References and Notes

(1) Paper XVII: H. E. Smith, A. W. Gordon, and A. F. Bridges, *J. Org. Chem.*, **39**, 2309 (1974).
(2) (a) Vanderbilt University; (b) Tennessee State University.
(3) National Science Foundation Undergraduate Summer Fellow, 1973.
(4) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products", Pergamon Press, New York, N.Y., 1964, pp 165 and 166.
(5) G. Horvath and A. I. Kiss, *Spectrochim. Acta, Part A*, **23**, 921 (1967).
(6) P. A. Mullen and M. K. Orloff, *J. Chem. Phys.*, **51**, 2276 (1969).
(7) "UV Atlas of Organic Compounds", Vol. V, Plenum Press, New York, N.Y., 1971, G1/4.
(8) H. E. Smith, L. J. Schaad, R. B. Banks, C. J. Wiant, and C. F. Jordan, *J. Am. Chem. Soc.*, **95**, 811 (1973).
(9) J. M. Patterson, L. T. Burka, and M. R. Boyd, *J. Org. Chem.*, **33**, 4033 (1968).
(10) H. E. Smith and H. E. Ensley, *Can. J. Chem.*, **49**, 2902 (1971).
(11) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 4050 (1968).
(12) J. Del Bene, H. H. Jaffe, R. L. Ellis, and G. Kuehnlenz, "CNDO/S-CI Molecular Orbital Calculations with the Complete Neglect of Differential Overlap and Configuration Interaction", Program 174, Quantum Chemistry Program Exchange (QCPE), Indiana University, Bloomington, Ind.
(13) Magnetic transition moments were calculated according to the method described by J. Linderberg and J. Michl, *J. Am. Chem. Soc.*, **92**, 2619 (1970).
(14) J. Ridley and M. Zerner, *Theor. Chim. Acta*, **32**, 111 (1973).
(15) J. A. Schellman, *Acc. Chem. Res.*, **1**, 144 (1968).
(16) E. G. Hohn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).
(17) G. J. Karabatsos and D. J. Fenoglio, *Top. Stereochem.*, **5**, 167 (1970).
(18) W. H. Inskeep, D. W. Miles, and H. Eyring, *J. Am. Chem. Soc.*, **92**, 3866 (1970).
(19) Details of the coupled oscillator calculation with transition bond moment approximations can be found in ref 18.
(20) J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966).
(21) J. N. Murrell and A. J. Harget, "Semi-empirical self-consistent-field molecular orbital theory of molecules", Wiley-Interscience, New York, N.Y., 1972, p 46.
(22) P. Salvadori, L. Lardicci, R. Menicagli, and C. Bertucci, *J. Am. Chem. Soc.*, **94**, 8598 (1972).
(23) C. Djerassi, "Optical Rotatory Dispersion", McGraw-Hill, New York, N.Y., 1960, pp 164–167.
(24) H. E. Smith, S. L. Cook, and M. E. Warren, Jr., *J. Org. Chem.*, **29**, 2265 (1964).

High Pressure Studies. XVII.
Thermal Decomposition of Cyclic Azo Compounds[1,2]

Robert C. Neuman, Jr.,* and Ernest W. Ertley[3]

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. Received October 3, 1974

Abstract: The effects of pressure on the decomposition of the cyclic azo compounds, *cis*-3,6-diphenyl-3,4,5,6-tetrahydropyridazine (**1**), *cis*-3,7-diphenyl-1,2-diaza-1-cycloheptene (**2**), and *cis*-3,8-diphenyl-*cis*-1,2-diaza-1-cyclooctene (**3**), have been investigated in toluene at 60 or 65°. Kinetic studies give decomposition activation volumes for **1** and **2** of ca. +5.5 cm³/mol, while that for **3** is +7.1 cm³/mol. Product studies from 1 to 5000 atm show that the ratio of styrene to 1,2-diphenylcyclobutane from **1** decreased from 1.4 to 1.1, while the ratio of *cis*- to *trans*-1,2-diphenylcyclobutane increased from 2.5 to 4.6. The ratio of 1,5-diphenyl-1-pentene to 1,2-diphenylcyclopentane from **2** increased from 0.2 to 0.4, while the ratio of *cis*- to *trans*-1,2-diphenylcyclopentane increased slightly from 1.1 to 1.2. The ratio of 1,6-diphenyl-1-hexene to 1,2-diphenylcyclohexane products from **3** increased from 0.9 to 1.3, but the *cis*- to *trans*-1,2-diphenylcyclohexane ratio *decreased* from 1.0 to 0.6. The results are interpreted in terms of simultaneous two-bond scission of **1** and **2** to give the intermediate carbon diradicals as primary products. The data for **3** suggest one-bond C–N scission with the formation of a diazenyl diradical as the first diradical intermediate.

One mechanism for decomposition of cyclic azo compounds might be one-bond scission to give an unstable diradical (k_1) which could lose nitrogen (k_β) in competition with reclosure (k_{-1}) (eq 1).[4,5] If this occurred, we thought

$$N{=}N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N{=}N\cdot \overset{k_\beta}{\longrightarrow} N{\equiv}N \qquad (1)$$
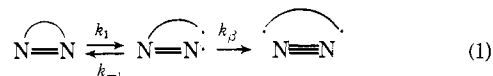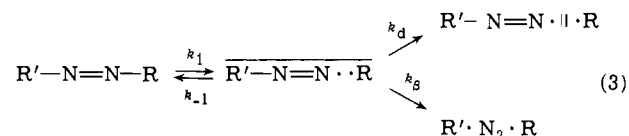
that it might be kinetically detectable by the effect of pressure on the decomposition rates.[6] The apparent activation volume for decomposition (eq 2) would depend not only on

$$\Delta V^*_{obsd} = \Delta V_1^* + RT\partial \ln (1 + k_{-1}/k_\beta)/\partial P \qquad (2)$$

that for the homolysis step (ΔV_1^*) but also on the pressure dependence of the competition between closure (k_{-1}) and β scission (k_β). Since that ratio might be expected to increase with increasing pressure [radical combination and homolytic scission (k_β) being accelerated and retarded, respectively, by pressure],[6] values of ΔV^*_{obsd} for such cyclic azo compounds would be larger than those for cyclic systems where concerted loss of nitrogen led directly to the final diradical shown in eq 1.

A basis for these assumptions is found in our observations

that activation volumes for decomposition of *acyclic* azo compounds are relatively small and constant when nitrogen is lost concertedly and much larger for a series of phenylazotriphenylmethanes (PhN=NCPh₃) which decompose via initial scission of just the N–CPh₃ bond (Table I).[7] However, it is likely that a substantial part of this difference for acyclic systems is due to a high-pressure effect on separative diffusion (k_d, eq 3).[6,8,9] The observed activation volume

$$R'{-}N{=}N{-}R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overline{R'{-}N{=}N\cdot\cdot R} \overset{k_d}{\underset{k_\beta}{\begin{array}{c}\nearrow R'{-}N{=}N\cdot\,\text{II}\cdot R \\ \searrow R'\cdot N_2\cdot R\end{array}}} \qquad (3)$$

for acyclic systems (eq 4) differs from that for cyclic systems (eq 2) by the inclusion of the rate constant k_d in the

$$\Delta V^*_{obsd} = \Delta V_1^* + RT\partial \ln [1 + k_{-1}/(k_\beta + k_d)]/\partial P \qquad (4)$$

differential term. Since pressure retardation of k_d is much greater than any effect on k_β, it is conceivable that the differential term in eq 4 is substantially greater than the analogous term in eq 2.

Table I. Activation Volumes for Decomposition of Acyclic Azo Initiators (R—N=N—R')

R	R'	T, °C	Solvent	ΔV^*, cm^3/mol
Me$_2$C(CN)		70	Toluene	+4[a]
Me$_2$C(Ph)		55	Cumene	+5.0[b]
			Chlorobenzene	+4.3[b]
Me$_2$C(p-MePh)		55	Cumene	+4[b]
Me$_3$CO		55	n-Octane	+4.3[c]
Ph$_3$C	p-NO$_2$Ph	60	Cumene	+20[b]
			n-Octane	+18[b]
			tert-Butylbenzene	+21[b]

[a] A. H. Ewald, *Discuss. Faraday Soc.*, 22, 138 (1956). [b] R. C. Neuman, Jr., G. D. Lockyer, Jr., and M. J. Amrich, *Tetrahedron Lett.*, 1221 (1972). [c] R. C. Neuman, Jr., and R. J. Bussey, *J. Am. Chem. Soc.*, 92, 2440 (1970).

