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THE NEOPHYL CARBENE REARRANGEMENT

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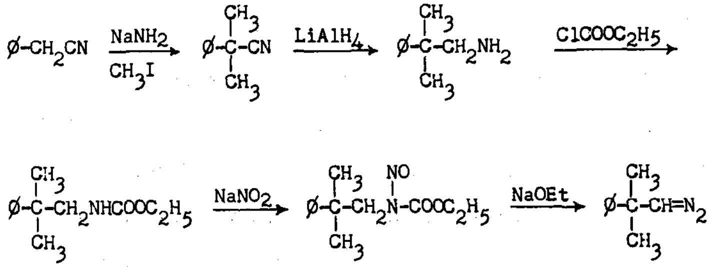
IN view of the extensive studies that have been made of rearrangements in the neophyl (2-methyl-2-phenylpropyl) system which proceed via carbonium ion[1] or radical[2] intermediates it was of interest to study rearrangements in this system which proceed via a carbene intermediate. Therefore, the thermal decomposition in an aprotic solvent of 1-diazo-2-methyl-2-phenylpropane, henceforth referred to as the neophyl diazo compound, was investigated. This work represents a preliminary study in the investigation of migration aptitudes in carbene rearrangements.

The neophyl diazo compound, I, was prepared by the following sequence of reactions;



$$\emptyset\text{-CH}_2\text{CN} \xrightarrow[\text{CH}_3\text{I}]{\text{NaNH}_2} \emptyset\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CN} \xrightarrow{\text{LiAlH}_4} \emptyset\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH}_2\text{NH}_2 \xrightarrow{\text{ClCOOC}_2\text{H}_5}$$

$$\emptyset\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH}_2\text{NHCOOC}_2\text{H}_5 \xrightarrow{\text{NaNO}_2} \emptyset\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH}_2\overset{\text{NO}}{\text{N}}\text{-COOC}_2\text{H}_5 \xrightarrow{\text{NaOEt}} \emptyset\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH=N}_2$$

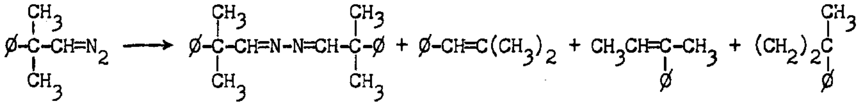
I

[1a] S. Winstein, B.K. Morse, E. Grunwald, D.C. Schreiber and J. Corse, J.Amer.Chem.Soc. 74, 1113 (1952); [b]S. Winstein and A.H. Fainberg, Ibid. 79, 1608 (1957); [c]R. Heck and S. Winstein, Ibid. 79, 3432 (1957); [d]W.H. Saunders and R.H. Paine, Ibid. 83, 882 (1961).

All compounds in this series were characterized. The presence and concentration of the neophyl diazo compound, I, was verified by its reaction with benzoic acid and subsequent identification of the resulting neophyl benzoate.

The thermal decomposition of the neophyl diazo compound, 0.1 molar in hexane, at 59°C over a period of 96 hr was observed. Results of two typical runs in this series are indicated in Table 1.

Table 1



$$\phi\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH{=}N_2 \longrightarrow \phi\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH{=}N\text{-}N{=}CH\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}\phi + \phi\text{-}CH{=}C(CH_3)_2 + CH_3CH{=}\underset{\phi}{C}\text{-}CH_3 + (CH_2)_2\overset{CH_3}{\underset{\phi}{C}}$$

I II III IV V

Run[c]	mmoles I	% N_2	% II[a]	Total % hydrocarbon	% III[b]	% IV[b]	% V[b]
12	86	75	54	35	49	8.5	43
15	85	70	45	36	51	9.0	40

[a] Found: C, 81.95; H, 8.08. Calc. for $C_{20}H_{24}N_2$: C, 82.14; H, 8.27.

[b] Expressed as percentage of total hydrocarbons.

