

Table I

Spectrum	Cl	Br	I	NCS	SnCl ₃	CN
N.m.r., δ _{Pt-H} (τ)	26.9	25.6	22.7	23.2	19.2	17.8
Infrared, ν _{Pt-H} (cm. ⁻¹)	2183	2178	2156	2112	2105	2041

between the two parameters (7.19 p.p.m.) suggests that it is a strong π-acceptor.

As a result of this combination of properties, five SnCl₃⁻ ligands may be coordinated about platinum to give [Pt(SnCl₃)₅]⁻³ without excessive buildup of electron density on the central metal atom. In addition, the formation of π-bonds from the filled 5p- and d-orbitals of the platinum to the vacant 5d-orbitals of the tin atoms would be expected to stabilize the trigonal bipyramidal configuration,³ as has now been established for [Pt(SnCl₃)₅]⁻³.

These same electronic properties are characteristic of such strongly *trans*-activating ligands as carbon monoxide. Accordingly, we have also examined the *trans* effect of the SnCl₃⁻ ligand by criteria expounded by Chatt and co-workers.^{4a,b} These investigators showed that the *trans* series, obtained by ranking ligands (X) in terms of their ability to shift the Pt-H infrared stretching frequency and H¹ n.m.r. frequency in *trans*-[(C₂H₅)₃P]₂PtHX compounds, conforms closely to that established earlier by ligand-exchange reactions.⁵

By similar examination of **3**, we now place the SnCl₃⁻ anion between NCS⁻ and CN⁻, the two most powerful ligands in the Chatt series, as shown in Table I (all values from ref. 4 except those for SnCl₃⁻).

This strong *trans*-activation undoubtedly plays an important role in the catalytic activity⁶ and facile ligand-exchange reactions⁷ observed for platinum metal-tin chloride complexes.

trans-Hydrido(trichlorotin)bis(triethylphosphine)-platinum(II) was prepared by reaction of equimolar quantities of *trans*-[(C₂H₅)₃P]₂PtHCl and SnCl₂·2H₂O in concentrated methanolic solution at 25°. White needles precipitated which, after recrystallization from methanol, melted at 100–101°. *Anal.* Calcd.: C, 21.91; H, 4.75; Pt, 29.7; Sn, 18.1. Found: C, 21.86; H, 4.70; Pt, 29.8; Sn, 17.8. The proton magnetic resonance spectrum of the ethyl groups showed equivalent coupling of the CH₃ protons to the two P³¹ nuclei in the complex, a condition characteristic of the *trans* configuration.⁸ The methyl resonance appeared as a five-line pattern (*J*_{P₂-CH₃} = 16 c.p.s., *J*_{CH₂-CH₃} = 7.8 ± 0.2 c.p.s.) which was partially collapsed to a 1:2:1 triplet by irradiation of the methylene signal.

The *m*- and *p*-fluorophenylplatinum complexes **1** and **2** were prepared similarly by treatment of the corresponding chloro compounds, FC₆H₄Pt(PEt₃)₂Cl, with stannous chloride in acetone. The presence of a coordinated SnCl₃⁻ group in complexes **1–3** was con-

(3) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

(4) (a) J. Chatt, L. A. Duncanson, and B. L. Shaw, *Chem. Ind. (London)*, 859 (1958); (b) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

(5) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

(6) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

(7) A. G. Davies, G. Wilkinson, and J. F. Young, *ibid.*, **85**, 1692 (1963).

