

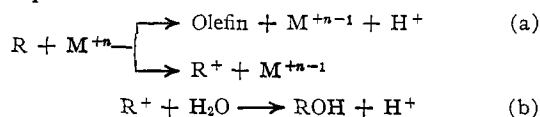
COMMUNICATIONS TO THE EDITOR

THE OXIDATION OF FREE RADICALS BY METAL IONS

Sir:

The effects of metal ions on free radicals have been delineated as reactions involving the modification of free radical activity¹ and oxidation-reduction.² Ligand transfer³ as a mode of an oxidation-reduction reaction has been described recently.^{2,4} We wish to report here some oxidation-reduction reactions which occur by electron transfer rather than ligand transfer.

The electron transfer mechanism for the oxidation of free radicals by metal ions is described by the equations



The distribution of the oxidation products between R^+ (solvolytic products) and olefin is dependent on the structure of the alkyl radical. Table I shows the oxidation of the simple alkyl radicals by cupric ion in aqueous solution to olefinic and alcoholic products.

TABLE I

PRODUCTS FROM THE OXIDATION OF ALKYL RADICALS BY CUPRIC SULFATE

Radical	Cupric ion, M	Olefin, %	Alcohol, %	ΔH_f^a (kcal./mole)
Methyl ^b	0.05	0	81	262
Ethyl ^b	.05	48	39	224
	.50	59	28	
<i>sec</i> -Butyl ^c	.05	19 ^d	65	180
<i>tert</i> -Butyl ^e	.05	9	82	166
Allylic ^e	.05	0	85	218

^a Heat of formation of the gaseous ion. ^b From *tert*-alkyl hydroperoxide and Ti^{+3} . ^c From photolysis of methyl ketone. ^d 24% *cis* and 76% *trans*-butene-2. ^e From *tert*-butoxy and butadiene.

In general there is a correlation between the heat of formation of the gaseous ion⁵ and the ease of oxidation of the radical to alcohol by cupric ion.⁶ The exception is the allyl radical whose anomaly is probably attributable to the different solvation requirements of the resonance stabilized carbo-

(1) J. Kochi and F. Rust, *J. Am. Chem. Soc.*, **83**, 2017 (1961).

(2) J. Kochi, *ibid.*, **78**, 4815 (1956); **79**, 2942 (1957). J. Kumamoto, H. De La Mare and F. Rust, *ibid.*, **82**, 1935 (1960).

(3) H. Taube, "Advances in Inorganic Chemistry and Radiochemistry," Editors, H. Emeleus and A. Sharpe, Academic Press, New York, N. Y., 1959, Chap. I.

(4) C. Bamford, A. Jenkins and R. Johnston, *Proc. Royal Soc.*, **A239**, 214 (1957).

(5) F. Field and J. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

(6) The implication is that the olefin is formed from the radical by a synchronous process involving electron transfer and loss of the β -proton.

nium ion compared to its saturated counterparts. Although it is possible in some cases that the solvolytic product arises *via* a ligand transfer process at present, we prefer the alternative two-step mechanism involving electron transfer and then solvation of the carbonium ion, especially with the allylic systems.

The oxidation of alkyl radicals by cupric ions is demonstrated by the preparative reactions. 1-Methyl cyclohexyl hydroperoxide reacts with ferrous sulfate⁷ in the presence of cupric sulfate to form 6-hepten-2-one in 95% yield. Tetrahydropyranyl-2-hydroperoxide reacts⁸ under similar conditions to form 3-buten-1-ol in approximately 20% yield. The cyclohexanone-hydrogen peroxide adduct⁹ is oxidized by the ferrous-cupric couple to 5-hexenoic acid in 76% yield.

Acyl radicals are quantitatively oxidized to carboxylic acid derivatives.¹⁰ Biacetyl is photolyzed in the presence of 0.05 M cupric ions to produce acetic acid quantitatively. In methanol methyl acetate is the exclusive product. Acetone similarly is oxidized to acetic acid and methanol. In neither case is carbon monoxide a product.

(7) E. Hawkins and D. Young, *J. Chem. Soc.*, 2804 (1950).

(8) N. Milas, R. Peeler and O. Mageli, *J. Am. Chem. Soc.*, **76**, 2322 (1954).

(9) M. Kharasch and G. Sosnovsky, *J. Org. Chem.*, **23**, 1362 (1958).

(10) D. Coffman, R. Cramer and W. Mochel, *J. Am. Chem. Soc.*, **80**, 2883 (1958).

