

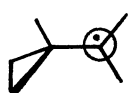
HOMOALLYLIC REARRANGEMENTS OF 4-SPIRO[2.4]HEPTYL RADICAL AND
4-SPIRO[2.5]OCTYL RADICAL

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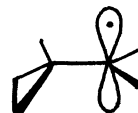
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Irradiation of azobis(4-spiro[2.4]heptane) and azobis(4-spiro[2.5]octane) afforded homoallylically rearranged products via the corresponding titled radicals, in which the rigid geometry locks the cyclopropylcarbiny radical in the stable bisected conformation.

Homoallylic rearrangement of cyclopropylcarbiny radicals into allylic radicals has been the subject of much interest.¹⁻⁶⁾ Recent studies of the cyclopropylcarbiny radical and related anion and cation radicals by esr spectroscopy have revealed that the cyclopropyl group preferentially adopts the bisected conformation 1 rather than the perpendicular conformation 2.⁶⁻⁹⁾ Further, Kochi indicated that the conversion of the cyclopropylcarbiny radical to the homoallylic radical requires the perpendicular conformation rather than the bisected conformation.⁶⁾ In view of this point, the chemical reactivities of 4-spiro[2.4]heptyl radical(3) and 4-spiro[2.5]octyl radical(4) are of interest since the structural rigidity would preclude the possibility of the perpendicular conformation.



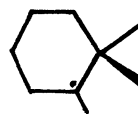
1



2



3



4

As precursors of the radical 3 and 4, the corresponding symmetrical azo compounds were prepared. There are several lines of convincing evidence that, for symmetrical azomethanes, decomposition occurs by a concerted, two-bond cleavage.¹⁰⁻¹² Spiro[2.4]heptan-4-one azine (5, mp 38.5-39,) ¹³ and spiro[2.5]octan-4-one azine (6, mp 86.5-87.5,) ¹³ were prepared on treatment of the corresponding ketones with hydrazine hydrate in yields of 80 % and 70 %, respectively. Treatment of 6 with lithium aluminum hydride in ether at reflux afforded azobis(4-spiro[2.5]octane) (8) ¹³ in 89 % yield: ν (cyclopropane) 3070, 1010 cm^{-1} , $\lambda_{\text{max}}^{\text{n-hexane}}$ 360 nm (ϵ 27), nmr δ 0.10-1.00 (m, 8H), 1.25-2.50 (m, 16H), and 2.75-3.16 (m, 2H). On the contrary, conversion of 5 to azobis(4-spiro[2.4]heptane) (7) was quite difficult. Thus, 5 was recovered on treatment with LiAlH_4 , $\text{H}_2/\text{Raney-Ni}$, and H_2/Pd , respectively, whereas the cyclopropane suffered ring-opening under more severe reduction conditions. The only successful condition was hydrogenation of 5 over platinum oxide in acetic acid at 11.5 atm at ambient temperature. Elution of the reaction mixture on alumina with n-hexane afforded 7 (mp 60-61,) ¹³ in 20 % yield: ν (cyclopropane) 3070, 1004 cm^{-1} , $\lambda_{\text{max}}^{\text{n-hexane}}$ 360 nm (ϵ 24), nmr δ 0.41 (s, 8H), 1.30-2.40 (m, 12H), 3.00-3.30 (m, 12H).

Irradiation of a solution of 7 (11 mmole/l) in n-hexane with a 500 w high-pressure mercury arc for 12 hr effected clean conversion into five products, ¹⁴ subsequently identified as 1-octylcyclopentene (9, 10 %), bis(spiro[2.4]heptan-4-yl) (10, 9 %), 2-[2-(1'-cyclopentyl)ethyl]spiro[2.4]heptane (11, 40 %), and bis(2-(1'-cyclopentyl)ethyl) (12, 18 %). These products were identified on the basis of their characteristic spectral properties as shown in Table 1.

