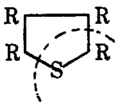
TABLE II

RATIOS OF LOSS TO RETENTION OF LABEL IN IONS IN THE SPECTRA OF LABELED TETRAPHENYLTHIOPHENES III AND IV

Ion and intensity in TPT	Ions compared	Ratio in III	Ratio in IV
77 ($C_6H_5^+$), 3%	95:77	0.6	2
121 ($C_6H_5CS^+$), 6%	139:121	0.9[a]	3[a]
165 ($C_{13}H_9^+$), 8%	201:183:165	*b*	*b*
267 (M − C_6H_5CS), 4%	285:303	1.0[c]	2.5[c]
278 (M − C_6H_6S), 4%	296:314	1.0[c,d]	1.1[c,d]
310 (M − C_6H_6), 6%	328–346	1.0[c,e]	1.7[c,e]

[a] Metastables of similar intensity ratio connect these to the molecular ion. [b] The peaks at 165 and 201 are buried in a rich doubly charged spectral region; the *m/e* 183 is at least a factor of 6 larger than either of these. [c] The ions formed by loss of the unsubstituted fragment (*m/e* 303, 314, 346) are taken as reference peaks. [d] The metastable for *m/e* 424 → 314 is present; the one for *m/e* 424 → 296 is buried in a doubly charged spectral region, and intensity comparisons cannot be made. [e] Both metastables (424 → 346, 328) are present but are distorted by other peaks.

which in the absence of experiments like these could have been formulated without formation of new bonds, as in V. The amount of scrambling is greater for the loss of the elements of benzene if this fragmentation is ascribed to direction by the heteroatom; here the process requires formation of a new C–H bond even at an elementary level of interpretation. Finally, the loss of C_6H_6S, a process requiring even more reorganization before fragmentation, shows almost complete equivalence of the different ring positions. All these observations fit a picture in which rearrangement is competitive with fragmentation, and in which obviously more complex pathways form products more slowly, so that a greater fraction of the products indicate a loss of positional identity. No comparison can be made with the loss of acetylene from thiophene,[2] since the analogous fragmentation does not occur in these compounds.



V

Our results extend those of Williams and support the photochemical analogy which he proposed.[2] On the one hand, the fact that heavy groups scramble like hydrogens in the thiophenes is accommodated by a process of formation of new bonds between C and S atoms of the ring, not simply hydrogen and aryl migrations about an intact thiophene nucleus. They support his concept of competitive rearrangement and fragmentation, particularly by contributing new kinds of fragmentations unavailable to the simple deuteriated molecules. Finally, they demonstrate the utility of the *p*-fluoro labeling technique as an adjunct in the determination of reaction mechanisms where some ambiguity possibly remains because of alternate interpretations of hydrogen–deuterium labeling results. The technique can also be applied to other systems, for example, quinones[11] and thiophene dioxides.[12] It does have limitations; it is impossible to use it to study scrambling in hexaphenylbenzene and pentaphenylpyridine, for example, because of the lack of sufficiently intense fragment ions in the spectra of these compounds.

Experimental Section

Mass spectra were recorded on a Hitachi RMU-6E instrument at 70 eV, with an ionizing current of 80 μA; the samples were introduced on the direct probe at temperatures between 60 and 100°. Melting points were determined on a Thomas–Kofler apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Samples of 2,4-bis(*p*-fluorophenyl)-3,5-diphenylthiophene (III) and 2,5-bis(*p*-fluorophenyl)-3,4-diphenylthiophene (IV) had been prepared in the course of another investigation.[12]

2,4-Bis(*p*-fluorophenyl)-3-diphenylfuran (I) was prepared from 2,4-bis(*p*-fluorophenyl)-3,5-diphenylcyclopentadienone[13] by singlet oxygen oxidation[14] to the substituted *cis*-dibenzoylstilbene, which was converted without isolation into the furan with Zn dust in refluxing acetic acid.[15] Chromatography on alumina and crystallization from ethanol gave product of mp 179–181°.

Anal. Calcd for $C_{28}H_{18}F_2O$: C, 82.33; H, 4.44. Found: C, 82.41; H, 4.43.

2,5-Bis(*p*-fluorophenyl)-3,4-diphenylfuran (II), mp 173–176°, was prepared analogously from 2,5-bis(*p*-fluorophenyl)-3,4-diphenylcyclopentadienone.[13]

Anal. Calcd for $C_{28}H_{18}F_2O$: C, 82.33; H, 4.44. Found: C, 82.41; H, 4.28.

Registry No.—I, 18741-99-6; II, 18749-93-4; III, 18742-00-2; IV, 18742-01-3.

