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THE THERMAL DECOMPOSITION OF CYCLOBUTANE CARBOXYALDEHYDE p-TOSYLHYDRAZONE[1]

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Missing amongst the numerous Tosylhydrazones whose decompositions have been studied is cyclobutane carboxaldehyde p-tosylhydrazone (I). Hydrazone I was synthesized by reacting a slight excess of cyclobutanecarboxaldehyde with p-tosylhydrazine at -80°. Due to the instability of hydrazone I, we were unable to purify the reaction product without causing decomposition*; mp 70-72^0 (dec); $_{max}$ 3200 cm^{-1} (N-H), 1590 cm^{-1} (C=N); NMR ($CDCl_3$) showed the aromatic protons centered at 2.40 , integration indicated that the high field portion of AB system contained 3H, the extra proton being the $-\overset{\overset{H}{|}}{C}=N-$ hydrogen. The cyclobutane tertiary hydrogen occurred as a broad multiplet at 7.09 and the remaining aliphatic protons appeared as a complex set of peaks from 7.27 to 8.59 (total of 10 H)**.

Pyrolysis of the hydrazone in alkaline medium was done under a stream of nitrogen and the products collected via a liquid nitrogen trap. The reaction products were analyzed and separated by vapor phase chromatography using a 15 ft. column packed with 30% di(2-ethylhexyl) sebacate on 60/80 Chromosorb P.

In a typical run, a mixture of 10 m mole of hydrazone I and 11 m mole of sodium hydride in oil dispersion were placed in a 50 ml three-neck flask equipped with a reflux condenser, nitrogen inlet and serum cap. By means of a syringe, 15 ml of diglyme was then injected, followed by 5.5 ml of 2M n-heptanol in diglyme. The reaction mixture was magnetically stirred and gradually heated by means of an oil bath to 195°. Rate of heating

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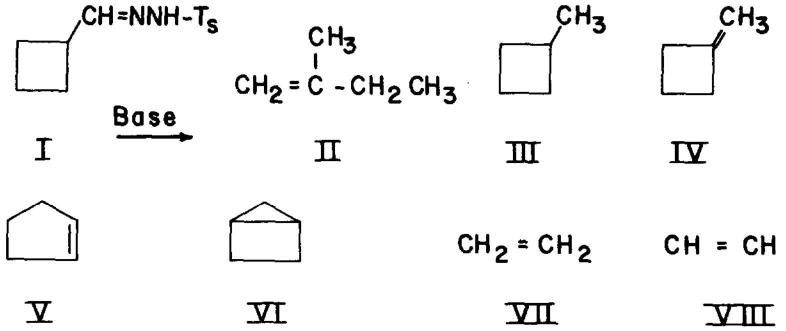
* The hydrazone was dried for at least 2 hours at 1 x 10^{-4} mm. or less at room temperature and stored at -20° until used.

** The NMR spectrum of the 2,4-dinitrophenyl hydrazone of cyclobutanecarboxaldehyde was qualitatively the same in the aliphatic region.

did not affect the composition of the hydrocarbon products. In the cases where metal salts were used as catalysts, one gram of the anhydrous metal salt was mixed with the tosylhydrazone I before addition of diglyme. The volatile hydrocarbon products were stored in dry ice until analysis and separation. The results are summarized in Table I.



The products were identified by comparison with published spectral data (IV[2] and VI[3]) or with authentic materials (III, V, VII and VIII). We tentatively identify hydrocarbon II as 2-methyl-1-butene. Positive identification of II was made difficult by a lack of material. We were unable to detect any bicyclo [1.1.1] pentane[4] in the hydrocarbon mixture.

Of particular interest is the formation of methylcyclobutane (III). It was at first thought that hydrocarbon III arose by hydride addition to the carbon-nitrogen bond[5, 6]; however, III was also a product when the base was not prepared in situ. The possibility that unreacted p-toluene sulphonylhydrazine was acting as a reacting agent was eliminated by the fact that the yield of III dropped tenfold when 20% excess of hydrazine was added to hydrazone I. Addition of 2% water to dry diglyme or running the decomposition in a protic solvent also lowered the yield of III. The reducing agent(s) is not known *.

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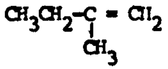
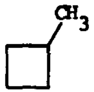
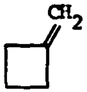
* Since the yield of III is reduced by the presence of protic solvent, speculation that at least part of this product arises from a carbonium ion intermediate is tempting; however, another possibility is hydride donation from the alkoxide. The referee has suggested that methylcyclobutane is the result of a Wolff-Kischner reduction as proposed by DuPuy[7]. A few other examples of a reduced product resulting from a basic medium tosylhydrazone decomposition are known to us[8, 9]. We have run other tosylhydrazone decompositions using the condition described and have not observed reduced products. This lack of ubiquity in observing reduced products, though not ruling out a Wolff-Kischner reduction, causes concern in our mind.

