mμ, log $\epsilon \sim 3.1$) absorbed one equivalent of hydrogen (Pd/C, ethanol) to give norbornane (92%) plus three unidentified compounds (8%).[11] The formation of norbornane greatly restricts the possible structures for V. Since V is neither nortricyclene nor norbornylene, we believe that the assigned structure, tricyclo[4.1.0.0^{3,7}]heptane, must be correct and that V is derived from II by insertion in the 3-position.

The formation of IV and V by self-insertion has encouraged us to attempt extensions of this reaction. In effect, one has at hand a two-step synthesis: addition of a dihalocarbene[12] to an appropriate olefin followed by generation of the cyclopropylidene with an organometallic reagent. Currently, we are trying to define the scope of this approach. Preliminary results suggest that it will be possible to form a number of new highly-strained systems.[13]

[11] Hydrogenation of bicyclo[2.1.0]pentane gives cyclopentane, R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957).

[12] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954), and later papers; P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956), and later papers.

[13] For example, 8,8-dibromobicyclo[5.1.0]octane appears to undergo similar reactions.

[14] National Science Foundation Summer Fellow, 1959.

[15] National Institutes of Health Predoctoral Fellow, 1960–1961.

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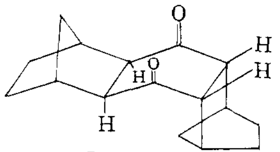
INTERACTIONS OF HOMOCONJUGATED 1,4-CHROMOPHORES IN BOAT CYCLOHEXANE DERIVATIVES[1]

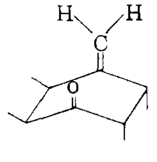
Sir:

The alteration of characteristic ultraviolet spectra by interactions between non-adjacent chromophores is of considerable theoretical interest.[2] In the case of unsaturated ketones,[2–6] these interactions are even more intriguing because of the analogy[2b,3,4] with anchimeric effects of the olefinic group in solvolysis of the toluenesulfonates of the related alcohols. We now have completed the preparation of an instructive series of unsaturated ketones which have 1,4-olefinic and carbonyl groups across from each other in a boat cyclohexane ring, and we report in the present Communication the striking ultraviolet spectra which these ketones display.

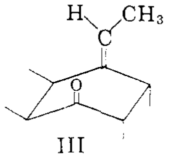
The new ketones are derived from diketone[7] I, m.p. 165°, obtained from hydrogenation of the bis-cyclopentadiene–benzoquinone adduct and subsequent isomerization. The alcohol,[8] m.p. 175–176°, from addition of isopropyllithium to the diketone gives rise to a mixture of unsaturated ketones on treatment with thionyl chloride in pyridine. From this mixture the γ,δ-unsaturated ketone[7,8] IV, m.p. 155–157°, can be isolated in pure condition. Osmium tetroxide oxidation of ketone IV, then lead tetraacetate cleavage of the resulting glycol, regenerates diketone I in high yield. Analogs of ketone IV, the γ-ethylidene ketone[8] III, m.p. 53–55°, and the γ-methylene ketone[8] II, m.p. 66–67°, were prepared by the action of the appropriate Wittig reagent on diketone I. In the case of III, the structure was confirmed by oxidation back to diketone I, as was done for IV.



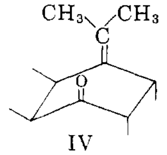
I



II



III



IV

Besides the low[9] and high wave length absorptions at *ca.* 187 and 300 mμ shown by the monoketone[7c] V, all three unsaturated ketones display new absorption bands at intermediate wave lengths. As summarized in Table I, the new bands for the three ketones occur at 210–239 mμ with ϵ values of 3,000–4,000 in heptane, and at 214–

TABLE I

ULTRAVIOLET SPECTRA OF SEVERAL KETONES[a]

V		II		III		IV	
mμ	ϵ	mμ	ϵ	mμ	ϵ	mμ	ϵ
				Heptane			
185.2[b]	2800	185[b]	10,700	185.9[b]	11,000	188	8500
						194(sh)	8220
		209.5	3,110	219	2,720	239	3940
300.6	29	298.4	32	301.6	27	306	31
				95% EtOH			
187.3[c]	3600	187.6[c]	11,240	187 6[c]	11,450	192[c]	9000
						199(sh)	8500
		214(sh)	1,810	224.5	1,455	244	2530
297	34	297	43	297	33	302(sh)	50

[a] Cary 14 Recording Spectrophotometer, 0.01 cm. cell and dry nitrogen flush employed for far ultraviolet region. [b] Not a maximum. [c] Doubtful maximum.

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[1] Research sponsored by the Office of Ordnance Research, U. S. Army.

[2] *E.g.*, (a) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959); (b) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

[3] P. D. Bartlett and B. E. Tate, *ibid.*, **78**, 2473 (1956).

[4] (a) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952); (b) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

[5] (a) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); (b) R. C. Cookson and N. Lewin, *Chemistry and Industry*, 984 (1956).

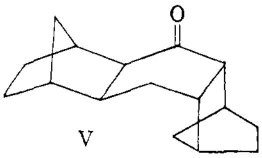
[6] (a) C. A. Grob and A. Weiss, *Helv. Chim. Acta*, **43**, 1390 (1960); (b) C. A. Grob and A. Gagneux, unpublished work quoted by Labhart and Wagnière.[2a]

[7] (a) S. Winstein, *Experientia Supplementum II*, 137 (1955); (b) S. Winstein, page 29 of Abstracts of 15th National Organic Chemistry Symposium of the American Chemical Society, Rochester, New York, June 17-20, 1957; (c) L. de Vries, R. Heck, R. Piccolini and S. Winstein, *Chemistry and Industry*, 1416 (1959).