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ON A TRANSANNULAR PHOTODESMOTIC TRANSITION¹

Sir:

We wish to report the use of solvent effects to identify a transannular electronic transition involving a carbon-carbon double bond and a carbonyl group. We further suggest that such transitions, which lead to a bond in the excited state between atoms not bonded in the ground state, be called *photodesmotic* (from the Greek, $\phi\omega\tau\omicron\delta\epsilon\sigma\mu\omicron\varsigma$, link caused by light).² In many cases, photodesmotic transitions will be intramolecular charge-transfer transitions,³ but exceptions will exist when the two groups are equivalent.⁴ The present case, *trans*-5-cyclodecenone, is typical of those in which the transition in question is located close to 2000 Å., and therefore near the absorption positions

(1) This communication may be considered as "Effect of Solvent on Spectra. VIII."

(2) We thank Professor H. M. Howe, Classics Department, for his advice in this matter.

(3) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959).

(4) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan *J. Am. Chem. Soc.*, **82**, 5450 (1960).

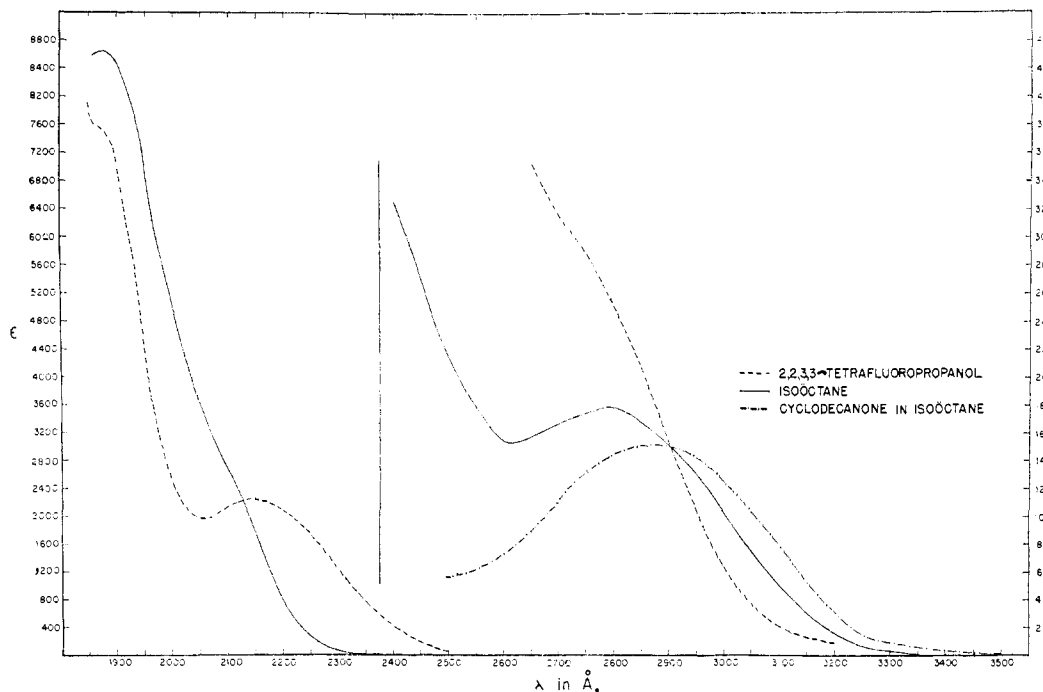


Fig. 1.—Absorption curves for *trans*-5-cyclodecenone.

for other electronic transitions in the molecule. Only rigorous purification of the ketone and the availability of the highly polar solvent 2,2,3,3-tetrafluoropropanol (TFP)⁵ permitted definite identification of the photodesmotic transition.

trans-5-Cyclodecenone was synthesized by chromic acid oxidation of *trans*-5-cyclodecenol⁷ and purified by preparative gas phase chromatography (conditioned 10% 1,2,3-tris-(2-cyanoethoxy)-propane on Chromosorb, 2.4 m., 170°), then four recrystallizations from pentane at -78°. The purity of the *trans*-ketone was judged to be 98-99% by gas phase chromatographic analysis on a Golay column.⁸ Its boiling point was 74-75° (0.9 mm.), n_D^{25} 1.4982, and showed infrared absorption at 3.55 μ , 5.92 μ and 10.14 μ (*trans*-double bond) with no band at 14.2 μ (*cis*-double bond) for the pure liquid. *Anal.* calcd. for C₁₀H₁₆O: C, 78.89; H, 10.59. Found: C, 78.80; H, 10.59.

