Tetrahedron Letters No.50, pp. 5049-5052, 1967. Pergamon Press Ltd. Printed in Great Britain.

LEWIS ACID CATALYZED DECOMPOSITION OF DIAZOALKANES

Bro. H. Philip, M.K. Lowery, James Havel[1]
Lewis College, Lockport, Ill. 60441

(Received in USA 14 August 1967)

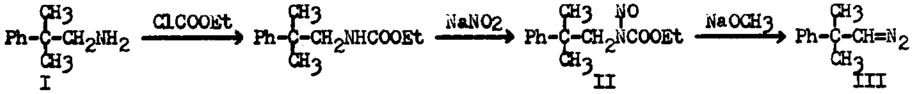
Shapiro[2] has recently shown that the products of the aprotic basic decomposition of camphor tosylhydrazone are significantly altered by the presence of metal ions. The percentage of camphene, the product expected of a carbonium ion process, increased from 1% to 50% as the base was changed from silver carbonate to lithium hydride to aluminum isopropoxide. He postulated a carbene-Lewis acid complex as the rearranging intermediate.

We have observed phenyl and alkyl shifts in the Lewis acid catalyzed decomposition of 2-phenyl-2-methyl diazopropane. The possible involvement of the carbonium ion as an explanation of these rearrangements was eliminated by a careful study of the proton catalyzed decomposition.

To a 0.1 M solution of 2-phenyl-2-methyl diazopropane*, III, in hexane less than 1/10 the stoichiometric equivalent of acid was added**. The reactions were complete in less than ten minutes as indicated by the loss of color and the quantitative evolution of nitrogen. The results are given in Table I.

---

* 2-Phenyl-2-methyl diazopropane, III, was prepared in excellent yield as shown below.

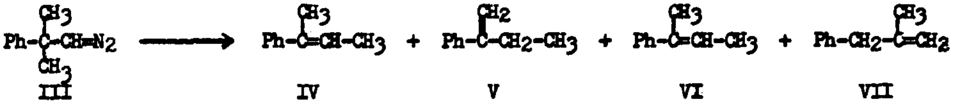


$$\underset{\text{I}}{Ph\text{-}C(CH_3)_2\text{-}CH_2NH_2} \xrightarrow{ClCOOEt} Ph\text{-}C(CH_3)_2\text{-}CH_2NHCOOEt \xrightarrow{NaNO_2} \underset{\text{II}}{Ph\text{-}C(CH_3)_2\text{-}CH_2N(NO)COOEt} \xrightarrow{NaOCH_3} \underset{\text{III}}{Ph\text{-}C(CH_3)_2\text{-}CH{=}N_2}$$

No nitrogen was evolved during the reaction of the nitrosourethan, II, with sodium methoxide and the subsequent hydrolysis indicating no carbonium ion rearrangement took place via the diazotic acid, a possibility clearly indicated by Moss[3].

** In the absence of catalysts the half-life of III is about two days in hexane at 69°. All proton and Lewis acid decompositions were carried out at room temperature with half-lives varying from seconds to five minutes.

TABLE I[a,d]



$$Ph\text{-}C(CH_3)_2\text{-}CH{=}N_2 \longrightarrow Ph\text{-}C(CH_3){=}CH\text{-}CH_3 + Ph\text{-}C({=}CH_2)\text{-}CH_2\text{-}CH_3 + Ph\text{-}C(CH_3){=}CH\text{-}CH_3 + Ph\text{-}CH_2\text{-}C(CH_3){=}CH_2$$

III IV V VI VII

Catalyst	% olefins	IV Trans	IV Cis	V	VI	VII	Ph/Me[b]
Benzoic acid	80[c]	5.5	8.3	9.0	24.0	52.0	6.7
Sulfuric acid	90	3.0	9.0	11.0	24.0	53.0	6.7
Acetic acid	70[c]	4.5	8.0	9.0	22.0	57.0	7.5

a.) Products were separated by v.p.c., using a 15 ft. DEGS column at 90°, and identified by comparison of their I.R. spectra with those of known samples.

b.) Phenyl to methyl migration aptitude. Corrected for the presence of two methyl groups.

c.) The ester products, obtained in about 20%, contained the esters of phenyl and methyl migration in about the same ratio as the corresponding olefins. Substantial amounts of neophyl ester, the unrearranged product, was observed.

d.) The mass balance in all cases was over 90%.

Essentially the same ratio of phenyl to methyl migration has been observed in other processes postulated to involve the neophyl cation, viz, the nitrous acid deamination of neophyl amine, I,[4] the deoxideation of neophyl alcohol, the electrolysis of the sodium salt of 3-phenyl-3-methyl butyric acid and the thermal decomposition of the nitrosourethan, II, and the corresponding nitrosobenzamide[5*]. This consistent behavior of the neophyl cation makes more dramatic the results of the Lewis acid catalyzed decompositions.

Boron trifluoride etherate, boron trichloride, trimethyl borate, aluminum chloride, aluminum isopropoxide and mercuric iodide catalyze the decomposition of 2-phenyl-2-methyl diazopropane in hexane. The results are given in Table II.

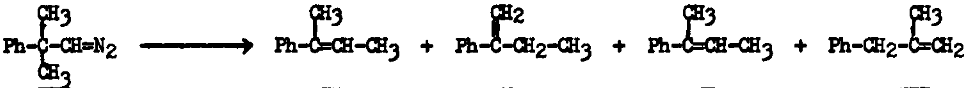
The unexpected aspect of this work is the near indiscriminate migration of phenyl or methyl observed from the boron trifluoride catalyzed decomposition and the gradual decrease in this indiscriminate character of the rearrangement as the Lewis acid is changed.