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Internal Diels–Alder Additions of 13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraenes

ALEXANDER L. JOHNSON AND HOWARD E. SIMMONS

*Contribution No. 1494 from the Central Research Department,
E. I. du Pont de Nemours and Company, Inc.,
Wilmington, Delaware 19898*

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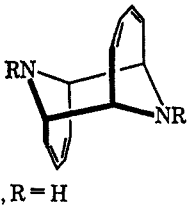
The syntheses of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (**1a**) and its derivatives from 1-cyanoazepine were reported previously.[1] Attempts



1a, R = H
b, R = $CH_2CH{=}CH_2$
c, R = $CH_2CH_2CH{=}CH_2$

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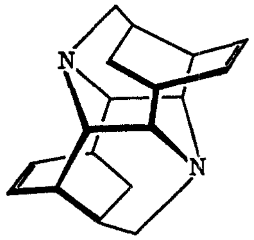
(1) (a) A. L. Johnson and H. E. Simmons, *J. Amer. Chem. Soc.*, **88**, 2591 (1966); (b) A. L. Johnson and H. E. Simmons, *ibid.*, **89**, 3191 (1967).

to form Diels–Alder adducts between simple derivatives of **1a** and external dienophiles were unsuccessful, presumably because of the rigidity of the system. By restricting the motion of the dienophile, internal Diels–Alder condensations have now been observed. In the 13,14-diallyl (**1b**) and 13,14-bis(3-butenyl) derivatives (**1c**),[1] the terminal double bond of the substituent will react with the conjugated diene system at 180° to give low to fair yields of more highly condensed products.

Examination of molecular models suggests that **1b** would be more likely to react in the mode indicated by formula **2**, whereas **1c** would be more likely to react in the opposite sense, *e.g.*, **3**. Stable products were isolated by hydrogenation of the thermal reaction mixtures of **1b** and **1c** and are assigned the respective structures **4** and **6**. Compound **4** is the parent compound of the new 19,20-diazaheptacyclo-$[6.4.2^{3,6}.2^{9,12}.1^{1,8}.1^{2,7}.1^{13,19}.1^{17,20}]$eicosane ring system and compound **6** is the 17-butyl derivative of the new 17,18-diazapentacyclo$[6.4.2^{3,6}.2^{14,17}.1^{1,8}.1^{2,7}]$octadecane ring system. Both structures **4** and **6** consist entirely of relatively strainless six- and seven-membered rings, and are stable, distillable materials. The alternative structures **5** and **7** were ruled out from the mass spectra of these compounds. Generally, the principal fragment seen in the mass spectra of 13,14-diazatricyclo-$[6.4.1.1^{2,7}]$tetradecane derivatives **8** is the protonated half-parent ion[1] ($^1/_2$ M + 1). For structure **5**, therefore, we would expect to find a low-intensity parent ion (M = 270) and a high intensity ($^1/_2$M + 1) peak. In the compound derived from **1b**, however, the base peak is the parent ion (M = 270); instead of having the clearcut fragmentation of the type described above, intense groups of peaks are found throughout the spectrum, *e.g.*, near *m/e* 190 (53.1%), 189 (50.6%), 175 (20.7%), 148 (40.7%), 136 (23.1%), 122 (26.3%), 106 (23.2%), 94 (28.5%), 80 (32.5%), 67 (31.6%), 53 (25.0%) and 41 (52.9%). This can be explained by the very rigid and compact structure **4**.



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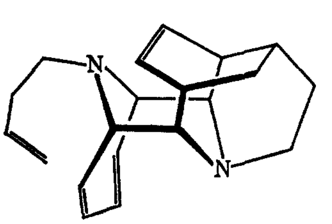

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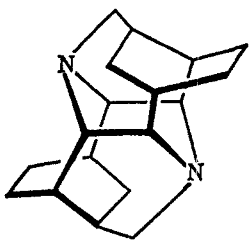

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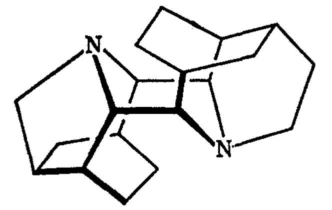

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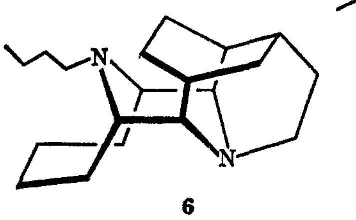

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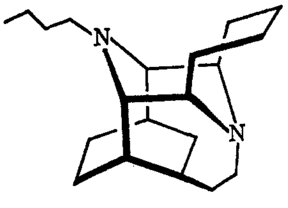

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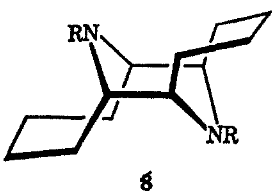

8

In the compound derived from **1c**, the parent ion (M = 302, 11.3%) cleanly loses a propyl fragment from the 17-butyl group (M − C_3H_7 = 259, 100%) and undergoes substantial cleavage of the central bonds with moderately intense peaks at *m/e* 154 (12.2%), 152 (10.5%), 151 (13.6%) and 107 (23.5%).