The effects of pressure on the thermal decomposition rates and products of the cyclic azo compounds 1–3 have
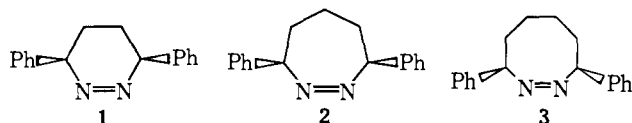
been investigated, and the results are reported here.[10] The data are consistent with ultimate formation of the carbon diradicals (4, x = 2–4), and it seems most likely that compounds 1 and 2 lose nitrogen in a concerted process. The
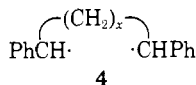
pounds 1 and 2 lose nitrogen in a concerted process. The magnitude of the decomposition activation volume for 3, however, is slightly greater than those for 1 and 2. Together with an unusual dependence of its product ratios on pressure, the data for 3 are not inconsistent with one-bond scission as generally outlined in eq 1.

Results

Six-Membered Azo Compound. Both the synthesis and thermal decomposition of 1 (cis-3,6-diphenyl-3,4,5,6-tetrahydropyridazine) were complicated by the formation of the cyclic hydrazone 5. The facile rearrangement of 1 to 5 (eq 5) has been well documented.[11] Its presence during synthesis

(5)
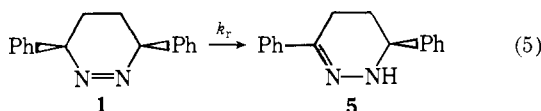
thesis was demonstrated by isolation and characterization, while its formation during kinetic runs was apparent from its uv absorbance band at 285 nm. Rate constants for loss of 1 at 60.0° in toluene followed by monitoring its uv λ_{max} at 383 nm are the sum of those for homolytic scission (k_{N_2}) and for rearrangement (k_r) (Table II). Attempts by uv to determine the concentrations of hydrazone formed during the kinetic runs were not successful, and the low concentrations of azo compound in these runs (0.004 M) precluded GLC analysis of the infinite time samples. However, GLC analyses of completely decomposed toluene solutions (60°) initially 0.1 M in azo compound permitted the determination of the absolute yields of all hydrocarbon products (Table III). These data were used to extract values for k_{N_2} assuming that hydrazone 5 was the only additional product, and that hydrocarbon products arose only from homolytic scission (k_{N_2}), and that the same amount of rearrangement occurred in the kinetic samples and in the more concentrated product samples. This latter supposition is supported by a comparison of the apparent decomposition rate constants determined by us at 64.7° (ethylbenzene) using uv (0.004

Table II. Rate Constants for Thermal Decomposition of 1 in Toluene

P, atm	T, °C	k_{obsd}[a] × 10^5, sec^{-1}	k_{N_2}[b] × 10^5, sec^{-1}	k_r[c] × 10^5, sec^{-1}	% HC[d]
1	60.0	7.85 ± 0.05	6.63	1.22	84.5
1350	60.0	7.19 ± 0.31	5.42	1.77	75.4
2310	60.0	6.16 ± 0.16	4.28	1.88	69.4
3300	60.0	5.48 ± 0.20	3.51	1.97	64.0
4290	60.0	4.62 ± 0.20	2.74	1.88	59.2
5260	60.0	4.70 ± 0.17	2.59	2.11	55.2
1[e]	60.0	8.37 ± 0.10			
1[e]	64.7	14.6 ± 0.3			
1[e,f]	64.7	13.1 ± 0.2			
1[e-g]	64.7	10			

[a] Determined by uv analysis except as indicated. [b] $k_{N_2} = (k_{obsd})$· (% HC) × 10^{-2}. [c] $k_r = k_{obsd} - k_{N_2}$. [d] Calculated from a smoothed graph of the data given in Table III. [e] Solvent, ethylbenzene. [f] Determined by gas evolution. [g] K. Kopecky and S. Evani, *Can. J. Chem.*, 47, 4041 (1969).

Table III. Product Yields from Decomposition of 0.1 M Solutions of 1 in Toluene (60°)

	% yield[a,b]			
		1,2-Diphenylcyclobutane		Total[c]
P, atm	Styrene	Cis	Trans	% HC
1	41.5	41.7	16.8	84.5
1350	37.4	46.3	16.3	74.2
2310	38.1	47.9	13.9	69.1
3300	38.3	49.1	12.6	73.8
4290	35.3	52.1	12.6	62.6
5260	35.8	52.6	11.5	53.7
1[d]	41.6	41.0	17.4	

[a] Normalized to 100%; additionally, we detected 1-phenyltetralin in about 0.5% yield at all pressures. [b] All yields represent per cent of azo compound giving rise to the particular product. [c] Based on the yield of styrene and cis- and trans-1,2-diphenylcyclobutane; the hydrazone 5 is presumed to constitute the bulk of the product balance. [d] Solvent, benzene; 64°; K. Kopecky and S. Evani, *Can. J. Chem.*, 47, 4041 (1969).

M) and gas evolution (0.05 M) (Table II). The gas-evolution rate constant is k_{N_2}, while the uv value is $k_{N_2} + k_r$. The results indicate 11% rearrangement in the low-concentration uv sample, comparable to the results obtained for the more concentrated product sample.

Decomposition of 0.1 M solutions of 1 in toluene at 60° with added p-ethylstyrene at 1 and 4100 atm did not lead to any loss of p-ethylstyrene. This indicates that the nonquantitative hydrocarbon yields were not the result of polymerization of the reaction product styrene.

Kopecky studied both the rates and products of decomposition of 1.[11] Our kinetic results and product yields at atmospheric pressure are in reasonable agreement with his data (Tables II and III).

Seven-Membered Azo Compound. In contrast with 1, thermal decomposition of 2 (cis-3,7-diphenyl-1,2-diaza-1-cycloheptene) was not complicated by competing rearrangement to a hydrazone. Nitrogen evolution at atmospheric pressure was quantitative, no absorption band characteristic of hydrazone was visible in any uv spectra, and product yields monitored by GLC were essentially the same at each pressure. Rate constants for thermolysis of 0.0067 M solutions of 2 in toluene were determined at 65° by monitoring the decrease in the azo band at 395 nm (Table IV). Products were analyzed using totally decomposed solutions initially 0.1 M in 2. Yields were calculated assuming identical thermal conductivities of the three isomeric products and normalized to 100% (Table V).

Overberger has previously studied the decomposition of this compound.[12] Our kinetic data are in agreement with

Table IV. Rate Constants for Thermal Decomposition of 2 in Toluene[a]

P, atm	T, °C	$k_{obsd} \times 10^5$, sec^{-1}
1	65.0	8.02 ± 0.04
1190	65.0	6.16 ± 0.06
2290	65.0	5.01 ± 0.05
3230	65.0	4.19 ± 0.05
4180	65.0	3.38 ± 0.03
5220	65.0	3.02 ± 0.05
1[b]	65.0	7.88 ± 0.02
1	60.0	4.13 ± 0.04
1[c,d]	61.0	3.80

[a] Determined by uv analysis. [b] Determined by gas evolution. [c] Solvent, xylene. [d] C. G. Overberger and J. G. Lombardino, J. Am. Chem. Soc., 80, 2317 (1958).