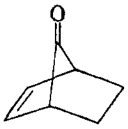
[8] Satisfactory carbon and hydrogen analyses were obtained for the new compounds here mentioned.

[9] The much more intense low wave length absorption of the unsaturated ketones II → IV compared to the mono-ketone V must involve the olefinic as well as the carbonyl group.

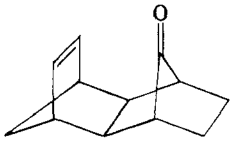
244 mμ with ε values of 1,500–2,500 in ethanol. The solvent dependence of the new bands is appropriate for $\pi\rightarrow\pi^*$ transitions, and the present results bear out the expectation[4b] that stereoelectronic factors are favorable for relatively strong 1,4-interactions in suitable conformations. In the language of Labhart and Wagnière,[2a] who have given a theoretical treatment of the coupling of olefinic and carbonyl groups in unsaturated ketones, the transition is $\pi_2\rightarrow\pi_3$, and it may be characterized as a charge-transfer $\pi\rightarrow\pi^*$ transition, an electron being excited from a molecular orbital resembling the bonding olefinic molecular orbital (π_c) to one resembling the anti-bonding carbonyl molecular orbital (π_0^*).



V



VI



VII

The charge-transfer $\pi\rightarrow\pi^*$ absorption of the unsaturated ketones II→IV occurs at wave lengths within the range usually associated with the analogous absorption of classically conjugated α,β-unsaturated carbonyl compounds.[10] Also, the solvent sensitivity and the effect of terminal methyl groups in ketones II→IV are quite comparable to those observed with α,β-conjugated substances.[10]

As regards the long wave length $n\rightarrow\pi^*$ absorption at *ca.* 300 mμ, none of the ketones II-IV shows the high extinction coefficient characteristic of many other ketones with a neighboring olefinic or phenyl group.[5a] This lack of enhancement of $n\rightarrow\pi^*$ absorption is expected from the theory of Labhart and Wagnière.[2a] According to them, increased $n\rightarrow\pi^*$ absorption is due to mixing of the p_n orbital on oxygen with the olefinic π_c orbital, permitting the $n\rightarrow\pi^*$ absorption to "steal" intensity from the $\pi_2\rightarrow\pi_3$ transition. On this basis, wherever symmetry causes the p_n-π_c overlap integral to be zero, no enhancement of $n\rightarrow\pi^*$ absorption is to be expected.[11a] This is just the situation in ketones II-IV. The situation is similar in 7-norbornenone[12] VI and the *endo-exo*-fused ketone VII reported recently.[11] Both VI and VII show charge-transfer $\pi\rightarrow\pi^*$ bands, but neither shows enhanced $n\rightarrow\pi^*$ absorption.

Both theory and available facts suggest that incidence of anchimeric acceleration of ionization of toluenesulfonates will not correlate with the occurrence of enhanced $n\rightarrow\pi^*$ absorption in the corresponding unsaturated ketone. On the other hand, much better correlation is predicted and observed between incidence of anchimeric acceleration of toluenesulfonate ionization and occurrence of charge-transfer $\pi\rightarrow\pi^*$ absorption in the corresponding ketones.

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GENERALIZED POLYMERIZATION MECHANISM OF MULTI-VINYL MONOMERS. BICYCLO- AND TRICYCLO-INTRAMOLECULAR PROPAGATION[1]

Sir:

The occurrence of the intra-intermolecular reaction step sequence in the polymerization of monomers having two terminal vinyl groups at appropriate distances to permit ring closure leads to polymer chain structures consisting of methylene-linked rings and has been observed and studied in a variety of divinyl systems, first by Butler and Angelo[2] and subsequently by many other investigators.

The relative rates of the two competitive propagation steps of the first active chain end, reacting intramolecularly with the second double bond or intermolecularly with a new monomer molecule, are dependent on a number of factors including potential ring size and reaction type and conditions. Although even for optimum monomers leading to 5- or 6-membered rings the intra-inter rate ratio is not so preponderantly large as to preclude the occurrence in the polymer chain of some pendant vinyl groups resulting from uncompleted cyclization steps and even appreciable extents of cross-linking at high concentrations, the rate ratio is nevertheless large enough with favorable monomers to yield soluble and essentially saturated polymers under usual concentration conditions. Notwithstanding the extensive investigations to date on widely varied divinyl and diolefinic monomers, the theoretically interesting and versatile possibilities of the general case which includes more than one intramolecular propagation step to properly available vinyl groups using suitable triolefinic or even tetraolefinic monomers has not yet been considered nor investigated. Here it could be similarly expected, in view of the ready formation of bicyclic ring systems, that more than one intramolecular ring closure step could occur in consecutive sequence, each predominating, respectively, over the competitive intermolecular propagation step.

Our studies on the polymerization reactions of some representative monomers having three and four unconjugated double bonds have established the occurrence of this generalized mechanism to yield new polymer chain structures comprising

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(10) (a) R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 76 (1942); (b) L. Dorfman, *Chem. Reviews*, **53**, 47 (1953).

(11) (a) S. Winstein, Welch Foundation Symposium, "Molecular Structure and Chemical Change," in Houston, Texas, November 7–9, 1960; (b) R. Hansen, unpublished work.

(12) C. J. Norton, Ph.D. Dissertation ,Harvard University, 1955.

(1) This research was supported in part by the Army, Navy and Air Force under Signal Corps contract DA-36-039sc-78105.

(2) G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957).