[c] Total number of runs investigated was 15.

The hydrocarbons were isolated by distillation under reduced pressure. The possibility of double bond migration in III and IV, as well as stereo isomeric forms of IV rendered the resolution of this mixture difficult. Indeed the infrared spectra indicated the presence of terminal olefin. By hydrogenation of the mixture and subsequent analytical scale gas chromatography the percentage of 1-methyl-1-phenylcyclopropane, V, and an unresolved mixture of iso- and sec-butylbenzene were determined. The mixture of iso-

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[2a] W.H. Urry and M.S. Kharasch, J.Amer.Chem.Soc. 66, 1438 (1944); [b]S. Winstein and F.H. Seubold, Ibid. 69, 2916 (1947); [c]W.H. Urry and N. Nicolaides, Ibid. 74, 5163 (1952); [d]F.H. Seubold, Ibid. 75, 2532 (1953).

and sec-butylbenzene was isolated by preparative scale VPC and determined by comparison of its infrared spectrum with that of mixtures of the authentic hydrocarbons. The percentage composition of the isolated mixture of iso- and sec-butylbenzene was further verified by a differential infrared spectrum and the near identity of its index of refraction with that of the mixture of authentic hydrocarbons. A differential infrared spectrum of the complete hydrogenated mixture further substantiated the percentage of 1-methyl-1-phenylcyclopropane.

The most interesting aspect of these results is that the phenyl/methyl migration aptitude in this rearrangement is about 10:1. This can be contrasted with the lack of methyl migration in radical rearrangements[2,3] and the 3000-300:1 phenyl/methyl migration aptitudes characteristic of normal carbonium ion rearrangements.[1d] This result is consistent with the postulate that the carbenic intermediate is a highly reactive electrophilic species.[4] Although the agreement is fortuitous, it is of interest to note that Curtin[5] stated that 10 is a conservative estimate for the phenyl/methyl migration ratio in the deamination of 1-amino-2-phenylpropanol-2, a rearrangement of the type postulated to proceed via the very reactive "Hot" carbonium ion.[6]

Another interesting aspect of these results is the 1.2 ratio of phenyl migration to insertion product. A great predominance, as high as 19:1, of hydrogen migration to insertion product from a variety of systems has been noted by other workers.[7] From these results a <u>tentative</u> order of migration

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[3] M.A. Muhs, <u>Diss.Abstr.</u> <u>14</u>, 765 (1954).

[4] R.C. Woodworth and P.S. Skell, <u>J.Amer.Chem.Soc.</u> <u>81</u>, 3383 (1959).

[5] D.Y. Curtin and S. Schmukler, <u>J.Amer.Chem.Soc.</u> <u>77</u>, 1107 (1955).

[6] J.D. Roberts, C.C. Lee, W.H. Sounders Jr., <u>J.Amer.Chem.Soc.</u> <u>76</u>, 4501 (1954). A. Streitwieser Jr., <u>J.Org.Chem.</u> <u>22</u>, 861 (1957). D.J. Cram and J.E. McCarty, <u>J.Amer.Chem.Soc.</u> <u>79</u>, 2866 (1957).

[7] L. Friedman and H. Shechter, <u>J.Amer.Chem.Soc.</u> <u>81</u>, 5512 (1959); <u>Ibid.</u> <u>82</u>, 1002 (1960); L. Friedman and J. Berger, <u>Ibid.</u> <u>83</u>, 501 (1961). G.L. Closs, Abstracts of Papers presented at the 138th Meeting of the <u>Amer.Chem.Soc.</u>, September, 1960, New York, p. 9-P.

aptitudes, hydrogen phenyl methyl, might be postulated for carbene rearrangements. This order is not inconsistent with that observed in rearrangements that proceed via carbonium ions.[8]

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[8] C.K. Ingold, Structure and Mechanism in Organic Chemistry pp. 475-477. Cornell University Press, Ithaca (1953).