(8) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

firmed by the presence of a doublet infrared vibration at 330 cm.⁻¹ assignable to Sn-Cl stretching. This absorption seems to be typical of complexes bearing the SnCl₃⁻ ligand including [Pt(SnCl₃)₅]⁻³

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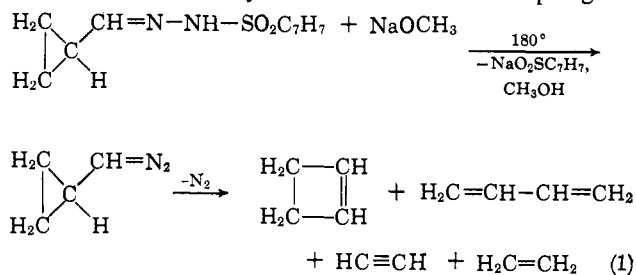
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Intramolecular Processes in Carbenic and Cationic Decomposition of Cyclopropanecarboxaldehyde *p*-Tosylhydrazone

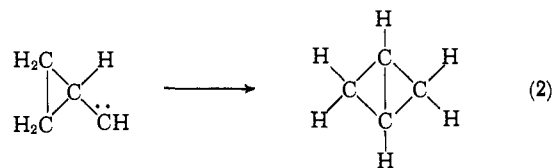
Sir:

Aldehyde and ketone *p*-tosylhydrazones react with bases in aprotic solvents at 90–180° to give diazo compounds which decompose by carbenic processes.^{1a,b} In proton-donor solvents decomposition of *p*-tosylhydrazones by bases occurs primarily by cationic mechanisms involving diazonium and/or carbonium ion intermediates.¹

Cyclopropanecarboxaldehyde *p*-tosylhydrazone (I) has been reported² to react with sodium methoxide in aprotic solvents to give (eq. 1) cyclobutene (60–67%) by ring expansion, 1,3-butadiene by reorganization, and ethylene and acetylene by fragmentation, along with unidentified hydrocarbons. In attempting to



prepare cyclobutene from I and sodium methoxide in Diethyl Carbitol or triglyme, Frey^{3a} informed us that the principal product (~80%) of their experiment was a hydrocarbon isomeric with cyclobutene and 1,3-butadiene. The hydrocarbon was subsequently identified^{3b} as bicyclo[1.1.0]butane, and it was suggested^{2b} that this product is formed (eq. 2) by intramolecular insertion of cyclopropylcarbene into one of its four equivalent secondary carbon-hydrogen bonds. We



wish to report our additional studies on base-catalyzed decomposition of I and emphasize the importance of experimental conditions on the paths and the apparent carbenic and cationic mechanisms of reaction of this system.


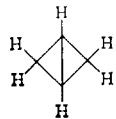
The effects of the number of equivalents of sodium methoxide and of the proton-donor capacity of sol-

(1) (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (b) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

(2) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).

(3) (a) H. M. Frey, private communication, Sept. 30, 1963; (b) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964).

Table I. Decomposition of Cyclopropanecarboxaldehyde *p*-Tosylhydrazone (I) by Sodium Methoxide or the Sodium Salt (II) of I in Various Environments

Reactant	NaOCH ₃ ^a	Solvent	Yield, ^b %	% composition of principal hydrocarbons ^c				
					$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$		$\text{HC}\equiv\text{CH}$	$\text{H}_2\text{C}=\text{CH}_2$
I	1.8	DEC ^d	89	41	39	3	8	9
	1.1	DEC	~85	83		3	5	5
	1.1	DEC	80	85	3	2	4	4
	1.0	DEC ^e	~95	82	3		5	5
	0.8	DEC	55	26	6	57	4	7
	1.1	Et ₃ COH	82	95	Trace	3	<i>f</i>	<i>f</i>
	1.1	EG ^g	27	16	4	79	<i>f</i>	<i>f</i>
II		Pyrolysis ^h	60	61-62	38			
		Pyrolysis ⁱ	100	33-0	44-100		0-10	0-13
		DEC ^j	62-71	34	32	16	8	7
		DEC-1.25% H ₂ O	76	50	3	34	4	10
		DEC-10% EG	68	28	8	64		
		EG	53	15	6	74		

