Kinetic Studies of Reactions Leading to Cyclopropylcarbinyl Radicals. Cyclopropyl-Substituted Azomethanes and Hexacyclopropylethane

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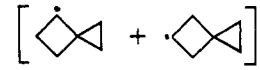
Abstract: Kinetic studies on the decomposition reactions of a series of symmetrically substituted azomethanes suggest that the increase in rate seen upon substitution of a cyclopropyl group for a methyl or isopropyl substituent directly attached to the incipient radical center may properly be used to support a postulated stabilization of product radicals by cyclopropyl conjugation. We rule out alternative explanations involving the relief of ring strain, with ring cleavage simultaneous with C–N bond cleavage. Arguments are presented that these azoalkane decompositions reflect product-radical stabilities free of the distorting influence of the transition state charge polarization which in many radical reactions imparts carbonium ion character to the developing radical center. It is reasoned that the great stability of the cyclopropylcarbinyl cations would make such distortions particularly important in systems where kinetic results are thought to reflect cyclopropylcarbinyl radical stabilities. Rates of decomposition at 135° (relative to 2,2′-azoisobutane) are 26.8, 362, and 2540 in compounds in which, respectively, one, two, and all three of the methyls of each *t*-butyl group are replaced by cyclopropyl groups. The preparation of hexacyclopropylethane is described and its unusually rapid pyrolysis ($k_{295°} = 1.31 \times 10^{-3}$ sec^{-1}) is proposed to be a further manifestation of the stability of the tricyclopropylcarbinyl radical.

The ability of the cyclopropyl group to interact with an adjacent radical center has been the subject of much interest in recent years.[1-13]

Although many reactions which are thought to involve the generation of cyclopropylcarbinyl radicals as intermediates show rate enhancements, questions can be raised as to the nature of the interaction with the cyclopropyl substituent which is responsible for the acceleration. The rate enhancement could arise (a) from resonance stabilization of a transition state leading to a cyclopropylcarbinyl radical or (b) from a concerted ring cleavage with the driving force originating from a relief of ring strain. If the interaction is a conjugative one it is possible that transition state polarization introduces enough resemblance to the cyclopropyl carbonium ion to invalidate conclusions based on a supposed resemblance of the transition state to a free radical.

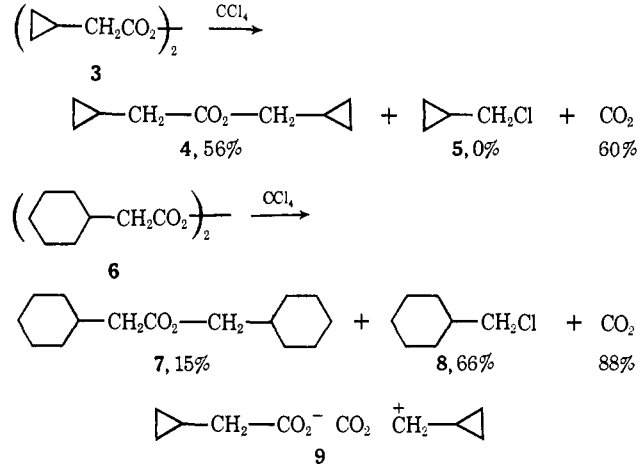
To shed more light on these and other questions, we have studied the rates of decomposition of a series of cyclopropyl-substituted azo alkanes, compounds with structures designed to minimize polar contributions to transition state descriptions. The relevance of these data to the question of the stability of cyclopropylcarbinyl radicals is discussed.

Gas-phase photochlorination of methylcyclopropane has been shown[6] not to involve formation of a "bicyclobutonium" type radical intermediate, although Walling and Fredricks[5] have evidence that the photochlorination with *t*-butyl hypochlorite in the liquid phase does proceed with rate acceleration. These latter results are in contrast with results from the vapor phase chlorination of spirohexane. Applequist and Landgrebe[7] found an almost statistical product distribution resulting from the intermediate radicals **1** and **2**. This suggests that little stabilization is provided through cyclopropyl conjugation in **1**.



1 **2**

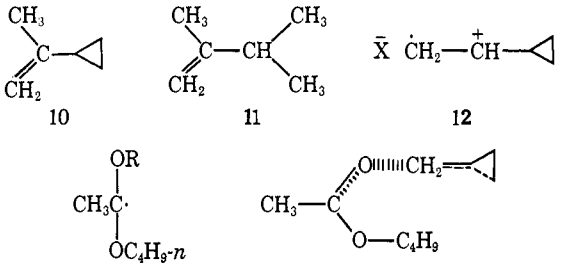
Hart and coworkers[1] have studied the thermal stability of cyclopropaneacetyl peroxide (**3**) and found it to decompose 55 times faster than cyclohexaneacetyl peroxide (**6**). While the rate difference may attest to the greater relative stability of the cyclopropylcarbinyl radical, Hart has pointed out that the conspicuously different product distributions leave open the possibility



(1) (a) H. Hart and D. P. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959); (b) H. Hart and R. A. Cipriani, *ibid.*, **84**, 3697 (1962).
(2) (a) C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951); (b) C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *ibid.*, **71**, 2661 (1949).
(3) E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963).
(4) E. S. Huyser and D. T. Wang, *ibid.*, **29**, 2720 (1964).
(5) C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, **84**, 3326 (1962).
(6) E. Rank, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *ibid.*, **83**, 1987 (1961).
(7) D. E. Applequist and J. A. Landgrebe, *ibid.*, **86**, 1543 (1964).
(8) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 4.
(9) D. C. Neckers and A. P. Schaap, *J. Org. Chem.*, **32**, 22 (1967).
(10) D. H. Gibson and C. H. DePuy, *Tetrahedron Lett.*, 2203 (1969).
(11) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Am. Chem. Soc.*, **91**, 1877, 1879 (1969).
(12) J. E. Schultz, Ph.D. Thesis, University of Illinois, 1963.
(13) J. C. Martin, J. E. Schultz, and J. W. Timberlake, *Tetrahedron Lett.*, 4629 (1967).

that the reaction is more accurately described as electrocyclic or ionic (**9**).

