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THE THERMAL REARRANGEMENT OF PHENYLNITRENE TO CYANOCYCLOPENTADIENE

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The remarkable generation of cyclopentadienyl radicals by the thermal or photochemical decarbonylation of phenoxy radicals has been documented by mass spectrometric, (1a, b) flash photolytic (2) and chemical techniques (3). Thermally generated anilino (4) and phenylthiyl (5) radicals also fragmented to cyclopentadienyl radicals at temperatures greater than 850°, thus suggesting that this type of reaction might be general for aryl radicals at high temperatures. With this in mind, we have discovered an interesting variant of this thermal process involving phenylnitrene in which ring contraction occurs without fragmentation (6).

Our specific interest in the ring contraction of phenylnitrene resulted from mass spectrometric experiments where phenyl azide was thermally decomposed at low pressures (ca. 10^{-3} Torr) and short contact times (ca. 1 msec) in a fused-silica capillary furnace coupled directly to the ionization chamber of a mass spectrometer (7). Initially, the mass spectrum for phenyl azide with the oven cold and with use of low energy electrons for simplicity consists in part of peaks at m/e 119 ($C_6H_5N_3$), m/e 93 ($C_6H_5NH_2$), and m/e 91 (C_6H_5N). Upon heating, the peak corresponding to the parent (m/e 119) decreased starting at 300°. The 91 peak similarly decreased in intensity up to 500° and then increased to a maximum at 800°. The 93 peak increased throughout this range. Dimers at m/e 182 and 184 increased to a maximum at 550° and then decreased although some still remained at 800°. The appearance potential (AP) of m/e 91 was found to depend on the pyrolysis temperature; 25°, 9.1 ev; 500°, 9.25 ev; 800°, 9.7 ev.

The observed behavior and the results of previous investigations (8) suggest the following reactions:

$$C_6H_5N_3 \longrightarrow C_6H_5N: + N_2 \qquad (1)$$

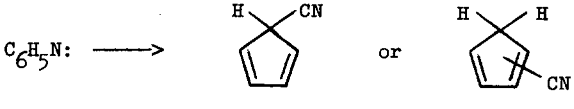
$$2\ C_6H_5N: \longrightarrow C_6H_5N{=}NC_6H_5\ (m/e\ 182) \qquad (2)$$

$$C_6H_5N: + H\ (wall) \longrightarrow C_6H_5NH \qquad (3)$$

$$2\ C_6H_5NH \longrightarrow C_6H_5NH{-}NHC_6H_5\ (m/e\ 184) \qquad (4)$$

$$C_6H_5NH^{\cdot} + H\ (wall) \longrightarrow C_6H_5NH_2 \qquad (5)$$

However, the decrease of the dimers at m/e 182 and m/e 184 cannot result from their thermal decomposition, since neither azobenzene nor hydrazobenzene are found to decompose at furnace temperatures as low as 550°. The increase of m/e 91 at 550° coupled with its large increase in appearance potential with increasing temperature suggests that phenylnitrene, which is the presumed precursor for the dimers, is diverted by rearrangement to a non-reactive species (1) starting at about 550° (reaction 6) (9).



1a 1b (6)

An ionization potential (IP) of 9.7 ev (AP (91) at 800°) is reasonable for 1. The electron impact IP for cyclopentadiene in our instrument is 9.0 ev and an increase of 0.75 ev was previously observed for cyanocyclopentadienyl radical compared to cyclopentadienyl (1b), thus suggesting that IP for cyanocyclopentadiene should be about 9.7 ev as observed.