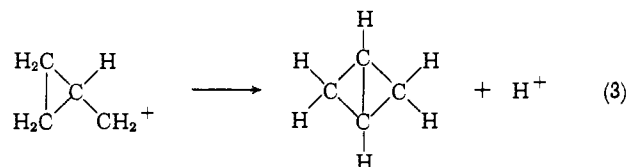
^a Prepared fresh from sodium and methanol or by titration of new commercial material. ^b Based on volume of gas evolved. ^c Analyzed on β,β' -oxydipropionitrile and Dowtherm v.p.c. columns. ^d Purified Diethyl Carbitol. ^e Ref. 2. ^f Undetermined. ^g Ethylene glycol. ^h 80 mm. ⁱ Atmospheric pressure. ^j II contained some methanol of crystallization.

vents on decomposition of I are summarized in Table I. If I is decomposed by excess sodium methoxide either heterogeneously in Diethyl Carbitol, an aprotic solvent, or homogeneously in triethylcarbinol, a poor proton donor,⁴ cyclobutene and 1,3-butadiene are the principal hydrocarbons produced; bicyclo[1.1.0]butane is a minor product (2-3%) under such conditions. In the presence of near-equivalent quantities of sodium methoxide, formation of the bicyclic hydrocarbon becomes more significant (~12%); if insufficient sodium methoxide (0.8 equiv.) or ethylene glycol is used, bicyclo[1.1.0]butane (57-79%) becomes the principal product.

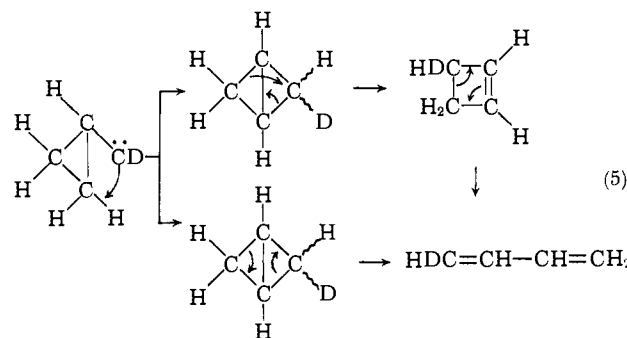
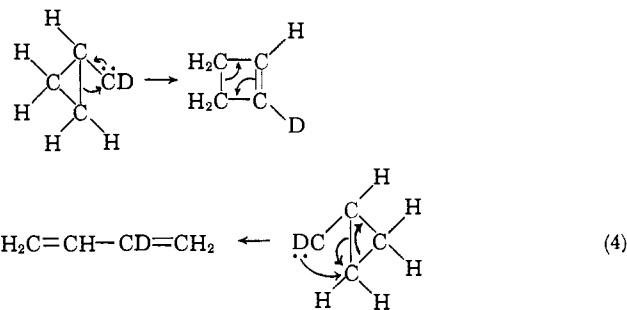
A study has also been made (Table I) of decomposition in various environments of the sodium salt (II) of I as prepared and isolated from reaction of I with sodium methoxide. Pyrolyses of II at 125-135° and at various pressures give cyclobutene and 1,3-butadiene as major products along with acetylene and ethylene; bicyclo[1.1.0]butane could not be detected. Thermolysis of II as a slurry in Diethyl Carbitol at 180° yields cyclobutene (34%) and 1,3-butadiene (32%) along with bicyclo[1.1.0]butane (16%). Of greater significance is that decomposition of II in Diethyl Carbitol containing 1.25% water or 10% ethylene glycol or in pure ethylene glycol results primarily in formation of bicyclo[1.1.0]butane.

Decomposition of II in aprotic solvents thus yields cyclobutene and 1,3-butadiene as principal products as previously reported²; bicyclo[1.1.0]butane is nearly negligible or a minor product under conditions which avoid cationic processes. Conversion of I to bicyclo[1.1.0]butane is greatly enhanced in environments of increased proton activity as possibly derived from the presence of water, methanol, parent tosylhydrazone (I),^{5a} *p*-toluenesulfonic acid, or incompletely neutralized solvents.^{5a} It is thus suggested that bicyclo[1.1.0]butane is not formed primarily by carbenic decompo-

sition of II but rather by cationic processes involving intramolecular reaction of cyclopropylcarbonium (eq. 3) or cyclopropylmethyl diazonium intermediates.^{5b}