The choice of solvents for the spectroscopic measurements was dictated by the desire for a wide range of polarity, with *Z*-values being used as the criterion.⁹ Absorption curves were measured in iso-octane (*Z* 60.1), acetonitrile (*Z* 71.3), methanol (*Z* 83.6), and tetrafluoropropanol (*Z* 96.3).⁶ The maxima are listed in Table I, while the curves for iso-octane and TFP are reproduced in Figure

(5) We are grateful to Dr. A. C. Haven, Jr., of the Organic Chemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., for a generous supply of the fluoro alcohol. The purification procedure of Pih-kuei C. Huang is described in a forthcoming publication.⁴

(6) E. M. Kosower and G. S. Wu, *ibid.*, **83**, in press (1961).

(7) W. D. Closson and H. L. Goering, unpublished work.

(8) If an impurity were responsible for the absorption assigned to the photodesmotic transition, the ϵ required would have to exceed 100,000.

(9) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

1 along with the low intensity absorption curve for cyclodecanone⁶ in iso-octane.

The low-intensity long wave length band is readily assignable as an $n \rightarrow \pi^*$ -transition on the basis of its low intensity¹⁰ and the shift of the maximum to shorter wave lengths with increasing solvent polarity.¹¹ It may be noted that the

TABLE I

ABSORPTION MAXIMA FOR *Trans*-5-CYCLODECENONE SOLVENT

Iso-octane		Acetonitrile	
λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
2790	18	2765	20
1880	8700		
Methanol		TFP	
2722	22	^a	
		2145	2300
		(1880) ^b	7500

^a Occulted by photodesmotic band. ^b For comparison of intensity; maximum not observed.

absorption intensity is not unusual for a cyclo-alkanone (*cis*-5-cyclodecenone, iso-octane, λ_{max} 2899 (15), cyclodecanone,⁶ λ_{max} 2883 (15)) in contrast to the examples treated by Labhart and Wagnière³ and summarized by Cookson and Wariyar.¹² More importantly, the maximum for the $n \rightarrow \pi^*$ transition is shifted to shorter wave lengths in comparison with the *cis*-ketone and the saturated ketone, the shift being approximately 3 kcal./mole, or 0.13 ev. Although the theory³ suggests that

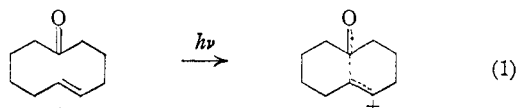
(10) J. W. Sidman, *Chem. Revs.*, **58**, 689 (1958).

(11) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958).

(12) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

the shift should be to longer wave lengths, it seems likely that the repulsion between the filled π -orbital of the double bond and the π^* -electron of the $n \rightarrow \pi^*$ -excited state is greater than the lowering (of E_s , cf. ref. 3) achieved by interaction of the π^* -electron with the π^* -orbital of the double bond. A shift which may be similar has been observed for bicyclohepten-7-one.¹³

It may be noted in the figure that a shoulder on the high intensity absorption in isoöctane shifts to longer wave lengths in the more polar solvent, TFP, and, in fact, appears as a maximum.¹⁴ The solvent effect on the maximum demonstrates that the excited state is considerably more polar than the ground state since the absorption band present at ca. 2050 Å. in isoöctane shifts to 2145 Å. in TFP. This absorption region is thus identifiable as that arising from the photodesmotic transition (eq. 1).



The shorter wave length absorption is due to a combination of an $n \rightarrow \sigma^*$ -transition of the carbonyl¹⁵ and the $\pi \rightarrow \pi^*$ -transition of the double bond.¹⁶ The decrease in intensity in this region for the change in solvent from isoöctane to TFP (at 1880 Å., $\Delta\epsilon$ is 1200) corresponds quite closely to the change in intensity observed for acetone at 1900 Å. with a solvent change from isoöctane to water (Z 94.6).¹¹ It has been reported that cyclohexene has a maximum at 1833 Å. (ϵ 7500) in hexane,¹⁷ while there is relatively little difference between the maximal positions for *cis*- and *trans*-2-butenes.¹⁸

A convincing demonstration of a photodesmotic transition using solvent effects was given recently by Leonard, Milligan, and Brown¹⁹ for 1-thiacyclooctan-5-one. It is worthy of note that the adsorption intensity observed for the PD transition of the thia ketone in cyclohexane (2500) is very close to that for the PD transition of the *trans*-cyclo-decane in isoöctane (2300).