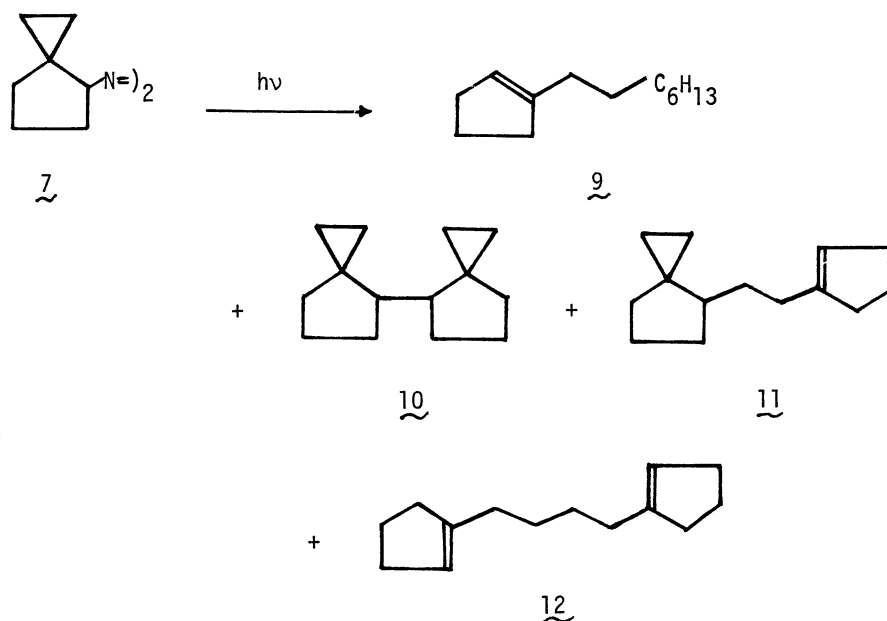
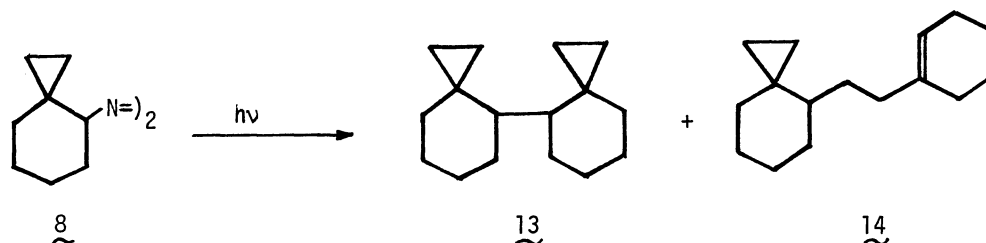


Table 1. Spectral Data of the Photo-products of Azo Compounds, 7 and 8

Compounds	mass (m/e)	ir (cm ⁻¹) ^{a)}	nmr (δ)
<u>9</u>	180	1620	0.65-1.0 (m, 6H), 1.0-2.4 (m, 17H), 5.24 (m, H)
<u>10</u>	190	3060, 1000	0.1-0.6 (m, 8H), 1.0-2.0 (m, 14H)
<u>11</u>	190	3060, 1650, 1000	0.0-0.7 (m, 4H), 0.8-2.5 (m, 17H), 5.25 (m, H)
<u>12</u>	190	1650	1.2-2.45 (m, 20H), 5.24 (m, 2H)
<u>13</u>	218	3070, 1005	0.0-0.8 (m, 8H), 1.1-2.4 (m, 18H)
<u>14</u>	218	3060, 1660, 1000	0.1-0.3 (m, 4H), 0.6-2.2 (m, 21H), 5.3 (m, H)

a) The absorptions near 1650 cm⁻¹ are caused by the stretching vibration of the C=C group, and others by the C-H stretching vibration of the cyclopropane.

Furthermore, irradiation of the azo compound 8 gave bis(spiro[2.5]octan-2-yl) (13, 39 %) and 2-[2-(1'-cyclohexenylethyl)]spiro[2.5]octane (14, 37 %). The structures of 13 and 14 rest on their spectral characterization.



These results can be rationalized by assuming spiro radicals, 3 and 4. The rigid geometry of the radical 3 locks the cyclopropylcarbonyl radical in the stable bisected conformation. Kochi suggested⁶⁾ that homoallylic rearrangement requires a $\pi/2$ rotation about the R₂C-cyclopropyl bond in the bisected conformation, resulting in interaction of p-orbital of the odd electron with the ring antibonding orbital. The ring opening of 3 would be strongly retarded because of the rigid geometry. However, a considerable amount of products derived from homoallylic rearrangement (9, 11 and 12) was obtained. Further, radical 4 is more flexible and therefore less locked into the bisected conformation, and hence homoallylic rearrangement of 4 should occur more easily than that of 3. Nevertheless, the result was inverse. Thus, the ratio of the products bearing a cyclopropyl ring to those derived from cleavage of a cyclopropane was $(2 \times \underline{10} + \underline{11})/(\underline{11} + 2 \times \underline{12} + \underline{9}) = 0.67$ for 3 and $(2 \times \underline{13} + \underline{14})/\underline{14} = 3.1$ for 4.

These results indicate that the conversion of the cyclopropylcarbonyl radical to the homoallylic radical does not necessarily require the perpendicular conformation. The effects of the cyclopropane to the radical seem to be manifestation of the ring strain.^{4,15)} The esr study of these radicals is under investigation.

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