Table V. Product Yields from Decomposition of 0.1 M Solutions of 2 in Toluene (65°)

	% yield[a]		
	1, 5-Diphenyl-1-pentene	1, 2-Diphenylcyclopentane	
P, atm		Cis	Trans
1	16.8	44.2	39.0
1330	20.6	41.1	38.3
2330	23.1	40.8	36.1
3310	24.5	40.1	35.4
4220	25.8	40.5	33.7
5220	27.4	39.5	27.4
1[b,c]	20	35	45

[a] Normalized to 100%; calculated from GLC analyses assuming identical thermal conductivities. [b] Solvent, xylene, 132°. [c] C. G. Overberger and C. Yaroslavsky, Tetrahedron Lett., 4395 (1965).

his (Table IV), but the product data from his study at a much higher temperature show an inverted ratio of cis- to trans-1,2-diphenylcyclopentane compared with our results (Table V).[13]

Eight-Membered Azo Systems. Synthesis of 3,8-diphenyl-1,2-diaza-1-cyclooctene gave a major and minor product which had, respectively, been assigned the trans-diphenyl (6) and cis-diphenyl (3) geometries by Overberger.[14] In agreement with his observations, we found that 3 decomposed at a convenient rate at 60° (Table VI), while the other isomer was exceptionally stable (2.6 × 10^{-7} sec^{-1}, toluene, 90°). This stability precluded high-pressure studies
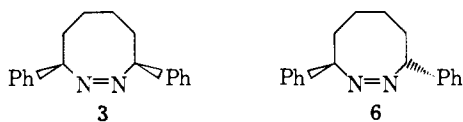
of its thermal-decomposition kinetics, and data are available only for 3 whose rate constants were determined using 0.010 M solutions by following the disappearance of the azo band at 385 nm. Like 2, hydrazone formation was not observed, and the yields of the hydrocarbon products from 0.10 M solutions of 3 were quantitative (Table VII). In this case, as with 1, the reaction products were individually isolated and used to calibrate the GLC analyses of the decomposition reaction mixtures.

It seemed strange to us that the reactivities of 3 and 6 should be so different. Ultimately, we noted that, while the uv azo band of 3 (λ_{max} 385, ϵ 125) was similar to those of 1 (λ_{max} 383, ϵ 300) and 2 (λ_{max} 395 nm, ϵ 178), that for the "trans" isomer of the eight-membered system (λ_{max} 367, ϵ 45) was much more like those found for acyclic azo compounds (e.g., azocumene,[15] λ_{max} 365, ϵ 45). Since the latter have a trans geometry about the azo linkage, we concluded that the "trans" eight-membered isomer was not 6, but most probably 7. Subsequently, this proposal was strengthened by observations of Overberger.[16]

Table VI. Rate Constants for Thermal Decomposition of 3 in Toluene[a]

P, atm	T, °C	$k_{obsd} \times 10^5$, sec^{-1}
1	60.0	4.82 ± 0.03
1088	60.0	3.61 ± 0.03
2120	60.0	2.72 ± 0.01
3075	60.0	2.19 ± 0.02
4170	60.0	1.64 ± 0.02
5440	60.0	1.46 ± 0.03
1[b,c]	60.0	5.04 ± 0.02
1[b,c]	70.0	16.8 ± 0.1
1[b,c]	80.0	52.7 ± 0.7
1[b,d,e]	80.0	23

[a] Determined by uv analysis except as indicated. [b] Determined by gas evolution. [c] ΔH^*, 25.1 kcal/mol; ΔS^*, +3 eu. [d] Solvent, tetralin. [e] C. G. Overberger et al., J. Am. Chem. Soc., 91, 3226 (1969).

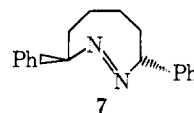Table VII. Product Yields from Decomposition of 0.1 M Solutions of 3 in Toluene (60°)

	% yield[a]			
	1,6-Diphenyl-1-hexene	1,2-Diphenyl-cyclohexane		
P, atm		Cis	Trans	Total
1	46.8	25.9	27.3	98
1090	49.4	23.2	27.4	97
2120	51.3	21.0	27.7	99
3080	52.3	19.6	28.1	95
4170	53.5	18.3	28.2	99
5440	55.5	16.8	27.7	99
1[b]	47.5	24.0	28.5	
1[c,d]	32.6	15.7	51.7	93

[a] Individual product yields normalized to 100%; total yield is that actually calculated from the experimentally determined yields of the individual products. [b] Solvent, tetralin; 60°. [c] Solvent, tetralin; no temperature reported. [d] C. G. Overberger et al., J. Am. Chem. Soc., 91, 3226 (1969).

Table VIII. Product Yields from Photolysis and High-Temperature Thermolysis of 3 and 7

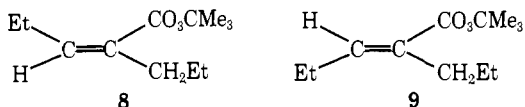| Compd and conditions	P, atm	% yield[a]			
		1,6-Di-phenyl-1-hexene	1,2-Diphenyl-cyclohexane		
			Cis	Trans	Total
3, hv, 25°[b]	1	57.9	23.8	18.8	97
	1390	66.7	18.3	15.0	102
	2690	71.1	15.7	13.1	99
	1[c,d]	63.0	20.0	17.0	
7, hv, 25°[b]	1	42.4	26.3	31.4	102
	1390	50.0	22.2	27.8	101
	2690	57.2	17.8	25.1	99
	1[d,e]	64.6	15.4	20.0	
3, Δ	1[f]	40.0	30.1	29.9	100
	1[d,g]	30.4	14.7	48.3	
7, Δ	1[f]	47.5	26.3	26.1	
	1[d,g]	50.4	16.6	27.9	

[a] See footnote a, Table VII. [b] Solvent, toluene except as noted. [c] Solid-state photolysis, 19°. [d] C. G. Overberger et al., J. Am. Chem. Soc., 91, 3226 (1969). [e] Solid-state photolysis, 0°. [f] Solvent, toluene, 134°. [g] Solvent, tetralin, no temperature reported.

Although kinetic data for 7 were not obtained, product yields for its thermal decomposition were determined from 0.1 M samples thermolyzed at high temperatures (Table VIII). In addition, product yields from the photochemical decomposition of both 3 and 7 at atmospheric and high pressure have been determined using a high-pressure optical cell (Table VIII).

Discussion

Rates of decomposition of all three azo compounds are decreased by increasing pressure. The effects on **1** and **2** appear to be about the same, while **3** is retarded to a greater extent (Figure 1). The activation volumes for **1** and **2** (ca. +5.5 cm³/mol) are very similar to those observed for decomposition of acyclic azo radical initiators which decompose by simultaneous two-bond scission (Table I). Thus, these data are compatible with a two-bond scission mechanism for **1** and **2** or a one-bond scission process (eq 1) in which return (k_{-1}) does not occur. The larger value of ΔV^* for **3** could indicate decomposition via one-bond scission (eq 1) with return ($k_{-1} > 0$) and an increase in the ratio k_{-1}/k_β with increasing pressure (eq 2). While the value of +7 cm³/mol for ΔV^*_{obsd} is substantially less than those observed for acyclic azo compounds known to undergo one-bond scission with return,[17] it is comparable to values of ΔV^*_{obsd} for decomposition of a pair of isomeric *tert*-butyl vinyl peresters (**8**, +6.8 cm³/mol; **9**, +9.0 cm³/mol) which

$$\underset{H}{\overset{Et}{>}}C=C\underset{CH_2Et}{\overset{CO_3CMe_3}{<}}\qquad\underset{Et}{\overset{H}{>}}C=C\underset{CH_2Et}{\overset{CO_3CMe_3}{<}}$$
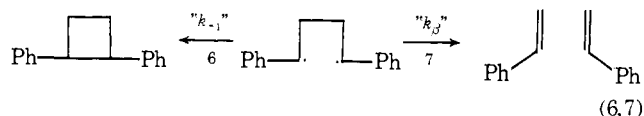$$\textbf{8}\qquad\qquad\qquad\textbf{9}$$

most certainly decompose via one-bond scission with some geminate return.[18] When one-bond scission occurs in open-chain systems, a range of values of $\Delta V^*_{obsd} > \Delta V^*_1$ is expected depending on the magnitude and pressure dependence of $k_{-1}/(k_\beta + k_d)$ (eq 4).[6] Thus, a value of +7 cm³/mol for **3** could accommodate a "return mechanism" particularly since separative diffusion of the radical centers in a diradical does not occur to the extent expected when the radicals are not connected.