Cyanocyclopentadiene was confirmed by its chemical isolation and characterization using the technique of flash vacuum pyrolysis (FVP) (3). In these experiments phenyl azide was pyrolyzed in a large oven (3) at conditions closely duplicating those of mass spectrometric experiments and the pyrolysate was rapidly quenched on the surface of a large liquid N_2-cooled Dewar. The quenched pyrolysate was then separated by vacuum distillation into a volatile and involatile portion which were then characterized by chromatography (preparative glpc and/or elution). The data of Table 1 summarizes the results of these experiments. Cyanocyclopentadiene was characterized by conversion to the sodium salt by the method of Webster (10), the nmr in trifluoroacetic acid and deuterochloroform solvents, and the mass spectrum of its dimer. The rapid dimerization of 1 (6,10) was minimized by keeping it at low temperatures or in dilute solution throughout isolation and analytical procedures. Where necessary, the analytical data (Table 1) were corrected for dimerization. Unsuccessful attempts were

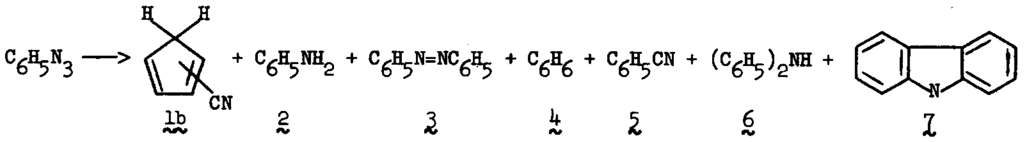


TABLE 1

FVP of Phenyl Azide[a]

	Product Distribution (%)[c]						
T°C	1[b]	2	3	4	5	6	Involatile Residue[c]
600	9	4	2	7	3	2	38
650	24	2	4	7	1	4	31
700	46	3	2	9	2	3	27
700	50	4	1	7	3	3	27
700[d]	49	4	1	5	2	3	19
750	45	3	0.4	8	2	3	24

a) Average pressure in oven was about 0.07 Torr; rate of sample introduction was about 3 mg/min; contact time was about 3 msec; analysis by glpc.

b) Corrected for varying amounts of dimerization.

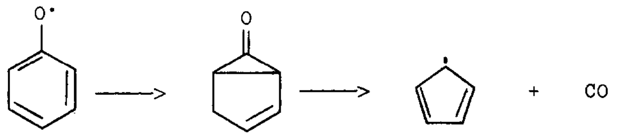
c) Mole % yields except for involatile residue which is wt. involatile residue/initial sample wt. x 100.

d) Pyrolysate was quenched in an ammonia matrix.

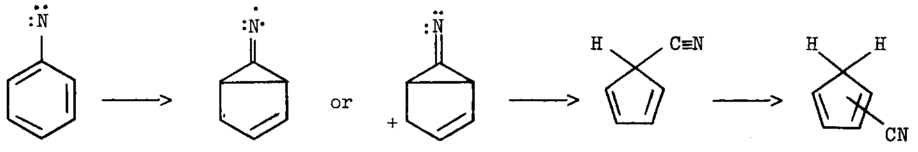
made to detect the 5-substituted isomer (1a) by low temperature nmr. The question of whether the isolated cyanocyclopentadiene is the 1 or 2-isomer or a mixture of both was not resolved (11). The other products were identified by comparison with authentic samples utilizing ir, nmr, uv, and glpc retention times. The carbazole (7) which was generated in lower yields than azobenzene, was isolated by elution chromatography and could not be conveniently determined by glpc. The involatile residue represents the uncharacterized, black, amorphous portion of the material remaining on the quenching Dewar surface. The reproducibility of the data is exemplified by the series of experiments at 700°. In one case (row 5, Table 1), the pyrolysate was mixed with a large excess of ammonia gas before quenching at -196° (matrix isolation). By using this isolation technique, we were able essentially to eliminate the dimerization of cyanocyclopentadiene in subsequent vacuum distillations without otherwise altering the product distribution.