Experimental Section[2]

19,20-Diazaheptacyclo$[6.4.2^{3,6}.2^{9,12}.1^{1,8}.1^{2,7}.1^{13,19}.1^{17,20}]$eicosane (4).—13,14-Diallyl-13,14-diazatricyclo$[6.4.1.1^{2,7}]$tetradeca-3,5,9,-11-tetraene (**1b**) (1 g) was degassed and sealed *in vacuo*. After it had been heated at 180° for 2 hr, the tube was cooled and the contents were dissolved in 150 ml of 90% methanol containing 1% of hydrochloric acid. This mixture was hydrogenated over platinum oxide (1.0 g) in a Parr shaker at 25° for 16 hr. The methanol was stripped from the filtered hydrogenation mixture, and the aqueous concentrate was made basic with sodium hydroxide and filtered. The crude residue (0.31 g) was sublimed twice at 100° (0.1 mm) to give pure 19,20-diazaheptacyclo-$[6.4.2^{3,6}.2^{9,12}.1^{1,8}.1^{2,7}1^{13,19}.1^{17,20}]$eicosane (**4**): mp 164–167°; no $\lambda_{max}^{CH_3OH}$ 205–400 mμ; ν_{max}^{KBr} 2995, 2985, 2955, 2915, 2895, 2870, 2860, 2790, 1470, 1455, 1440 and 1425 cm^{-1}.

Anal. Calcd for $C_{18}H_{26}N_2$: C, 79.95; H, 9.09; N, 10.36; mol wt, 270.41. Found: C, 79.92; 80.05; H, 9.09, 9.00; N, 10.64, 10.66; mol wt, 270; M + 1/M = 0.1998 (theory[3] 0.2063).

17-Butyl-17,18-diazapentacyclo$[6.4.2^{3,6}.2^{14,17}.1^{1,8}.1^{2,7}]$octadecane (6).—The thermal reaction was carried out as above with 0.85 g of 13,14-bis(3-butenyl)-13,14-diazatricyclo$[6.4.1.1^{2,7}]$tetradeca-3,5,9,11-tetraene (**1c**).[1] Short-path distillation of the crude thermal product at 100° (0.1 mm) gave 0.2 g of an unstable colorless oil. This was 17-(3-butenyl)-17,18-diazapentacyclo-$[6.4.2^{3,6}.2^{14,17}.1^{1,8}.1^{2,7}]$octadeca-4,9,11-triene (**3**): $\nu_{max}^{CCl_4}$ 3060 and 1645 cm^{-1} ($CH{=}CH_2$ and $C{=}C$); δ ($CDCl_3$) 6.3–5.5 and 5.2–4.8 (nine vinyl protons), 3.4 (four tertiary bridgehead protons next to nitrogen), 2.85 (four NCH_2 protons), 2.5–2.0 (nine protons).

Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.58; H, 8.90. Found: C, 81.30, 81.38; H, 8.84, 8.96.

A total of 20.38 g of the bis(3-butenyl) derivative **1c** was heated in two batches at 180° for 3 hr. The crude product was immediately hydrogenated as described above. The methanol was stripped, the concentrate was basified with sodium hydroxide and extracted with chloroform. The residue obtained from the dried extracts was purified by short-path distillation at 120° (0.1 mm): yield 4.66 g (27%) of the viscous liquid 17-butyl-17,18-diazapentacyclo$[6.4.2^{3,6}.2^{14,17}.1^{1,8}.1^{2,7}]$octadecane (**6**); $\nu_{max}^{CCl_4}$ 2960, 2930, 1540 and 1450 cm^{-1}; no $\lambda_{max}^{CH_3OH}$ 205–400 mμ; δ (CCl_4) 3.40–1.91 (four NCH_2 and four tertiary bridgehead protons next to nitrogen), 1.80–1.20 (23 methylene and methine protons), 1.0 (three CH_3 protons).

Anal. Calcd for $C_{20}H_{34}N_2$: C, 79.41; H, 11.33; mol wt, 302. Found: C, 79.15; H, 11.57; mol wt, 302; M + 1/M = 0.2150 (theory[3] 0.2292).

Registry No.—**3,** 18746-03-7; **4,** 18746-04-8; **6,** 18746-05-9.

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[2] Melting points are uncorrected and were determined in a Mel-Temp capillary apparatus. Infrared spectra were determined on a Perkin-Elmer 221 instrument and ultraviolet spectra on a Cary Model 14 instrument. Nuclear magnetic resonance spectra were determined on a Varian Associates A-60 spectrometer and mass spectra on a CEC 21-103 spectrometer.

[3] J. H. Beynon and A. E. Williams, "Tables for Use in Mass Spectroscopy," Elsevier Publishing Co., Amsterdam, The Netherlands, 1963.