If one assumes that ΔV^*_1 for decomposition of **3** is in the range of +5 to +6 cm³/mol,[19] the quantity $RT\partial \ln (1 + k_{-1}/k_\beta)/\partial P$ (see eq 2) would by necessity range from +1 to +2 cm³/mol. It is not possible to calculate unique values of k_{-1}/k_β as a function of pressure without knowing the atmospheric pressure value of k_{-1}/k_β. Therefore, using a range of arbitrary values of $(k_{-1}/k_\beta)_0$, we have calculated corresponding groups of values of $(k_{-1}/k_\beta)_P$. These have then been used to calculate differences in the activation volumes for diradical closure and β scission ($\Delta V^*_{-1} - \Delta V^*_\beta$). Some representative values of this $\Delta\Delta V^*$ are given in Table IX for values of ΔV^*_1 equal to +5.0, +5.5, and +6.0 cm³/mol.[19]

The values of $\Delta\Delta V^*$ (Table IX) are negative in agreement with the expectation that activation volumes for radical combination (ΔV^*_{-1}) and homolytic scission (ΔV^*_β) are negative and positive, respectively,[6] and their magnitudes are not unreasonable. We have shown that activation volumes for single-bond homolysis can be in the vicinity of +5 cm³/mol[6,8] and, if this were the case for ΔV^*_β, some of the results in Table IX would accommodate small negative values of ΔV^*_{-1}. These correspond to low values for $(k_{-1}/k_\beta)_0$ where recyclization is relatively unimportant compared with β scission.

The product data for decomposition of **1** also provide a model for $\Delta\Delta V^*$. The pressure dependence of the ratio of cyclobutanes to styrene gives the difference in activation volumes for diradical closure and β scission (eq 6,7); from

$$\text{Ph}\underset{\substack{6}}{\overset{"k_{-1}"}{\longleftarrow}}\text{Ph}\quad\text{Ph}\underset{7}{\overset{"k_\beta"}{\longrightarrow}}\underset{\text{Ph}}{\overset{}{\nearrow}}\quad\underset{\text{Ph}}{\overset{}{\parallel}}$$
$$(6,7)$$

these data, a value for $\Delta V^*_{-1} - \Delta V^*_\beta$ between −1 and −2 cm³/mol is estimated. While this range is consistent with some results shown in Table IX for **3**, it corresponds to high
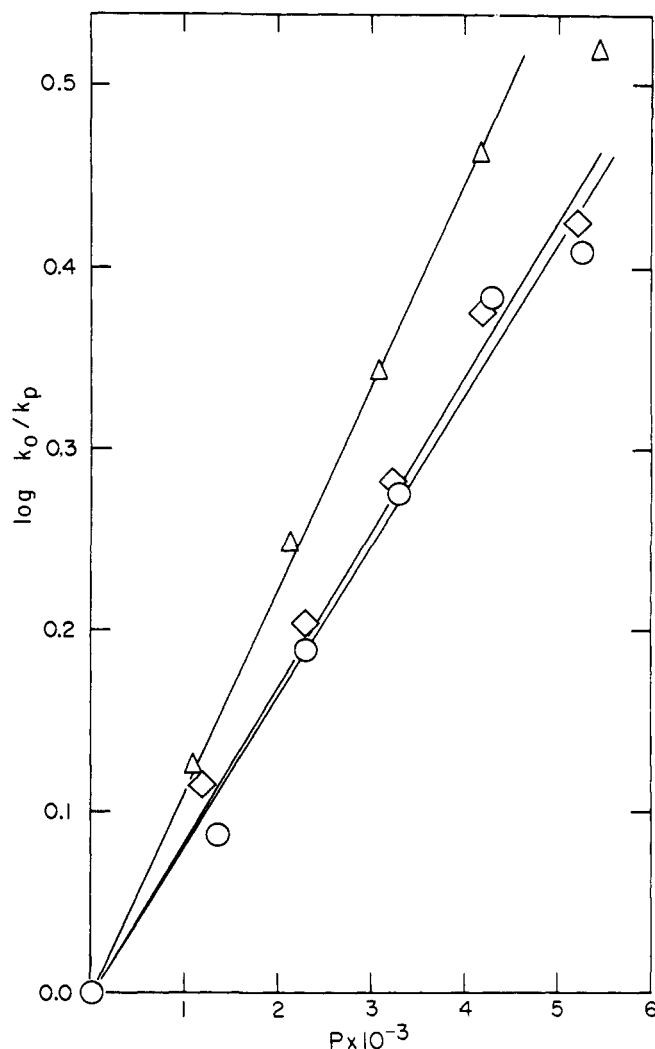

Figure 1. Pressure dependence of the rates of decomposition of the cyclic azo compounds **1** (O, 60°), **2** (◊, 65°), **3** (△, 60°) in toluene.

Table IX. Calculated Values of $\Delta V^*_{-1} - \Delta V^*_\beta$ for Decomposition of **3** (60°) as a Function of $(k_{-1}/k_\beta)_0$ and ΔV^*_1

	$\Delta V^*_{-1} - \Delta V^*_\beta{}^{a,b}$		
$(k_{-1}/k_\beta)_0$	$\Delta V^*_1 = +5.0$	+5.5	+6.0
0.1	−9	−9	−7
0.5	−5	−4	−3
1.0	−4	−3	−2
10.0	−2	−2	−1

^{a}All ΔV^* values in units of cm³/mol. ^{b}Calculated from a least-squares analysis of values of log $(k_{-1}/k_\beta)_P$ and P using the equation $(\Delta V^*_{-1} - \Delta V^*_\beta) = (2.303\ RT/P) \log [(k_{-1}/k_\beta)_0/(k_{-1}/k_\beta)_P]$.

ratios of $(k_{-1}/k_\beta)_0$ where reclosure of diradical **10** occurs much more frequently than loss of nitrogen. However, the behavior of the 1,4 diradical (eq 6,7) may be a poor model for **10**. β scission in the former leads to stable molecules of

$$\text{Ph}\underset{\text{N=N}}{\overset{}{\longleftrightarrow}}\text{Ph}$$
$$\textbf{10}$$
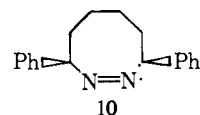
styrene, while the same process from **10** gives another diradical. In terms of Hammond's postulate, more bond stretching would be expected to occur to eliminate nitrogen from **10** than to cleave the C–C bond to give styrene (eq 7). If this were so, the expected larger value of ΔV^*_β for **10** would give a more negative value of $\Delta V^*_{-1} - \Delta V^*_\beta$ than those

Table X. Product Ratios from Thermal Decomposition of 1, 2, and 3 and from Photolysis and High-Temperature Thermolysis of 3 and 7

Compd	P, atm	Cis/trans[a]	Olefin/cis[b]
1[c]	1	2.48	1.00
	1350	2.84	0.81
	2310	3.45	0.80
	3300	3.90	0.78
	4290	4.13	0.68
	5260	4.57	0.68
2[d]	1	1.13	0.38
	1330	1.07	0.50
	2330	1.13	0.57
	3310	1.13	0.61
	4220	1.20	0.64
	5220	1.44	0.69
3[e]	1	0.95	1.81
	1090	0.85	2.13
	2120	0.76	2.44
	3080	0.70	2.67
	4170	0.65	2.92
	5440	0.61	3.30
3, hν[f]	1	1.27	2.43
	1390	1.22	3.64
	2690	1.20	4.53
7, hν[f]	1	0.84	1.61
	1390	0.80	2.25
	2690	0.80	3.21
3, Δ[f]	1	1.00	1.33
7, Δ[f]	1	1.01	1.81

[a] Ratio of cis-cycloalkane product to trans-cycloalkane product. [b] Ratio of olefin product to cis-cycloalkane product. [c] Ratios from data in Table III. [d] Ratios from data in Table V. [e] Ratios from data in Table VII. [f] Ratios from data in Table VIII.

from the 1,4 diradical and a correspondingly smaller value of $(k_{-1}/k_\beta)_0$.

