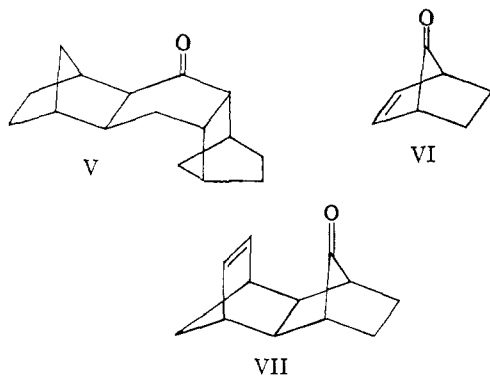


244  $m\mu$  with  $\epsilon$  values of 1,500–2,500 in ethanol. The solvent dependence of the new bands is appropriate for  $\pi \rightarrow \pi^*$  transitions, and the present results bear out the expectation<sup>4b</sup> that stereo-electronic factors are favorable for relatively strong 1,4-interactions in suitable conformations. In the language of Labhart and Wagnière,<sup>2a</sup> 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 ( $\pi_c$ ) to one resembling the anti-bonding carbonyl molecular orbital ( $\pi_0^*$ ).



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  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>10</sup> Also, the solvent sensitivity and the effect of terminal methyl groups in ketones II–IV are quite comparable to those observed with  $\alpha,\beta$ -conjugated substances.<sup>10</sup>

As regards the long wave length  $n \rightarrow \pi^*$  absorption at *ca.* 300  $m\mu$ , none of the ketones II–IV shows the high extinction coefficient characteristic of many other ketones with a neighboring olefinic or phenyl group.<sup>5a</sup> This lack of enhancement of  $n \rightarrow \pi^*$  absorption is expected from the theory of Labhart and Wagnière.<sup>2a</sup> According to them, increased  $n \rightarrow \pi^*$  absorption is due to mixing of the  $p_n$  orbital on oxygen with the olefinic  $\pi_c$  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  $p_n$ - $\pi_c$  overlap integral to be zero, no enhancement of  $n \rightarrow \pi^*$  absorption is to be expected.<sup>11a</sup> This is just the situation in ketones II–IV. The situation is similar in 7-norbornenone<sup>12</sup> VI and the *endo-exo*-fused ketone VII reported recently.<sup>11</sup> 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<sup>1</sup>

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<sup>2</sup> 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

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

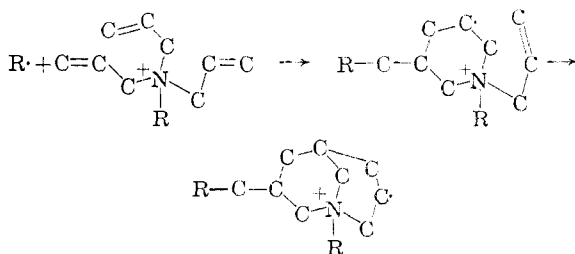
(11) (a) S. Winstein, Welch Foundation Symposium, “Molecular Structure and Chemical Change,” in Houston, Texas, November 7–9, 1960; (b) R. Hansen, unpublished work.

(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).

methylene-linked bicyclic or tricyclic rings. For example, from data summarized in Table I on polymers prepared from triallylammmonium bromide and tetraallylammmonium bromide at several monomer and initiator concentrations, it is evident from the soluble, non-crosslinked and largely saturated character of these polymers that the reaction sequence and resultant chain structure as illustrated for triallylammmonium bromide occurs



Interestingly, even with the tetraallyl derivative the above radical propagates once again intramolecularly to form a bridged tricyclic repeating unit. Especially at the lower concentrations, the intramolecular *vs.* intermolecular selectivity for these monomers remains very high for both the second and third cyclization steps, leaving relatively few pendant double bonds. The effects of monomer and initiator concentration on residual unsaturation are those expected.