TABLE*

BASE[b]	SOLVENT AND CATALYSTS	% Composition of Reaction Mixture[a]				
		 $CH_3CH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}=CH_2$				
		II	III	IV	V	VI
NaH and n-heptanol	Dry Diglyme	0	13.6	17.7	56.5	12.2
Na-heptoxide[c]	Dry Diglyme	0.2	10.0	30.0	37.2	22.6
NaH and n-heptanol	Dry Diglyme and 20% T_sNHNH_2	0	1.3	15.8	71.5	11.4
NaH and n-heptanol	Diglyme and 2% H_2O	0	4.0	17.8	63.0	15.2
NaH	m-Cresol	1.5	5.3	1.3	91.9	0
NaH	Ethylene glycol	0.9	2.1	3.8	92.5	0
$NaOCH_2CH_2OH$[d]	Ethylene glycol	0.5	1.7	5.0	92.8	0
NaH and n-heptanol	Dry Diglyme CuCl	2.6	1.9	24.0	71.5	0
NaH and n-heptanol	Dry Diglyme $CuSO_4$	4.8	4.6	29.1	61.5	0
NaH and n-heptanol	Dry Diglyme $NiCl_2$	4.1	10.4	13.6	71.9	0

* See the following page for table footnote

Decomposition in protic solvents totally eliminates bicyclo[2.1.0]pentane (VI) and drastically lowers the yield of methylenecyclobutane (IV) while the production of cyclopentene (V) is enhanced. If these results are interpreted with the generalization that cationic intermediates prevail in protic media and carbenoid intermediates predominate under aprotic conditions[10], one would assume that a carbenoid intermediate in aprotic solvent is responsible for IV, V and VI. The total elimination of VI in protic solvents suggests the suppression of at least part or perhaps all of the carbenoid pathway of decomposition. The appearance of IV and V in protic media decomposition would on this basis then be attributed to cationic intermediates**.

One further point of interest is the elimination in aprotic media of bicyclo[2.1.0]-pentane from the products when anhydrous transition metal salts are present. This result is in sharp contrast with the use of cupric salts to catalyze the supposed formation of carbenoid intermediates from diazo compounds[13,14***,15]. These results differ from the observations of Shapiro[9] on the effect of trivalent ions since the yield of IV increases with the presence of transition metal ions, whereas in protic media it decreased. Hence, a simple cationic intermediate as proposed by Shapiro is not likely in this case

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** A priori, one is not able to rule out totally suppression of carbenoid intermediates in protic media[11,12]. Experiments like those reported by Shapiro[12] would be useful in determining the extent of participation of such species in protic media.

*** Nozaki et al. have shown asymmetric induction in carbenoid reactions in the presence of a disymmetric copper chelate. They propose the intermediate is bonded to the metal as a fifth ligand.

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* <u>Footnotes to Table</u>

(a) Ethylene and acetylene were also detected in small quantities (< 1%), but were not analyzed quantitatively. On several occasions a polymer was formed in small quantities when the product mixture was removed from the dry-ice bath. No evidence on the structure of the polymer or its monomer(s) is available.

(b) Sodium methoxide was also used, but due to the problem of separating methanol from the hydrocarbon products, n-heptanol was chosen.

(c) A saturated solution of sodium heptoxide (15 m mole) was prepared by dissolving sodium metal in n-neptanol, hence an excess of n-heptanol was present in this experiment. The difference in hydrocarbon yields between the <u>in situ</u> and externally prepared sodium heptoxide reactions is probably due to a slightly greater excess of base used in the externally prepared base reaction or perhaps in part to the excess alcohol.

REFERENCES

1. This work was supported by the National Research Council of Canada.
2. NMR Spectra Catalog N.S. Bhacca, L.F. Johnson and J.N. Shoolery, National Press 1962.
3. (a) H.P. Chesick, J.Amer.Chem.Soc., **84**, 3250 (1962). (b) R. Criegee and A. Rimmelin, Ber., **90**, 414 (1957).
4. K.B. Wibert, D.S. Connor and G.M. Lampman, Tetrahedron Letters, 531 (1964).
5. R.M. McDonald and R.A. Krueger, J.Org.Chem., **31**, 488 (1966).
6. L. Caglioti, Tetrahedron, **22**, 487 (1966).
7. C.H. DePuy and D.H. Froemsdorf, J.Am.Chem.Soc., **82**, 634 (1960).
8. A.C. Udding, J. Strating, A. Wynberg and J.L.M.A. Schlatmann, Chem.Comm., 657 (1966).
9. R.H. Shapiro, Tetrahedron Letters, 3401 (1966).
10. A. Nickon and N.H. Werstiuk, J.Amer.Chem.Soc., **88**, 4543 (1966) and references therein.
11. J.A. Smith, H. Shechter, J. Bayless and L. Friedman, J.Am.Chem.Soc., **87**, 659 (1965).
12. R.H. Shapiro, J.H. Duncan and J.C. Clopton, ibid., **89**, 471 (1967).
13. W. von E. Doering, E.T. Fosel, and R.L. Kaye, Tetrahedron, **21**, 25 (1965).
14. H. Nozaki, S. Moriuti, H. Takaya and R. Noyori, Tetrahedron Letters, 5239 (1966)
15. W. Kirmse, "Carbene Chemistry", Academic Press, New York, 1964, pp. 12-13.