The product data from decomposition of 3 also suggest one-bond scission. In contrast with the other two cyclic azo compounds 1 and 2, the relative amount of trans- compared with cis-cycloalkane from 3 increases with pressure (Table X). This would be consistent with pressure retardation of nitrogen loss from 10 permitting rotation to occur to give 11 (eq 8). This diazenyl radical (11) could then yield 1,2-di-

(8)
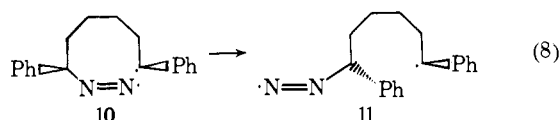
phenylcyclohexane by displacement of nitrogen[4] (a process expected to be pressure accelerated) or by closure of the trans 1,6 diradical resulting from unassisted loss of nitrogen

Scheme I
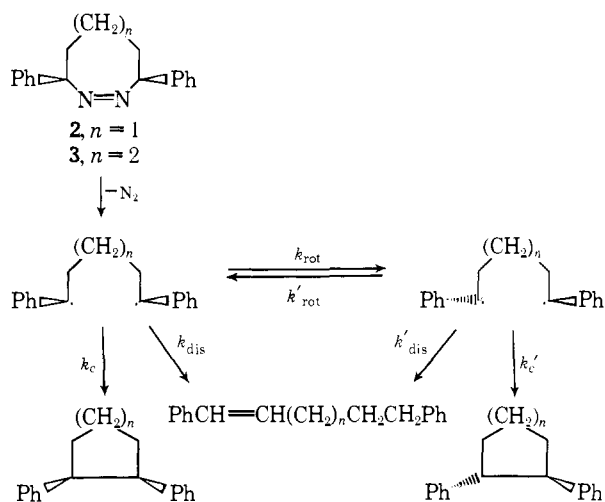
from 11. However, the results should also be examined in terms of a mechanism for product formation not involving diazenyl diradicals. Such a mechanism for 2 and 3 is outlined in Scheme I. A mechanism for 1 differs in that the disproportionation steps are replaced by β scission to give styrene (see eq 7).

Based on Scheme I, the ratio of cis- to trans-cycloalkane formed by decomposition of 2 or 3 depends on the ratio of closure of the "cis" diradical (k_c) compared with its rotation to give the "trans" diradical (k_{rot}) modified by the fraction of the latter which closes (k'_c) to trans-cycloalkane (eq 9).[4] In order to evaluate the various rate ratios, it is nec-

$$\left[\frac{(cis)}{(trans)}\right]_{cis} = \frac{k_c}{k_{rot}\left(\frac{k'_c}{k'_{rot} + k'_{dis} + k'_c}\right)} \quad (9)$$

essary to enter into Scheme I not only from 2 or 3, but also from their corresponding trans isomers. However, the trans-1,2-diphenyl isomer of 2 is apparently unknown,[12] while that from 3 does not have a cis geometry about the azo linkage (see 7). While this does not absolutely preclude 7 from serving as a precursor of the "trans diradical" in Scheme I, it makes this possibility uncertain. A limited amount of data is available for thermolysis of 3 and 7 under the same conditions (Table VIII), and we have attempted to use these product ratios to calculate rate-constant ratios in Scheme I using Bergman's equations.[4] Neither our data, nor those of Overberger, give reasonable results. In particular, negative rate-constant ratios are obtained. This might be expected if 7 did not give the "correct" trans diradical, or if diazenyl diradicals are intermediates in the decomposition of 3 and/or 7.

Although an exact analysis of Scheme I is not possible for either 2 or 3, qualitative considerations can be applied to the kinetic expression for $[(cis)/(trans)]_{cis}$ (eq 10) arising

$$\left[\frac{(cis)}{(trans)}\right]_{cis} = \frac{k_c}{k'_c}\frac{k'_{rot}}{k_{rot}} + \frac{k_c}{k'_c}\frac{k'_{dis}}{k_{rot}} + \frac{k_c}{k_{rot}} \quad (10)$$

from rearrangement of eq 9. It is to be expected that the pressure dependence of each of the rate constants k_c, k_{rot}, and k_{dis} would be essentially the same as that of their respective analogs k'_c, k'_{rot}, and k'_{dis}. Hence the ratios k_c/k'_c and k'_{rot}/k_{rot} should be constant with changing pressure. While the magnitude of the changes is not clear, it would seem that both of the ratios k'_{dis}/k_{rot} and k_c/k_{rot} should increase with increasing pressure since cyclization and disproportionation should be accompanied by volume contractions, while rotation might be expected to occur with at least a small volume increase.[20] Thus, we would predict, based on Scheme I, that the ratio $[(cis)/(trans)]_{cis}$ should increase at least slightly with pressure. This trend is observed for 2, but not for 3 (Table X), and the contrast, in our view, provides further evidence for the intermediacy of diazenyl radicals from 3.

The ratio of olefin to cis-cycloalkane based on entry from 2 or 3 to Scheme I depends on the ratios k_{dis}/k_c, k'_{dis}/k'_c and the ratio of trans- to cis-cycloalkane (eq 11). Since for

$$\left[\frac{(olefin)}{(cis)}\right]_{cis} = \frac{k_{dis}}{k_c} + \frac{k'_{dis}}{k'_c}\left[\frac{(trans)}{(cis)}\right]_{cis} \quad (11)$$

2 $[(trans)/(cis)]_{cis}$ decreases slightly with increasing pressure, while there is a big increase in $[(olefin)/(cis)]_{cis}$ (Table X), the rate constant ratios k_{dis}/k_c and k'_{dis}/k'_c must increase indicating that pressure favors disproportionation over cyclization for the diradicals formed from 2. There is a similar increase in disproportionation to cyclization products from 3, and the origin is probably similar to that from 2. However, analysis is complicated if intermedi-

ate diazenyl radicals are present. It is interesting to note that pressure also increases the relative amount of disproportionation to radical coupling between separated radicals.[6,8,21]

The product ratios arising from direct photolysis of **3** (Table X) show the same increase in disproportionation compared with coupling with increasing pressure as seen in the thermolysis experiments (Table X). However, it is interesting to note that the cis/trans ratio is now greater than unity at all pressures and relatively insensitive to pressure. This pressure insensitivity of cis/trans is also observed on photolysis of **7** but, in this case, the cis/trans ratio is less than unity at all pressures. While the data are limited, these results suggest that direct photolysis of **3** (and **7**) might proceed by concerted loss of nitrogen, or that the intermediate diazenyl radicals lose nitrogen via β scission before undergoing other reactions to any significant extent, because they possess excess vibrational energy. In line with Porter's observations, it is conceivable that photolysis of **7** proceeds by isomerization of the *trans*-azo linkage to a cis configuration before homolysis.[22] However, it should be noted that the product data for photolysis of **3** and **7** cannot be fit by Bergman's equations.[4] Just as with thermolysis, negative rate constant ratios are obtained.

The product data from **1** can be analyzed using the broad features of Scheme I and replacing the disproportionation steps (k_{dis}, k'_{dis}) with β-scission reactions which yield styrene (k_{sty}, k'_{sty}). Kopecky has carried out a detailed study of the atmospheric-pressure kinetics and products of decomposition of **1** and its *trans*-1,2-diphenyl isomer.[11] At 63° (solvent, benzene), he calculates that the ratios of rate constants for β scission to coupling from the cis and trans diradicals, respectively, are the similar values 0.56 and 0.73. If it is assumed that the cis and trans diradicals give exclusively *cis*- and *trans*-cycloalkane, respectively, and that pressure affects the ratio of β scission to coupling about the same for the two diradicals, it then follows that the dramatic increase in the *cis/trans*-cyclobutane ratio with increasing pressure is the result of fewer cis diradicals interconverting to trans diradicals with increasing pressure (i.e., a pressure-induced increase of k_c/k_{rot}). Alternatively, the same conclusion arises from an analysis of the pressure dependences of the various rate-constant ratios in eq 12 which

$$\left[\frac{cis}{trans}\right]_{cis} = \frac{k_c}{k'_c}\frac{k'_{rot}}{k_{rot}} + \frac{k_c}{k'_c}\frac{k'_{sty}}{k_{rot}} + \frac{k_c}{k_{rot}} \quad (12)$$

is derived from eq 10 by substitution of k'_{sty} for k'_{dis}. The ratios k_c/k'_c and k'_{rot}/k_{rot} are expected to be independent of pressure, while k'_{sty} and k_c should be retarded and accelerated by pressure, respectively. To accommodate the increase in [cis/trans]$_{cis}$, the rate constant k_{rot} must therefore decrease with pressure, and/or the last ratio k_c/k_{rot} must increase substantially.

