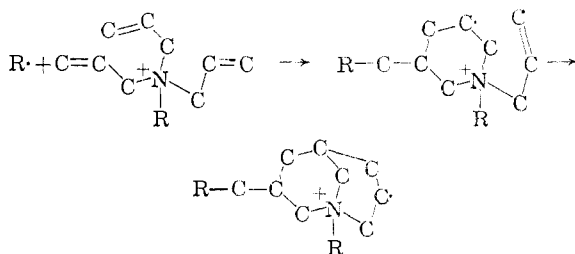


methylene-linked bicyclic or tricyclic rings. For example, from data summarized in Table I on polymers prepared from triallylammmonium bromide and tetraallylammmonium bromide at several monomer and initiator concentrations, it is evident from the soluble, non-crosslinked and largely saturated character 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^a

Monomer concn., g./g. H ₂ O	Cat. concn., g./g. mon.	Conversion, % ^b	Resid. unsatn., ^c 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

^a Conditions: H₂O solvent at 60.0° using *t*-butyl hydroperoxide initiator. ^b All polymers completely soluble in H₂O and CH₃OH. ^c 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 D₂O 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 C₆H₅C(CH₃)₂ONa whose concentration corresponded to a mol. wt. of 2500 was taken as indication of a mol. wt. ≥ 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 prepared³ 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.

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

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THE STRUCTURE OF ZAPOTIDINE¹

Sir:

We wish to report that the sulfur-containing alkaloid zapotidine,² 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,³ 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).

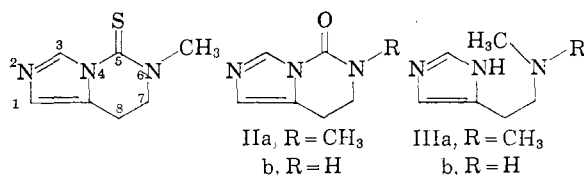
(2) F. A. Kincl, J. Romo, G. Rosenkranz and F. Sondheimer, *J. Chem. Soc.*, 4163 (1956).

(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).

rare for a thiourea derivative to occur in Nature.⁴

Zapotidine, m.p. 96–98°,² C₇H₉N₃S,² contains one N-methyl group (Found: N-methyl, 8.88), no S-methyl, O-methyl or C-methyl groups and no active hydrogen functions. On attempted microhydrogenation (platinum, acetic acid), no hydrogen was absorbed after one hour. The n.m.r. spectrum⁵ showed two aromatic proton peaks (at 505 cps. due to the C-3 proton and at 408 cps. due to the C-1 proton), an N-methyl proton peak (at 213 cps.) and two aliphatic proton peaks (triplets centered at 220 cps. due to the C-7 protons and at 183 cps. due to the C-8 protons).

Zapotidine on being boiled with ethanolic silver nitrate solution, with gradual addition of aqueous sodium hydroxide,⁶ yielded the urea derivative IIa, m.p. 115–116°, C₇H₉N₃O (Found: C, 55.71;



H, 6.11; N, 27.12; S, 0.00); $\lambda_{\text{max}}^{\text{EtOH}}$ 222 m μ (ϵ 8,100); $\nu_{\text{max}}^{\text{KBr}}$ 1713 cm⁻¹. The ultraviolet and infrared data are compatible with those reported for the corresponding des-methyl compound IIb.³ The n.m.r. spectrum⁵ showed peaks at 485 cps. (C-3 proton), 405 cps. (C-1 proton), a triplet at 209 cps. (C-7 protons), 188 cps. N-methyl protons) and a triplet at 182 cps. (C-8 protons). Integration of the n.m.r. peaks showed a total of nine protons to be present.