That the neophyl cation cannot accommodate these results is evident from our study of the proton catalyzed decompositions. Further, a carbonium ion process would require the presence of water. We have been scrupulously careful to avoid the presence of water. Indeed

---

* The particulars of these reactions will be published shortly.

TABLE II[a]



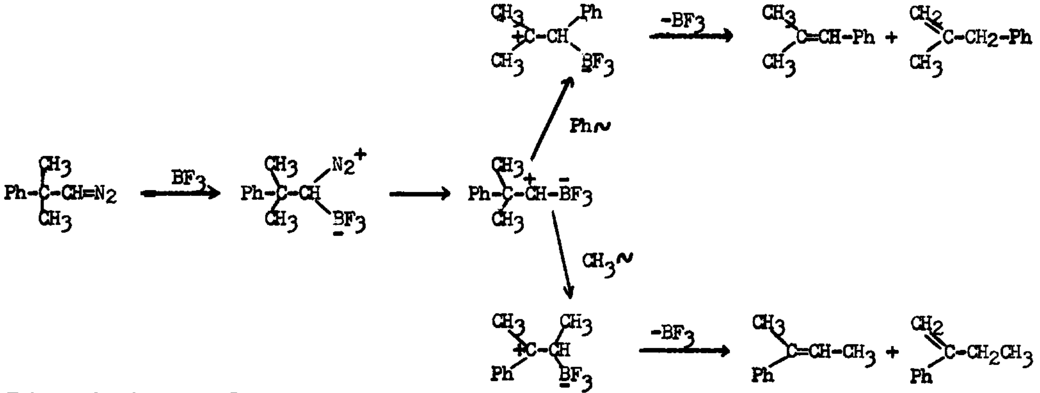
III IV V VI VII

Catalyst[b]	% N_2	% olefin	IV trans	IV cis	V	VI	VII	Ph/Me[c]
BF_3[d]	100	90	4.4	53.0	5.1	21.0	16.0	1.2
BCl_3	100	95	7.6	14.2	11.2	21.6	45.5	4.0
$B(OCH_3)_3$	94	90	7.4	14.0	13.0	16.0	49.0	3.8
$AlCl_3$	95	95	5.9	14.0	20.0	23.0	37.0	3.0
$Al(i\text{-}OC_3H_7)_3$	90	78	6.3	8.3	24.7	21.0	37.8	2.9
HgI_2	100	95	2.7	12.1	0.8	77.4	7.3	11.1

a.) The results are the average of at least three runs. The correlation between various runs was excellent.
b.) The catalyst was always less than 0.1 x mmoles of III.
c.) Phenyl to methyl migration aptitude. Corrected for the presence of two methyl groups.
d.) Added as boron trifluoride etherate.

when precautions are not taken to avoid water, or 5 ul of water is intentionally introduced (giving a 5×10^{-3} M. concentration of water) the same ratio of phenyl to methyl migration as found in the proton catalyzed decomposition is observed.*

A mechanistic pathway which accommodates the experimental results is indicated below.**



This mechanism postulates the actual rearranging species to be a lewis acid-carbene complex.

---

* This observation has been made when the catalyst was either BF_3, BCl_3 or $AlCl_3$.

** The details which result in the distribution between terminal and internal olefins are being investigated.

Since a change in the Lewis acid would involve a different rearranging species, the mechanism nicely accommodates the variation of product composition with Lewis acid catalyst.

The rearrangement involves charge separation. This electrostatic work is compensated for by the formation of a 3° cation and the relief from the unfavorable inductive effect resulting from the presence of both an electron deficiency and an electron-withdrawing substituent on the carbenic site. Analogies for the latter effect are apparent in the anti-Markownikoff additions of HX to vinyl groups bearing $-Si(CH_3)_3$[6] or $-CF_3$[7] substituents.

$$CH_2{=}CH{-}Si(CH_3)_3 + HX \longrightarrow XCH_2{-}CH_2{-}Si(CH_3)_3$$

$$CH_2{=}CH{-}CF_3 + HX \longrightarrow XCH_2{-}CH_2{-}CF_3$$

One might expect that the more electronegative the Lewis acid species in the carbene complex, the more reactive the electrophilic site adjacent to it. It is interesting that in cases where the electronegativity of the Lewis acid species may be similar, the aluminum chloride-aluminum isopropoxide and the boron trichloride-trimethyl borate, the observed ratio of phenyl to methyl migration is the same. The range of Lewis acids studied shows that the electron deficiency in the carbene complexes can be made either more or less discriminating for phenyl or methyl migration than is the neophyl cation.

The occurrence of 1,3 shifts in carbene complexes is under examination using suitable isotopic labeling experiments.

REFERENCES

(1) Partial support of this investigation from the National Science Foundation, Grant No. G14476 is gratefully acknowledged. M.K.L. and J.H. were National Science Foundation Undergraduate Research Participants.

(2) R.H. Shapiro, *Tetrahedron Letters*, 3401 (1966). R.H. Shapiro, J.H. Duncan and J. C. Clopton, *J. Amer. Chem. Soc.*, *89*, 1442 (1967).

(3) R.A. Moss, *J. Org. Chem.*, *31*, 1082 (1966).

(4) James Keating, B.S. Thesis, St. Mary's College, Winona Minn. (1962).

(5) James Havel, B.S. Thesis, Lewis College, Lockport, Illinois. (1967).

(6) H.D. Kaesz, F.G.A. Stone, *Organometallic Chemistry*, H. Zeiss, Editor, p. 117. Reinhold Publishing Co., New York (1960) and references contained therein.

(7) A.L. Henne and S. Kaye, *J. Amer. Chem. Soc.*, *72*, 3369 (1950).