It is possible to estimate the pressure effect on the ratios k_{sty}/k_c and k'_{sty}/k'_c using the data of Kopecky and that from Table X if it is assumed that both ratios change with pressure to the same extent. Substitution of the rate constants k_{sty} and k'_{sty} for k_{dis} and k'_{dis} in eq 11 gives eq 13

$$\left[\frac{styrene}{cis}\right] = \frac{k_{sty}}{k_c} + \frac{k'_{sty}}{k'_c}\left[\frac{trans}{cis}\right] \quad (13)$$

which applies to product ratios for decomposition of **1**. If the rate constant ratios change by the same factor α with change in pressure, the variation in α with pressure can be calculated using eq 14 and Kopecky's values of $(k_{sty}/k_c)_0$

$$\left[\frac{styrene}{cis}\right]_p = \alpha_p\left[\left(\frac{k_{sty}}{k_c}\right)_0 + \left(\frac{k'_{sty}}{k'_c}\right)_0\left(\frac{trans}{cis}\right)\right] \quad (14)$$

and $(k'_{sty}/k'_c)_0$ which are 0.73 and 0.56, respectively. Resulting values of α_p (P, atm) are: 1.2 (1 atm), 1.0 (1350, 2310, 3300 atm), 0.9 (4290, 5260 atm).[23] Thus the apparent effect of pressure on these ratios is small but in the predicted direction. Since the acceleration of k_c is small, it is likely that k_{rot} is substantially decreased by pressure for the 1,4 diradical from **1**.

Experimental Section

Solvents. Toluene, ethylbenzene, and pentane were thoroughly washed successively with sulfuric acid, water, and 10% sodium carbonate solution. They were then distilled (over sodium in the case of the aromatic solvents) and stored in brown bottles. Other solvents mentioned below were used without purification.

Glassware. All glassware used in the syntheses of **3,6-diphenyl-3,4,5,6-tetrahydropyridazine (1)** and in the handling of solutions of **1–3** and **7** was cleaned with a 3:1 mixture of sulfuric to nitric acid, rinsed with distilled water, soaked in dilute ammonium hydroxide for several hours, rinsed in distilled water, and thoroughly dried. Glassware cleaned by this procedure minimized the rearrangement of the cyclic azo compounds to their corresponding cyclic hydrazones.

Syntheses. Complete details of the syntheses of **1–3** and **7** have been published (see below), and our detailed procedures are outlined by Ertley.[2a] Particular difficulty was encountered in synthesis of **1** because of the facile rearrangement of **1** to the hydrazone **5**.

cis-**3,6-Diphenyl-3,4,5,6-tetrahydropyridazine (1)** was prepared following the scheme outlined by Kopecky[11a] beginning with the Diels–Alder adduct *cis*-**3,6-diphenyl-1,2-dicarbethoxy-1,2,3,6-tetrahydropyridazine** prepared using the method of Alder and Niklas[24] from a 45-g portion of *trans,trans*-1,4-diphenyl-1,3-butadiene (0.218 mol, Aldrich) and 45 g of diethyl azodicarboxylate (0.258 mol, Aldrich). The resulting solid crude product was recrystallized from glacial acetic acid (Du Pont), filtered, washed with water, and air dried. A second recrystallization from acetic acid yielded 73 g (88%), mp 132–133° (reported[24] 95%, mp 132–133°). Hydrogenation of this compound for 42 hr using the procedure of Kopecky and Evani[11a] gave *cis*-**3,6-diphenyl-1,2-dicarbethoxyhexahydropyridazine**. Recrystallization from methanol–water followed by drying under vacuum yielded 10.2 g (81%) of product, mp 80–84°. Further recrystallization did not raise the melting point (lit.[11a,24] 83–87 and 87°). Treatment of a 3.74-g (0.0098 mol) sample of this compound with concentrated aqueous base, subsequent acidification, and careful neutralization following Kopecky's procedures led to hydrolysis of the carboethoxy groups and decarboxylation to give the azo compound **1**. Long needles of **1** were deposited from an ether solution upon standing at 0° for 24 hr. The crystals were filtered, air dried, and stored under argon at 0°: 1.80 g, 78%; mp 111–113°; λ_{max} 383 nm ϵ 300 (toluene) (reported[11a] λ_{max} 385 nm ϵ 362). The azo compound was 93% pure by gas-evolution studies at 64.7°. All attempts to purify the azo compound by recrystallization, sublimation, and column chromatography failed because of the facile isomerization of **1** to **5**. Abundant yields of **3,6-diphenyl-2,3,4,5-tetrahydropyridazine (5)** were obtained from unsuccessful syntheses of **1**, mp 156–157° (lit.[11a] 157–158°).

cis-**3,7-Diphenyl-1,2-diaza-1-cycloheptene (2)** was prepared following the procedure outlined by Overberger[12a,25] beginning with **1,3-dibenzoylpropane**. The latter compound was prepared by the method of Fuson and Walker;[26] recrystallization from 95% ethanol followed by drying under vacuum gave a 58% yield of ivory-colored crystals, mp 64–66° (lit.[25] 65–67°). Reaction of 50.2 g of 1,3-dibenzoylpropane (0.2 mol) and 10 ml of hydrazine hydrate (0.2 mol, 99%, MCB) in 1200 ml of absolute ethanol followed by recrystallization from ethanol gave 30 g (60%) of **3,7-diphenyl-1,2-diaza-2,7-cycloheptadiene**, mp 161–162° (reported[25] 95%, mp 162.8–164.2°). Recrystallization of the crude **3,7-diphenyl-1,2-diaza-2,7-cycloheptadiene** from acetone as reported by Overberger[25] resulted in a yellow semisolid mass, which could not be purified. Hydrogenation of a 3.5-g sample of this compound, subsequent oxidation of the resulting product with mercuric oxide, followed by recrystallization from methanol gave 0.46 g (13%) of *cis*-**3,7-diphenyl-1,2-diaza-1-cycloheptene (2)**, mp 114.5–115.5° dec, λ_{max} 395 nm ϵ 178 in toluene, 100.6% gas evolution at 65.0° (reported[12a] mp 114–115°, λ_{max} 395 nm ϵ 127 in chloroform).

cis- and "*trans*"-3,8-diphenyl-1,2-diaza-1-cyclooctene (3 and 7) were prepared following procedures outlined by Overberger[14a] beginning with **3,8-diphenyl-1,2-diaza-2,8-cyclooctadiene.**[27] This latter compound was prepared by reaction of a hydrazine solution, prepared from 120 g of potassium acetate (1.2 mol, Baker and Adamson) and 60 g of hydrazine dihydrochloride (0.57 mol, MCB) in 750 ml of ethanol and 210 ml of water, and a suspension of 47.9 g of 1,6-diphenyl-1,6-hexanedione (0.18 mol, Aldrich) in 2.1 l. of ethanol. Recrystallization of the crude yellow product from ethanol followed by a second recrystallization from benzene yielded 37.9 g (81%) of pale-yellow crystals, mp 134–135° (reported[14a] 87% mp 135–136°). Hydrogenation of a 4.6-g sample of this compound and subsequent oxidation of the purified product with mercuric oxide gave after purification a light-yellow solid containing both 3 and 7. This was taken up in 130 ml of *n*-heptane (redistilled, Mallinckrodt) by warming to 55–60° for a few minutes and filtered. Long flat needles of ***cis*-3,8-diphenyl-*cis*-1,2-diaza-1-cyclooctene (3)**, 0.50 g, were deposited upon standing at room temperature overnight. The needles were recrystallized twice from methanol (reagent, redistilled, Mallinckrodt) to yield 0.34 g (3.7%) of 3, mp 116–117° dec, λ_{max} 381 ϵ 125 (toluene), 97% gas evolution at 60.0° [reported[14b] 4.3%, mp 115–116°, λ_{max} 381 ϵ 111 (chloroform)]. Upon cooling the *n*-heptane filtrate to 0°, flat needles of ***trans*-3,8-diphenyl-*trans*-1,2-diaza-1-cyclooctene (7)**, mp 85–87°, were deposited. Recrystallization from methanol yielded 2.0 g (22%) of product, mp 89–90°, λ_{max} 367 ϵ 45 (toluene) [reported[14b] 56%, mp 90–91°, λ_{max} 368 ϵ 45 (chloroform)].