TABLE I

POLYMERIZATION OF TRI- AND TETRAALLYLAMMONIUM BROMIDE<sup>a</sup>

Monomer concn., g./g. H <sub>2</sub> O	Cat. concn., g./g. mon.	Conversion, % <sup>b</sup>	Resid. unsatn., <sup>c</sup> double bond/mon.
Triallylammmonium bromide			
0.167	0.003	54	0.011
.50	.003	39	.111
.167	.01	72	.018
.50	.01	66	.31
1.0	.01	74	.30
Tetraallylammmonium bromide			
0.167	0.003	60	0.013
1.0	.003	52	.382
0.167	.01	80	.034
1.0	.01	83	.693

<sup>a</sup> Conditions: H<sub>2</sub>O solvent at 60.0° using *t*-butyl hydroperoxide initiator. <sup>b</sup> All polymers completely soluble in H<sub>2</sub>O and CH<sub>3</sub>OH. <sup>c</sup> Determined by quantitative hydrogenation under conditions known to saturate the monomer rapidly and completely.

The molecular weight range of a typical triallylammmonium bromide polymer was estimated from intrinsic viscosity data,  $[\eta] = 0.14$ , compared to 0.020 for the monomer and 0.023 for a model dimer, bis-(*N,N,N*-dimethylbenzyl)-ethylene diammonium bromide. Also, the maximum end group concentration and corresponding minimum molecular weight was determined by

quantitative n.m.r. measurements using a D<sub>2</sub>O solution of a cumene hydroperoxide-initiated polymer and scanning for phenyl proton absorption. The absence of this absorption and the presence of a small phenyl proton peak in a reference solution of C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>ONa whose concentration corresponded to a mol. wt. of 2500 was taken as indication of a mol. wt.  $\geq 5000$ .

Although limited by the comparative difficulty in obtaining a wide variety of suitable monomers, we have also examined to date some other representative examples. A triolefinic monomer, 3-vinyl-hexadiene-1,5, has been prepared<sup>3</sup> and polymerized using Ziegler catalysts. The soluble polymer obtained,  $[\eta] = 0.46$ , showed residual unsaturation *via* infrared analysis of *ca.* 0.65 double bond/monomer unit and therefore extensive 2,6-linked 2,2,1-bicycloheptyl (norbornyl) chain units, even though with this unsymmetrical monomer at least 0.33 double bond/monomer unit residual unsaturation is expected since only propagation to either of the two equivalent double bonds results in probable second ring closure to the 2,2,1-bicycloheptyl ring. Triallylmethylsilane also has been Ziegler-polymerized to soluble, solid polymers showing residual unsaturation (*e.g.* 0.38 double bond/monomer unit) indicative of a correspondingly large degree of 3,3,1-bicyclic ring content. Preliminary tests with triallyl orthoformate polymerized with azo-bis-isobutyronitrile also indicate the occurrence of appreciable extents of 4,4,2-bicyclic ring formation.

These completely novel polymer chain structures appear from present work to be capable of wide synthetic variation with respect to ring sizes and elemental composition and continuing investigation of the limits of this type reaction and further characterization of the resulting polymers is in progress.

(3) H. Levy and A. C. Cope, *J. Am. Chem. Soc.*, **66**, 1684 (1944).

(4) Hercules Powder Company Fellow, 1958-1960.

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### THE STRUCTURE OF ZAPOTIDINE<sup>1</sup>

Sir:

We wish to report that the sulfur-containing alkaloid zapotidine,<sup>2</sup> a constituent of the seed of the tree *Casimiroa edulis* Llave *et* Lex., possesses the unusual structure I (6-methylimidazo[1,5-*c*]-tetrahydropyrimidine-5-thione). This type of ring system has not been encountered previously in a natural product,<sup>3</sup> and it is moreover exceedingly

(1) "The Constituents of *Casimiroa edulis* Llave *et* Lex. VII." For Part VI, see F. Sondheimer and A. Meisels, *Tetrahedron*, **9**, 139 (1960).

(2) F. A. Kincl, J. Romo, G. Rosenkranz and F. Sondheimer, *J. Chem. Soc.*, 4163 (1956).

(3) K. Schlögl and H. Woidich (*Monatsh.*, **87**, 679 (1956)) have recently synthesized compounds containing the ring system present in I, including the closely related substance IIb. For a discussion of the infrared spectra, see J. Derkosch, K. Schlögl and H. Woidich, *ibid.*, **88**, 35 (1957).