These data show that the yield of cyanocyclopentadiene increased markedly with temperature, while the yields of the other characterized products varied insignificantly. Furthermore, we were able to isolate only one dimeric product of phenylnitrene (azobenzene). However, the decrease in involatile residue does qualitatively parallel the increase in cyanocyclopentadiene yield. We tentatively conclude that the cyanocyclopentadiene, as well as the aniline and azobenzene, and at least a part of the involatile residue result from phenylnitrene. Quenching conditions are being sought which will eliminate the involatile residue. Interesting precursors of benzene, benzonitrile, diphenylamine and carbazole can be proposed but these are more speculative (12). Preliminary results suggest that the yield of benzonitrile increases with pressure. The absence of significant effects on the product distribution when the pyrolysate was quenched in an ammonia matrix suggests that most of the products are formed before quenching.

One attractive scheme for the decarbonylation of phenoxy radical involves the intermediate **8**. By analogy, we suggest that the rearrangement of phenylnitrene involves **9**. The



8



9 **1a** **1b**

phenylnitrene must initially be formed in the singlet state. Its subsequent rearrangement can involve either the singlet state or the triplet ground state (14), while it is believed (15) that hydrogen abstraction and dimerization involve the triplet state. It is noteworthy that the rearrangement of phenylnitrene appears to occur at a lower temperature than the corresponding phenoxy radical decarbonylation (3).

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9. We can speculate on our failure to detect ØN: by low energy ionization. The essentially invariant AP (91) of 9.1 ev in the temperature range 25-500° may correspond to formation of a rearranged ion of much lower energy than that of ØN: which may have an IP greater than 9.1 ev. A high IP (ØN:) is suggested by IP (NH) which is 13.1 ev (Foner and Hudson, *J. Chem. Phys.*, **45**, 40 (1966)). Alternately, the gas phase dissociation of phenyl azide may be exothermic in which case AP (ØN:) would be less than IP (ØN:). The sensitivity for detection of ØN: would be correspondingly low. IP (ØN:) may also be greater than that of cyanocyclopentadiene (**1**) which would further reduce the sensitivity for detection of ØN: by low energy electrons.
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11. Nmr evidence (10) suggests that protonation of sodium cyclopentadienide by trifluoroacetic acid results in 2-cyanocyclopentadiene. The isomer resulting from thermal isomerization of 5-cyanocyclopentadiene would be predicted to be 1-cyanocyclopentadiene on the basis of the Woodward-Hoffmann rules (11a) and by analogy to methylcyclopentadiene (11b); a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965); b) S. McLean and R. Haynes, *Tetrahedron Letters*, 2385 (1964).
12. The following reactions have been considered for these products:

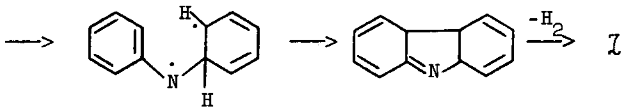
$$2\ C_6H_5N: \longrightarrow C_6H_5N{=}NC_6H_5^{*} \xrightarrow{\text{in part}} C_6H_5\cdot \ + \ \cdot N_2C_6H_5 \qquad (1)$$

$$C_6H_5N_2\cdot \longrightarrow C_6H_5\cdot \ + \ N_2 \qquad (2)$$

$C_6H_5\cdot \quad + \quad \text{wall} \longrightarrow C_6H_6$ (3)

$C_6H_5\cdot \quad + \quad CNC_5H_5 \longrightarrow C_6H_5CN \quad + \quad C_5H_5\cdot$ (4)

$C_6H_5N: \quad + \quad C_6H_6 \longrightarrow (C_6H_5)_2NH$ (5)



(6)

Reactions 1, 2, and 3 reasonably account for the substantial yield of benzene and imply that collisional deactivation of excited azobenzene is relatively inefficient at our low pressures. The detection of cyclopentadienyl radicals by esr[13] in the quenched pyrolysate from azobenzene offers some evidence for reaction 4 which is best rationalized as involving an addition-elimination sequence. We are not aware of any previous evidence for intermolecular insertion or addition reactions (5 and 6 respectively) involving phenylnitrene.

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