

Thermally Induced [3,3] Sigmatropic Rearrangement of *N*-Allylhydrazones

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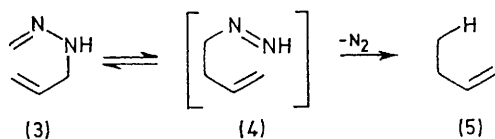
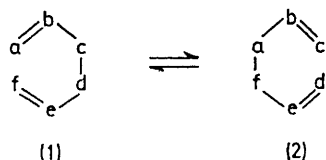
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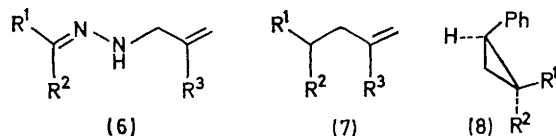
Summary The pyrolysis of various *N*-allylhydrazones (6) yields three types of products—allylated hydrocarbons (7), cyclopropanes (8), and radical fragmentation and combination products.

THE [3,3] sigmatropic rearrangement, (1) ⇌ (2), is known to be a useful tool in synthesis, *e.g.*, the Claisen and Cope rearrangements.¹ Whereas rearrangements involving a hetero-atom have been investigated extensively, few such reactions have been recorded in which two or more hetero-atoms are part of the rearranging system.² In this connection the equilibrium (3) ⇌ (4) appeared especially intriguing in view of the known tendency of monoalkyldiazines (4) to decompose into nitrogen and hydrocarbons.³ Since (3) is a keto-derivative, its transformation into (5) constitutes a simple method for the conversion of a carbonyl group into an allylmethine unit (Scheme 1).⁴



SCHEME 1

The hydrazones were prepared by the interaction of several carbonyl compounds with allylhydrazines, which, in turn, were obtained by alkylation of hydrazine with various allylic halides. A preliminary study of the pyrolysis

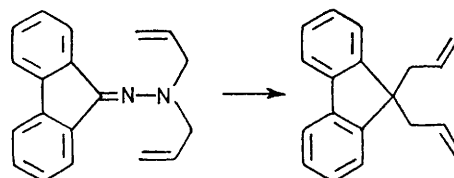


- a; R¹=R²=Ph, R³=H
 b; R¹+R²=*o,o'*-biphenyl, R³=H
 c; R¹=H, R²=Ph, R³=H
 d; R¹=R²=Me, R³=H
 e; R¹=Me, R²=Ph, R³=H
 f; R¹=H, R²=Ph, R³=Me
 a; R¹=Me, R²=H
 b; R¹=R²=H
 c; R¹=CHD₂, R²=Me

of the allylhydrazones in the Table was undertaken to determine the effect of temperature, various solvents, and catalysts. No significant catalytic effect was noted, and triethylene glycol was selected as solvent for all reactions. Three types of pyrolysis products were obtained—allylated hydro-

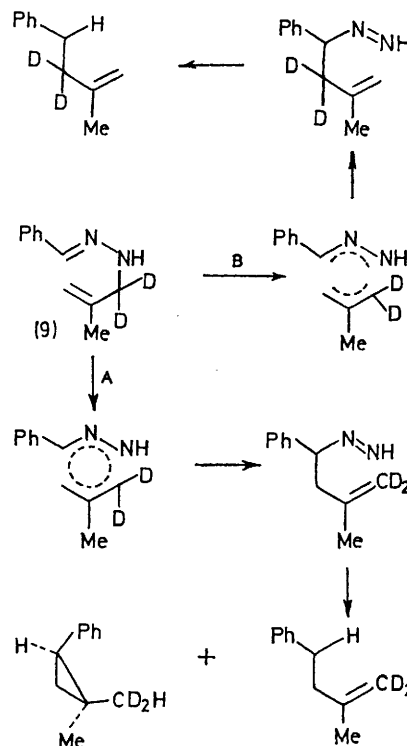
carbons (7), radical fragmentation and recombination products, and, unexpectedly, cyclopropanes (8). Highest yields of (7) were observed in the thermolysis of aromatic ketohydrazones.

It is apparent from the isolation of products derived from radical fragmentation and recombination that the reactions studied were not entirely concerted, if concerted at all, and suggested the novel possibility that two allyl units could be transferred onto the same carbon site by employing a bis-allylhydrazone. This was realized in one case studied, in 76% yield (Scheme 2).



SCHEME 2

In a separate experiment labelled hydrazone (9) was pyrolysed at 300°. The 2-methyl-4-phenylbut-1-ene isolated retained 91% of the label at the 1-position (¹H n.m.r.



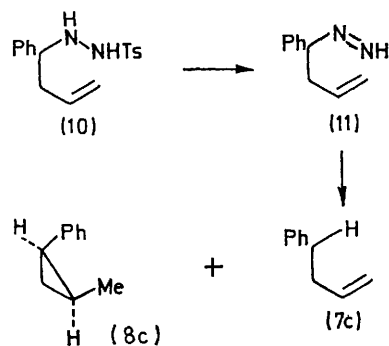
SCHEME 3

analysis). Thus, at least 82% of the rearrangement proceeded *via* a synchronous mechanism (Path A) and a maximum of 18% by a label scrambling route (possibly Path B) (Scheme 3).

TABLE. Thermolysis of triethylene glycol solutions of allylhydrazones.

Hydrazone	Product	T/°C	Time/h
(6a)	56% (7a); 20% Ph ₂ CH ₂	300	8
b	32% (7b); 13% 9,9'-difluorenyl	210	0.5
c	28% (7c); 8% (8a)	300	1.5
d	6% (7d); 5% diallyl	300	3
e	no (7e)	275	1
f	(7f) + (8b)	300	0.75

Convincing evidence that both olefinic and cyclopropane products arise from the same intermediate monodiazine (11) was obtained from the pyrolysis³ of tosylhydrazone (10) at 100° in ethylene glycol until nitrogen evolution ceased. Compounds (7c) and (8c) were the only volatile products produced in this reaction (Scheme 4).



SCHEME 4

The support of the Robert A. Welch Foundation is acknowledged.

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¹ Cf. A. Jefferson and F. Scheinmann, *Quart. Rev.*, 1968, **22**, 391.

² R. H. DeWolfe and W. G. Young, 'Allylic Reactions,' in 'The Chemistry of Alkenes,' ed. S. Patai, vol. I, Interscience, New York, 1964, p. 681.

³ E. M. Kosower, *Accounts Chem. Res.*, 1971, **4**, 193.