cis- and *trans*-1,2-diphenylcyclobutane were prepared beginning with *trans*-1,2-dibenzoylethylene (Aldrich). This compound was reduced[28] to give **1,2-dibenzoylethane,** mp 144–146° (lit.[28] mp 145–147°), which was further reduced[29] to give **1,4-diphenyl-1,4-butanediol,** mp 88–90° (lit.[29,30] 90–92, 89–90°). Treatment with hydrogen chloride gave **1,4-dichloro-1,4-diphenylbutane,** mp 102–103° (lit.[29] 102–104°), which was converted to **1,2-diphenylcyclobutene,** mp 51–52° (lit.[29] 51–53°), by treatment with sodium in liquid ammonia. Catalytic hydrogenation gave ***cis*-1,2-diphenylcyclobutane,** mp 37–38° (lit.[29] 38–39°). Treatment of this cis isomer with potassium *tert*-butoxide in dimethyl sulfoxide[29] gave an oil which was purified by GLC and shown by NMR to be identical with authentic ***trans*-1,2-diphenylcyclobutane.**[29,31]

1-Phenyltetralin. Beginning with α-tetralone (Aldrich), reaction with phenylmagnesium bromide gave **1-hydroxy-1-phenyl-2,3,4-trihydronaphthalene** which was subsequently dehydrated with 20% sulfuric acid to give **1-phenyl-3,4-dihydronaphthalene,** bp 158° (5 mmHg) [lit.[32] 158–160° (5 mmHg)]. This was catalytically hydrogenated to give 1-phenyltetralin: bp 154–156° (5 mmHg) [lit.[32,33] 154–156° (5 mmHg)]; NMR, τ 2.7–3.4 (multiplet, 9.1 H), 5.94 (triplet, $J = 6$ Hz, 0.93 H), 7.21 (triplet, $J = 6$ Hz, 1.9 H), and 7.70–8.45 (multiplet, 4.0 H).

cis- and *trans*-1,2-diphenylcyclohexane and *trans*-1,6-diphenyl-1-hexene were obtained from decomposition of 7 in refluxing cumene and isolated by preparative GLC. Recrystallization of the product identified as *cis*-1,2-diphenylcyclohexane from ethanol yielded 0.11 g of compound: mp 44.5–45.0° (reported[34,35] mp 46–46.5°); NMR τ 3.02 (singlet, 10.0 H), 6.86 (poorly resolved doublet, 1.9 H), and 7.8–8.7 (multiplet, 8.0 H). Recrystallization from ethanol of the fraction identified as the trans isomer gave 0.13 g of material: mp 51–52° (reported[36] mp 54–55°); NMR τ 3.06 (singlet, 10 H), 7.37 (poorly resolved triplet, 1.9 H), and 7.85–8.82 (multiplet, 8.0 H). The third fraction identified as *trans*-1,6-diphenyl-1-hexene was a colorless liquid: NMR τ 2.62–3.06 (multiplet, centered at τ 2.86, 10 H), 3.70–3.91 (overlapping doublets with some further splitting of the upfield doublet, $J = 15$ Hz, 1.9 H, olefinic protons), 7.30–7.60 (triplet, $J = 7$ Hz, 2 H, benzylic protons), 7.69–8.06 (quartet, $J = 6.6$ Hz, 2 H, allylic protons), 8.15–8.78 (multiplet, 4.2 H). The infrared spectra of the neat liquid showed the following absorption bands: 3040, 3029, 3011, 2960, 2924, 1598, 1491, 1460, 1259, 1075, 1030, 968, 962, 845, 800, 765, 745, and 690 cm^{-1} (reported[14a] 10.35 μ (966 cm^{-1})).

Isomerization of *cis*- to *trans*-1,2-Diphenylcyclohexane. A standard solution was prepared by adding 0.038 g of a 36:64 mixture of *cis*-1,2-diphenylcyclohexane and *trans*-1,2-diphenylcyclohexane to a 2.0-ml portion of dimethyl sulfoxide (distilled and stored over 4A molecular sieve). Half of this solution was combined with a 0.05-g portion of dry potassium *tert*-butoxide, transferred to a dry ampoule, and sealed under vacuum. The sealed ampoule was then

maintained at 90° for 48 hr. Comparison by GLC of the original solution with the sample heated with potassium *tert*-butoxide indicated that a substantial amount of the *cis*-1,2-diphenylcyclohexane had isomerized to *trans*-1,2-diphenylcyclohexane confirming the structural assignments of the cis and trans isomers.[37,38]

High-Pressure Apparatus and Techniques. Thermal decomposition of the azo compounds under pressure for kinetic and product studies was done using solutions of appropriate concentrations in Teflon cells which have been described.[39] Pressure was generated with an apparatus constructed by the Harwood Engineering Co., Walpole, Mass.[39] Samples were analyzed after removal from the pressure apparatus. Photochemical decompositions were carried out using a high-pressure optical cell which has been described[40] and light of wavelength >340 nm.

Product Studies. Products were analyzed by thermal conductivity GLC. Identification and quantitative analysis of all of the products from 1, 3, and 7 were facilitated by the use of authentic samples of these products. Decomposition of 2 gave three products by GLC analysis. They were identified by treatment of a sample of the product mixture with potassium *tert*-butoxide in dimethyl sulfoxide. That compound giving rise to the GLC peak which decreased was assumed to be *cis*-1,2-diphenylcyclopentane, that giving rise to the peak which increased was assumed to be *trans*-1,2-diphenylcyclopentane, while the third peak which was unchanged by treatment with base was assumed to be 1,5-diphenyl-1-pentene. It was also assumed that the relative thermal conductivities of these three products were identical since this was the case for the three products formed from decomposition of 3 (and 7).

Kinetic Studies. Procedures for the kinetic runs have been previously described.[39] The initial concentrations of 0.004, 0.007, and 0.01 M for 1, 2, and 3 were chosen to give initial absorbances of ca. 1.2 at the azo λ_{max}. No difference between degassed or nondegassed samples could be detected in either kinetic or product studies. Kinetic runs were carried out for two or three half-lives and "infinite-time" samples were decomposed for 10 half-lives. All samples were stored at 0° prior to analysis. Analysis was performed using a Cary 14 and quartz minicells (path length 10 mm, volume 0.7 ml, Precision Cells, Inc.). Errors reported for rate constants are those determined from least-squares analysis of the kinetic data.

References and Notes

(1) (a) Part XVI: G. D. Lockyer, Jr., D. Owen, D. Crew, and R. C. Neuman, Jr., *J. Am. Chem. Soc.*, **96**, 7303 (1974). (b) Support by the National Science Foundation is gratefully acknowledged.

(2) (a) Taken from the Ph.D. Dissertation of E. W. Ertley, University of California, Riverside, 1973. (b) Presented at the 1973 Pacific Conference on Chemistry and Spectroscopy, San Diego, Calif., Nov 3, 1973, paper 228.

(3) NDEA Predoctoral Fellow, 1969–1972.

(4) See R. G. Bergman and W. L. Carter, *J. Am. Chem. Soc.*, **91**, 7411 (1969).

(5) One-bond scission in acyclic azo compounds has been well documented: (a) S. Seltzer and F. T. Dunne, *J. Am. Chem. Soc.*, **87**, 2628 (1965); (b) W. A. Pryor and W. K. Smith, *ibid.*, **92**, 5403 (1970); N. A. Porter, M. E. Landis, and L. J. Marnett, *ibid.*, **93**, 795 (1971); K. Takagi and R. J. Crawford, *ibid.*, **93**, 5910 (1971).

(6) See R. C. Neuman, Jr., *Acc. Chem. Res.*, **5**, 381 (1972).

(7) This behavior of phenylazotriphenylmethanes is not restricted to just the *p*-NO$_2$-substituted isomer; unpublished results of G. D. Lockyer from this laboratory.

(8) R. C. Neuman, Jr., and M. Amrich, *J. Am. Chem. Soc.*, **94**, 2730 (1972).

(9) R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 657 (1971).

