to be first order in VII. The results are summarized in Table I.

Both of the products VIII and IX were reasonably stable to heating to 200° for 8–12 hr.

The data of Table I show only a threefold effect on the reaction rate over the series of solvents studied, well within the range of solvent effects observed in other Diels–Alder reactions.<sup>2</sup> Moreover, the relative rates do not vary appreciably over the temperature range (65°), nor is there a large effect of either solvent or temperature on the isomer ratios.

The above data may, of course, be interpreted as pertaining to two separate (one-step) reactions possessing different transition states<sup>8</sup> but having extraordinarily similar influences of solvents on their activation parameters. However, we would like to suggest the alternate explanation that the reaction is proceeding through a single transition state such as I to an intermediate (*cf.* II).<sup>11</sup> This intermediate may then continue through either of two subsequent, lower energy transitions similar to III and IV to the two observed products.

Additional support for the two-step intermediate II may be found in the structure of the vinylcyclobutanes (IX): only the 2-vinyl isomers were detected under conditions (g.l.p.c.) which should have shown the presence of >1% yield of either of the 3-vinyl isomers (assuming no unusual instability of the latter). The products (IX) are those which would be predicted by the accepted<sup>12–14</sup> two-step mechanism for a (cyclobutane-forming) thermal cycloaddition reaction.

Examination of the activation parameters for this reaction may disclose more subtle, but possibly more meaningful differences in the two reaction paths. The question of whether such differences would support the contention that dual, one-step mechanisms<sup>8</sup> are involved in the formation of VIII and IX, or merely reflect variations in the second, product-determining step of the two-step mechanism, which we favor, would appear to be subject to debate. Unfortunately, the present data are not suitable for comparison, but more complete studies of this aspect are in progress. Stereochemical examinations suggested by previous observations with other systems<sup>4,5,13</sup> are also under consideration.

In summary, it seems possible that study of this simple and yet versatile system may offer a fresh approach to the intricacies of the Diels–Alder and related reactions.

**Acknowledgment.** Numerous stimulating discussions with Professors Martin Stiles and J. C. Martin are greatly appreciated.

(11) The necessary involvement of the "secondary attractive forces" in retaining stereochemistry is assumed by analogy with earlier discussions.<sup>4</sup>

(12) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962).

(13) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).

(14) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

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## The Photodecomposition of Pivaloyl Azide

Sir:

In the Curtius rearrangement<sup>1</sup> carbonyl azides of the type R–CO–N<sub>3</sub> (R = alkyl or aryl) are converted to isocyanates (R–NCO) when decomposed by heat<sup>1</sup> or light.<sup>2</sup> Alkoxy carbonyl azides (RO–CO–N<sub>3</sub>) when decomposed by light<sup>3</sup> or heat<sup>4,5</sup> give carbalkoxy nitrenes (RO–CO–N) which insert into C–H bonds and add to double bonds in intermolecular reactions.

Carbonyl nitrenes (R–CO–N) have often been postulated as intermediates in the Curtius rearrangement,<sup>6–8</sup> and the lack of unrearranged intermolecular reaction products has been explained by assuming a very high rate of rearrangement to isocyanate.<sup>9</sup> This seemed to be in accord with the observation, first made by ApSimon and Edwards,<sup>10</sup> of the formation of intramolecular C–H insertion products in photolyses of carbonyl azides containing a C–H function in positions sterically favorable for cyclization. Furthermore, photolysis of benzazide in dimethyl sulfoxide<sup>11</sup> gave an addition product of C<sub>6</sub>H<sub>5</sub>–CO–N to the solvent in a reaction interpreted as the capture of the nitrene intermediate of the Curtius rearrangement. Also, ethyl azidoformate, shown to be a source of carbethoxy nitrene,<sup>3</sup> was observed to undergo some Curtius rearrangement in methanol solution.<sup>12</sup> The hypothesis of a common nitrene intermediate for rearrangement as well as for C–H insertion leaves unexplained the absence of intramolecular C–H insertion products in the thermal decomposition of ApSimon's compounds.<sup>10,13</sup>

In this communication we wish to show: (1) that in the photolysis (but not in the thermolysis) of pivaloyl azide (*t*-Bu–CO–N<sub>3</sub>, I) an intermediate capable of selective intermolecular reactions is formed; (2) that this intermediate possesses properties similar to those of carbethoxy nitrene, and (3) that the intermediate is not involved in the (thermal) Curtius rearrangement of pivaloyl azide.

We have studied the decomposition of pivaloyl azide (I) in hydrocarbon solvents. Thermolysis in cyclohexene and 2-methylbutane is rapid above room temperature and gives a virtually quantitative yield of

(1) For a detailed discussion of the Curtius rearrangement see P. A. S. Smith in P. DeMayo, "Molecular Rearrangements," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, p. 528 ff.

(2) L. Horner, E. Spietschka, and A. Gross, *Ann.*, **573**, 17 (1951).

(3) W. Lwowski and T. W. Mattingly, *Tetrahedron Letters*, 277 (1962); *J. Am. Chem. Soc.*, **87**, 1947 (1965); W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *ibid.*, **85**, 1200 (1963); W. Lwowski and T. J. Maricich, *ibid.*, **86**, 3164 (1964); **87**, 3630 (1965).

(4) R. J. Cotter and W. E. Beach, *J. Org. Chem.*, **29**, 751 (1964).

(5) M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Letters*, 2945 (1964).

(6) J. Stieglitz, *Am. Chem. J.*, **18**, 751 (1896).

(7) K. R. Brower, *J. Am. Chem. Soc.*, **83**, 4370 (1961).

(8) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 502; J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p. 656.

(9) *Cf.* R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(10) J. W. ApSimon and O. E. Edwards, *Proc. Chem. Soc.*, 461 (1961); *Can. J. Chem.*, **27**, 1930 (1963).

(11) L. Horner and A. Christmann, *Ber.*, **96**, 388 (1963).

(12) W. Lwowski, R. DeMauriac, T. W. Mattingly, Jr., and E. Scheiffle, *Tetrahedron Letters*, 3285 (1964).

(13) Prof. Huisgen kindly informed us in Oct. 1964 of positive trapping experiments. The photolyses of acetyl azide in benzonitrile and phenylacetylene gave 2-methyl-5-phenyl-1,3,4-oxadiazole or -oxazole, respectively. In thermolysis experiments with acyl azides no evidence for nitrene intermediates was obtained.