(13) C. J. Norton, Ph.D. Dissertation, Harvard University, quoted in ref. 4.

(14) Acetonitrile and methanol exhibit intermediate behavior (as expected) which will be illustrated in a full paper.

(15) Certain observations by W. Simpson have suggested that this transition might actually be $n_2 \rightarrow \pi^*$; M. Kasha, personal communication.

(16) Both of these transitions would be changed in energy according to the theory of ref. 3; since our experiments cannot evaluate this possibility, we refer to them as transitions in the isolated groups.

(17) D. W. Turner, *J. Chem. Soc.*, 30 (1959).

(18) J. T. Gary and L. W. Pickett, *J. Chem. Phys.*, **22**, 599 (1954).

(19) N. J. Leonard, T. W. Milligan and T. L. Brown, *J. Am. Chem. Soc.*, **82**, 4075 (1960).

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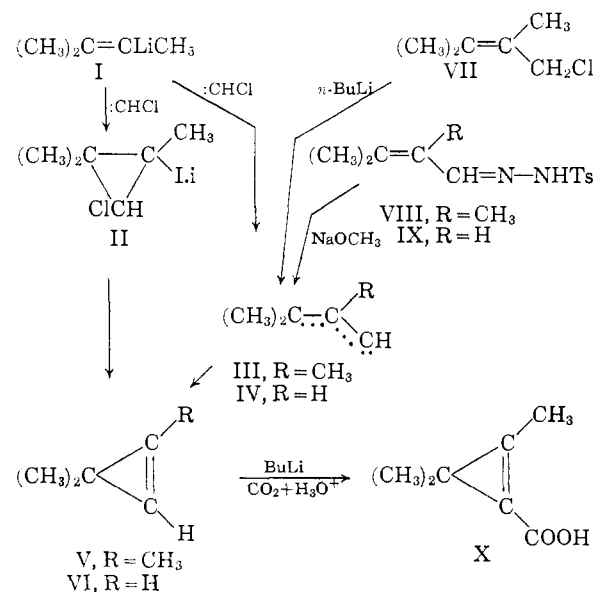
ALKENYL CARBENES AS PRECURSORS OF CYCLOPROPENES

Sir:

Recently we reported a novel synthesis of cyclopropenes based on the reaction of 1,2-dimethyl-

propenyllithium (I) with methylene chloride.¹ Two mechanisms were advanced, both capable of explaining the formation of 1,3,3-trimethylcyclopropene (V) under these conditions: chlorocarbene, generated from methylene chloride and alkenyllithium compound I, was postulated to add to the π -electrons of I to form the hypothetical intermediate II, or to react with the non-bonding electrons of the incipient carbanion of I to yield alkenylcarbene III. Intermediate II could give the observed cyclopropene V by β -elimination of lithium chloride, while alkenylcarbene III can be visualized to cyclize to the same product by rotation of the *gem*-dimethyl group through 90°. The concept that alkenylcarbenes might serve as precursors of cyclopropenes is an intriguing one and led to further investigations.

Attempting the formation of an alkenylcarbene by a more direct route, *n*-butyllithium was added to a solution of 1-chloro-2,3-dimethyl-2-butene (VII) in tetrahydrofuran at -15°. Carbonation and acidification of the reaction mixture yielded 16% of 2,3,3-trimethylcyclopropene-1-carboxylic acid (X), identical in all properties with a previously prepared sample.¹ This result is difficult to explain without invoking the alkenylcarbene intermediate III, generated by α -elimination of hydrogen chloride from VII.² Cyclization of the carbene



leads to V which is converted to 2,3,3-trimethylcyclopropenyllithium on reaction with *n*-butyllithium.³ Carboxylation of the latter gives X.

Another route which appeared to be promising for the preparation of alkenylcarbenes is the base catalyzed decomposition of tosylhydrazones of

(1) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 1003 (1961).

(2) For recent examples of α -elimination on alkyl halides under the influence of organo-alkali compounds see: W. Kirmse and W. v. E. Doering, *Tetrahedron*, **11**, 266 (1960); G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **24**, 26 (1960); L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **82**, 5758 (1960); **83**, 492 (1961); **83**, 500 (1961).

(3) About the acidity of the olefinic hydrogens in cyclopropenes see: K. B. Wiberg, R. K. Barnes and J. Albin, *ibid.*, **79**, 4994 (1957); and ref. 1.