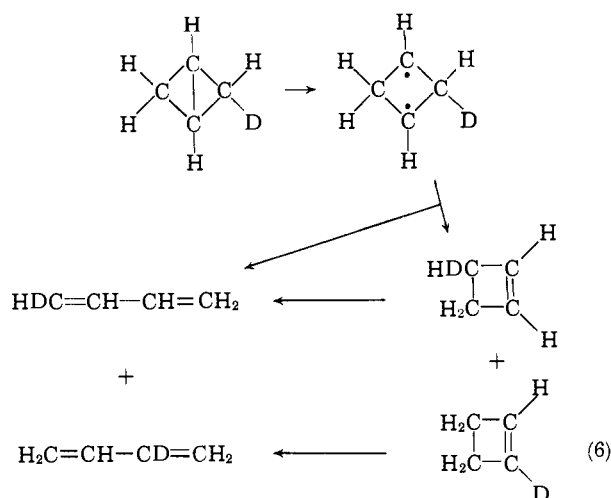


Lithium cyclopropanecarboxaldehyde-*d* tosylhydrazone has been pyrolyzed to determine if (1) carbon-skeleton rearrangement gives cyclobutene-1-*d* and 1,3-butadiene-2-*d* (eq. 4) and/or (2) β carbon-hydrogen insertion yields bicyclo[1.1.0]butanes-2-*d* as intermediates which isomerize to cyclobutenes-*d* and/or 1,3-butadienes-*d* via reorganization of external carbon-carbon bonds (eq. 5) or rupture of the internal carbon-carbon bond and subsequent rearrangement (eq. 6).



(4) J. Bayless, unpublished results.

(5) (a) I is a weak acid; if it is incompletely converted to II, *p*-toluenesulfonic acid is generated upon its thermolysis; (b) the possible role of hydrogen-bonded bivalent intermediates in this system is being studied.



Decomposition of the dry salt (125°, 8 mm.) yields only cyclobutene-1-*d* (44%) and 1,3-butadiene-2-*d* (56%) as C₄ products. The deuterio hydrocarbons formed are thus consistent with that derived by carbon-skeleton rearrangement of cyclopropylmethylidene-*d* as in eq. 4.^{6b} A similar mechanism is apparently involved in vacuum thermolysis of sodium 1-phenylcyclopropanecarboxaldehyde-*d* tosylhydrazone in that 1-phenylcyclobutene (78%) is formed containing deuterium only at the vinyl position.⁶ The 2-phenyl-1,3-butadiene obtained (16%), however, contains most of its deuterium at the 1 and 4 positions and thus may be derived by isomerization of intermediate 1-phenylbicyclo[1.1.0]butanes-2-*d*.

(6) (a) The positions and ratios of hydrogen and deuterium in the products were determined by n.m.r. methods. (b) An alternate but unlikely mechanism being investigated with other systems involves insertion of cyclopropylmethylidene-*d* between its methylene carbons to give bicyclo[1.1.0]butane-1-*d* which reorganizes via its external bonds to cyclobutene-1-*d* and 1,3-butadiene-2-*d*.

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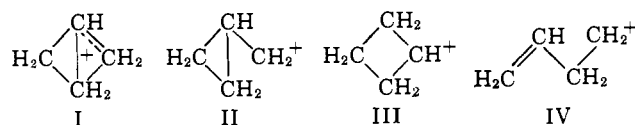
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Intramolecular Reactions of Cyclopropylcarbinyl, Cyclobutyl, and Allylcarbinyl Cationic Systems

Sir:

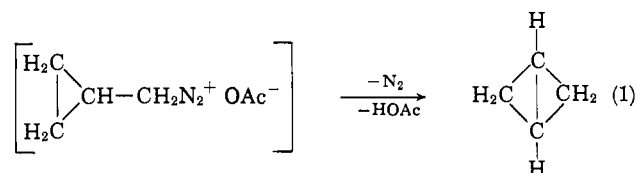
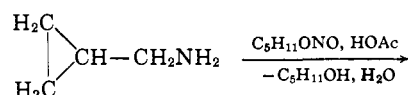
Carbonium ion reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl compounds result in extensive rearrangement.¹ The intermolecular products and the detailed mechanisms of such solvolyses vary according to the reagents and their environment.¹ In general, mixtures of cyclopropylcarbinyl, cyclobutyl, allylcarbinyl, and less frequently 1-buten-3-yl and 3-buten-1-yl derivatives are formed, possibly as derived from interconverting bicyclobutonium ions (I) and/or energetic classical cations (II-IV).¹ Recently decomposition of sodium cyclopropanecarboxaldehyde *p*-tosylhydrazone in proton-donor solvents was found to give bicyclo[1.1.0]butane as a major product along with cyclobutene, 1,3-butadiene, acetylene, and ethyl-

(1) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 3773 (1964), and references therein.

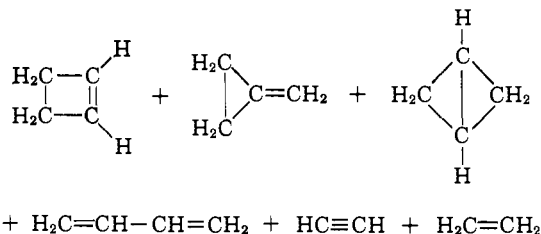
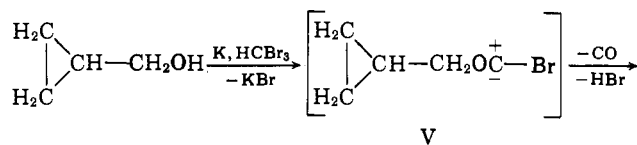


ene.² Bicyclo[1.1.0]butane and its isomeric C₄ hydrocarbons are apparently derived from intramolecular decomposition of high-energy cyclopropylmethylidiazonium ion intermediates. Since such processes have not been recognized previously, a study has been initiated (Table I) of the intramolecular reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl cationic systems as generated from various sources. The disciplines of such processes are contrasted with those of analogous carbenic systems.

Deamination of cyclopropylcarbinylamine hydrochloride with amyl nitrite gives low yields (7%) of hydrocarbons derived from intramolecular processes. Bicyclo[1.1.0]butane is not formed; the product is primarily a mixture of cyclopropylcarbinyl chloride (72%), cyclobutyl chloride (13%), and allylcarbinyl chloride (15%). Aprotic diazotization³ of cyclopropylcarbinylamine by amyl nitrite and acetic acid in chloroform results in extensive intramolecular insertion in which bicyclo[1.1.0]butane is the principal product (eq. 1).⁴ The intramolecular products are similar to that in cationic decomposition of sodium cyclopropanecarboxaldehyde *p*-tosylhydrazone in proton-donor solvents (Table I) and appear to be derived from poorly solvated cyclopropylmethylidiazonium ion intermediates which are highly energized. Alkaline deoxygenation of potassium cyclopropylcarbinol by bromoform,⁵ a reaction involving dibromocarbene and apparent collapse of a subsequent intermediate such as V, yields



carboxaldehyde *p*-tosylhydrazone in proton-donor solvents (Table I) and appear to be derived from poorly solvated cyclopropylmethylidiazonium ion intermediates which are highly energized. Alkaline deoxygenation of potassium cyclopropylcarbinol by bromoform,⁵ a reaction involving dibromocarbene and apparent collapse of a subsequent intermediate such as V, yields



(2) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **87**, 659 (1965).

(3) (a) L. Friedman and F. M. Logullo, *ibid.*, **85**, 1549 (1963); (b) aprotic diazotization of various amines will be described in subsequent publications by J. Bayless and L. Friedman.

(4) Cyclopropylcarbinyl (67%), cyclobutyl (20%), and allylcarbinyl (13%) acetates are formed via solvolytic routes.

(5) J. Hine, E. L. Pollitzer, and H. Wagner, *J. Am. Chem. Soc.*, **75**, 5607 (1953); P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959).