Lithium aluminum hydride reduction of zapotidine^{3,7} gave N α ,N α -dimethylhistamine (IIIa), characterized as the dipicrate, m.p. 231–233°, C₁₉H₁₉N₉O₁₄ (Found: C, 38.39; H, 3.31; N, 21.07). The latter derivative was identified (mixture m.p., infrared comparison) with an authentic sample (m.p. 231–233°).⁸

Boiling zapotidine in ethanol with 20% aqueous potassium hydroxide yielded N α -methylhistamine (IIIb), converted to the dipicrate, m.p. 188–190°, C₁₈H₁₇N₉O₁₄ (Found: C, 37.21; H, 3.04; N, 21.66; O, 37.50). This derivative was identified (mixture m.p., infrared comparison) with an authentic sample (m.p. 187–189°).⁹

The above-described findings unequivocally show zapotidine to possess structure I. Two other compounds isolated from *Casimiroa edulis*, N α ,N α -

dimethylhistamine (IIIa)^{8b,10} and casimiroedine,^{9b} are imidazoles structurally closely related to I and a biogenetic relationship between the three substances appears very probable. Moreover, it is tempting to speculate that biogenetically zapotidine is derived from 1-acetyl-(or thioacetyl)-histamine by ring closure and methylation. 1-Acetyl-imidazoles have been postulated to be of importance as part of the active sites of some enzymes.¹¹

We are indebted to Dr. S. Pinchas (Weizmann Institute of Science) for valuable discussions regarding infrared spectra, to Prof. R. T. Major (University of Virginia) for providing a sample of N α ,N α -dimethylhistamine dipicrate and to Prof. C. Djerassi (Stanford University) for a sample of N α -methylhistamine dipicrate.

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(11) For a review see E. A. Barnard and W. D. Stein in "Advances in Enzymology," ed. F. F. Nord, **20**, 51 (1958); but see also M. A. Marini and G. P. Hess, *J. Am. Chem. Soc.*, **82**, 5160 (1960).

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CHEMISTRY OF VANADIUM HEXACARBONYL, I: π -CYCLOHEPTATRIENYL-TRICARBONYL- VANADIUM(-1)

Sir:

Various complexes containing a transition metal bonded to a seven-membered carbocyclic system have been synthesized in the recent past, e.g., C₇H₈Cr(CO)₃,¹ C₇H₈Mo(CO)₃,¹ C₇H₈W(CO)₃,² and C₇H₈Fe(CO)₃.³ The first tropylium sandwich compound to be described was the ionic [C₇H₇Mo(CO)₃]BF₄; subsequently the neutral C₇H₇V(CO)₃H₅⁵ was reported.

We now wish to report the synthesis of a novel organometallic vanadium compound and present evidence which supports the assignment of its structure as tropylium-tricarbonyl-vanadium(-1).

Vanadiumhexacarbonyl was prepared from its diglyme-complexed sodium salt as described elsewhere⁶. The agitated mixture of 8.7 g. (0.04 mole) of V(CO)₆ and 18.4 g. (0.2 mole) of cycloheptatriene in 300 ml. of *n*-hexane was heated to its reflux temperature of about 65° for one hour, under nitrogen. During this time 2.7 liters of gas (S.T.P., 0.12 mole) were evolved, containing only a mere trace of hydrogen. Some fine brown amor-

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(3) H. J. Dauben, Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961).

(4) H. J. Dauben, Jr., and L. R. Honnen, *ibid.*, **80**, 5570 (1958).

(5) R. B. King and F. G. A. Stone, *ibid.*, **81**, 5263 (1959); **82**, 4557 (1960).

(6) R. P. M. Werner and H. E. Podall, *Chemistry & Industry*, 144 (1961).

(4) See M. G. Ettlinger and J. E. Hodgkins, *J. Org. Chem.*, **21**, 204 (1956).

(5) N.m.r. spectra were determined at 60 Mc. on a Varian V 4300-C spectrometer in deuteriochloroform solution with tetramethylsilane as internal standard.

(6) See A. E. Dixon, *J. Chem. Soc.*, **67**, 556 (1895); A. Kjaer and R. Gmelin, *Acta Chim. Scand.*, **10**, 1100 (1956).

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