(10) A preliminary report of the results of decomposition of 1 has been published: R. C. Neuman, Jr., and E. W. Ertley, *Tetrahedron Lett.*, **13**, 1225 (1972).

(11) (a) K. R. Kopecky and S. Evani, *Can. J. Chem.*, **47**, 4041 (1969); (b) K. R. Kopecky and J. Soler, *ibid.*, **52**, 2111 (1974).

(12) (a) C. G. Overberger and J. G. Lombardino, *J. Am. Chem. Soc.*, **80**, 2317 (1958); (b) C. G. Overberger and C. Yaroslavsky, *Tetrahedron Lett.*, 4395 (1965).

(13) Since *trans*-1,2-diphenylcyclopentane is expected to be more stable than the cis isomer, an increase in the trans/cis ratio with increasing temperature would not be unusual from a diradical intermediate.

(14) (a) C. G. Overberger and I. Tashlick, *J. Am. Chem. Soc.*, **81**, 217 (1959); (b) C. G. Overberger, J. W. Stoddard, C. Yaroslavsky, H. Katz, and J.-P. Anselme, *ibid.*, **91**, 3226 (1969).

(15) Determined by us in toluene; also see S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137 (1966).

(16) (a) C. G. Overberger, private communication; (b) C. G. Overberger, M. S. Chi, D. G. Pucci, and J. A. Barry, *Tetrahedron Lett.*, 4565 (1972).

(17) R. C. Neuman, Jr., G. D. Lockyer, Jr., and Michael J. Amrich, *Tetrahedron Lett.*, 1221 (1972).

(18) R. C. Neuman, Jr., and G. D. Holmes, J. Am. Chem. Soc., **93**, 4242 (1971).
(19) This range of +5 to +6 cm³/mol was chosen based on the values of +5.5 cm³/mol for decomposition of **1** and **2**.
(20) Relative motion of geminate radicals appears to be restricted by pressure,⁶,⁸ and the product data from **1** to be discussed below provide further support for a pressure retardation of bond rotation.
(21) C.-M. Backman, S. Claesson, and M. Szwarc, Trans. Faraday Soc., **66**, 3061 (1970).
(22) N. A. Porter and L. J. Marnett, J. Am. Chem. Soc., **95**, 4361 (1973).
(23) α_p is not 1.00 at atmospheric pressure, because we are comparing our experimental data, which differ slightly from Kopecky's at 1 atm, with Kopecky's rate constant ratios derived from his data. The trend in α_p with pressure is still valid.
(24) K. Alder and H. Niklas, Justus Liebigs Ann. Chem., **585**, 6 (1954).
(25) C. G. Overberger and J. J. Monagle, J. Am. Chem. Soc., **78**, 4470 (1956).
(26) R. C. Fuson and J. T. Walker, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 143.
(27) J. M. van der Zanden and G. DeVries, Recl. Trav. Chim. Pays-Bas, **75**,

1159 (1956).
(28) P. S. Bailey and R. E. Lutz, J. Am. Chem. Soc., **70**, 2412 (1948).
(29) R. M. Dodson and A. G. Zielske, J. Org. Chem., **32**, 28 (1967).
(30) R. E. Lutz and J. S. Gillespie, Jr., J. Am. Chem. Soc., **72**, 344, 2002 (1950).
(31) We thank Professor K. Kopecky for a sample of trans-1,2-diphenylcyclobutane.
(32) S. Evani, Ph.D. Dissertation, University of Alberta, Edmonton, Alberta, Canada, 1967.
(33) A. Zwierzak and H. Pines, J. Org. Chem., **28**, 3392 (1963).
(34) S. M. Parmerter, J. Am. Chem. Soc., **71**, 1127 (1949).
(35) P. Tomboulian, J. Org. Chem., **26**, 2652 (1961).
(36) J. W. B. Reesor, J. G. Smith, and G. F. Wright, J. Org. Chem., **19**, 940 (1954).
(37) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. G. Knipmeyer, J. Am. Chem. Soc., **83**, 4838 (1961).
(38) C. G. Overberger and J.-P. Anselme, Chem. Ind. (London), 280 (1964).
(39) R. C. Neuman, Jr., and J. V. Behar, J. Am. Chem. Soc., **91**, 6024 (1969).
(40) A. Zipp, Ph.D. Dissertation, Princeton University, Princeton, N.J., 1973.

Relation of ^{13}C NMR Shifts to the Effect of Methyl Substitution on Electronic Charge Distribution at Trigonal Carbons[1]

George A. Olah* and David A. Forsyth[2]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received November 14, 1974

Abstract: The effect of the substitution of methyl for hydrogen on the electronic charge distribution at the carbon undergoing substitution (C_α) is discussed in relation to the deshielding of C_α observed in ^{13}C NMR spectra. In particular, the effect of methyl substitution at trigonal carbons in carbocations is examined by considering the electron populations predicted by a variety of molecular orbital methods for the series of simple alkyl cations: methyl, ethyl, isopropyl, and tert-butyl. Also, the ^{13}C NMR spectra of a series of p-methyl-substituted benzene derivatives, including p-tolylcarbenium ions and related onium ions, were determined in order to study the possible constancy of the effect of methyl substitution on ^{13}C chemical shifts, i.e., the validity of the additivity relationship for substituent-induced chemical shifts (SCS). The SCS data are consistent with an interpretation supported by molecular orbital calculations in which the methyl group has a negative inductive effect that increases in magnitude as the extent of electron donation from methyl increases via hyperconjugation.

The traditional view of the electronic effect of the methyl group is that the methyl substituent is electron releasing (i.e., electron donor) compared with hydrogen, by both inductive and hyperconjugative mechanisms, when attached to an sp² hybridized carbon.[3] This view is in large part derived from consideration of methyl substituent effects in aromatic systems and from the energetic stabilization provided by methyl substitution at a trigonal carbon in carbocations and in electron-deficient transition states. The effects of substituents on carbenium ion stabilities are frequently attributed to the capability of the attached groups to disperse or neutralize the positive charge by electron donation to the positive center. Thus it is disturbing to find that several molecular orbital treatments of such simple ions as the tert-butyl and isopropyl cations indicate that the central carbon atom actually becomes more positive upon substitution of methyl for hydrogen.[4-10] Some recent experimental work which also indicates that a methyl group is not necessarily electron donating has been reviewed by Sebastian.[11]

^{13}C NMR studies are an integral part of the evidence concerning the electronic effect of the methyl group. Substitution of a methyl group for hydrogen consistently produces a deshielding of the α carbon in the ^{13}C NMR spectrum. The deshielding α effect of a methyl group has been attributed to a reduction in electron density at the α carbon in alkanes,[12] ketones,[13] and carbenium ions.[14] Although the dependence of ^{13}C chemical shifts on electron density is a well-recognized phenomenon, the importance of other fac-

tors governing chemical shifts is not well understood, and the use of the α effect of the methyl group as evidence for inductive electron withdrawal has been questioned on the basis of this uncertainty.[15] In regard to this question, the deshielding effect of α-methyl substitution is usually small and fairly regular at a variety of trigonal carbon atoms (ethene to propene, $\Delta\delta_{13C}$ 7.8 ppm;[16] benzene to toluene, $\Delta\delta_{13C}$ 8.9 ppm;[17] formic acid to acetic, $\Delta\delta_{13C}$ 10.9 ppm;[18] acetaldehyde to acetone, $\Delta\delta_{13C}$ 5.5 ppm;[19] isopropyl cation to tert-butyl cation, $\Delta\delta_{13C}$ 10.4 ppm),[14] which raises the possibility of a constant neighboring-group effect of the methyl group that is unrelated to a charge effect.

In this paper, we examine the problem of the relation of ^{13}C chemical shifts to the effect of methyl substitution on electronic charge distributions, with particular emphasis on improving our understanding of the methyl-group effect on charge distribution in carbocations. The emphasis of our work was directed toward clarifying the meaning of ^{13}C shifts in terms of hyperconjugative (resonance), polarizing, and inductive influences of the methyl group. In order that problems of interpretation be kept to a minimum, only methyl substitution at trigonal carbons bonded to carbon and hydrogen will be considered.

Results

To approach the problem of the effect of methyl substitution on charge distribution in carbocations, we first examined the electron populations predicted by a variety of mo-