Huyser and Wang[4] found that the photochemically induced addition of bromotrichloromethane or thiophenol to 2-cyclopropylpropene (**10**) was, respectively, 4.4 or 6.6 times more rapid than addition to 2,3-dimethyl-1-butene (**11**). However, since both trichloromethyl and thiyl radicals are good electron acceptors it is expected that transition state polarization toward the electronegative addend radical might in these cases provide a marked resemblance to a carbonium ion in the transition state as in **12**. Even a small resemblance of the transition state to the very stable cyclopropylcarbonium ion[8] might account for the observed rather small rate enhancements.



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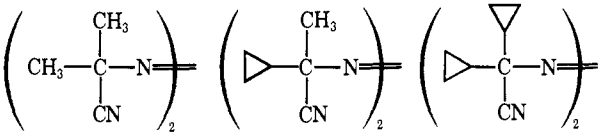
13 14

It has been found[4] that the cyclopropylcarbinyl group (R = cyclo-$C_3H_5CH_2$–) is eliminated as a radical, by β cleavage of radical **13**, 3.9 times more readily than is the *n*-butyl group. Product studies were not undertaken, however, so it is possible that concerted bond cleavage is occurring concomitant with O–C bond cleavage. The factor of almost four increase in rate of elimination could then be a consequence of a relief of ring strain (**14**). Neckers[9] has reported results from which it is concluded that for the systems studied, the "effects of a cyclopropyl group adjacent to radical sites are the manifestation of ring strain only."

The analogous reactions of cyclopropanol, which Gibson and DePuy[10] have found to be very susceptible to radical attack at the O–H bond, are also considered to involve simultaneous O–H and C–C bond cleavage. Kochi, Krusic, and Eaton's direct observation[11] by esr of the cyclopropylcarbinyl radical, generated by hydrogen abstraction from methylcyclopropane by the electronegative *t*-butoxy radical at temperatures below −140°, tells us that in this case fragmentation does not provide the driving force for the hydrogen abstraction which occurs preferentially at the methyl group. At temperatures above −140° ready ring cleavage to give the allylcarbinyl radical was observed. This leaves unanswered the question of how generally the accelerations seen at higher temperatures in reactions related to this are the result of concerted fragmentations in cyclopropylcarbinyl systems.

Overberger and coworkers[2] have found that 2,2′-azobis-2-cyclopropylpropionitrile (**16**) decomposes (80°, toluene) 25 times faster than azobisisobutyronitrile (AIBN **15**). Rate studies for decomposition of α,α'-azobis(dicyclopropylacetonitrile) (**17**) show that a similar rate acceleration results from the substitution of a second pair of cyclopropyl groups into the AIBN molecule. Product studies on **17** in the presence of an excess of hexaphenylethane account for 78% of the dicyclopropylcyanomethyl radicals in reaction products which have both cyclopropyl rings intact,[12,13] thus ruling out concerted ring cleavage as sole provider of the driving force for the decomposition.



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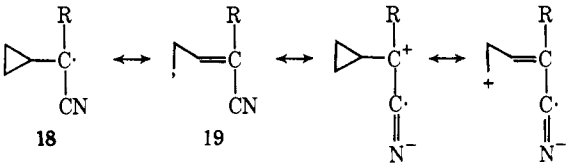
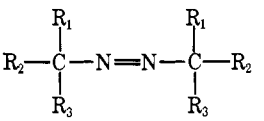
Evidence concerning the stability of cyclopropylcarbinyl radicals deduced from kinetic studies is valid only to the extent that the transition states being compared resemble the product radicals. Many free-radical reactions are thought to proceed through transition states that are much more charge polarized than either the starting materials or the products.[14] The cyanoalkyl radicals from decomposition of azo compounds such as **15**–**17** and the transition states leading to them may, moreover, show the results of a polarization toward the strongly electron-withdrawing cyano function. A possible resemblance of the transition state to the cyclopropylcarbonium ion is illustrated in resonance forms **20** and **21**, and it is possible that they make some contribution to the reduction in the free energy of activation for decomposition of **16** and **17**. Since the rate accelerations seen in radical reactions that develop cyclopropylcarbinyl radicals are so much smaller than those seen in ionizations leading to related carbonium ions,[15,16] only a small increase in the amount of positive charge on the central atom on going to the transition state could account for the observed effect.[5,17]



18 19 20 21

Results and Discussion

In a search for a system in which the rates of formation of variously substituted cyclopropylcarbinyl radicals could be studied conveniently by kinetic methods with a minimum of distortion of results by polar effects in the transition state, we decided to study the rates of decomposition of a series of azo compounds of type **22** which, lacking the strongly electron-withdrawing cyano function, would make it more nearly possible to isolate effects relating to radical stabilities.



22

Azo compounds resembling **22** have been studied by a number of workers,[18–34] and there are several lines of

(14) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 170.
(15) H. Hart and J. M. Sandri, *J. Am. Chem. Soc.*, **81**, 320 (1959).
(16) H. Hart and P. A. Law, *ibid.*, **86**, 1957 (1964).
(17) E. C. Friedrich, *J. Org. Chem.*, **34**, 528 (1969).
(18) C. G. Overberger, J.-P. Anselme, and J. G. Lombardino, "Organic Compounds, With Nitrogen–Nitrogen Bonds," The Ronald Press Co., New York, N. Y., 1966, p 32.

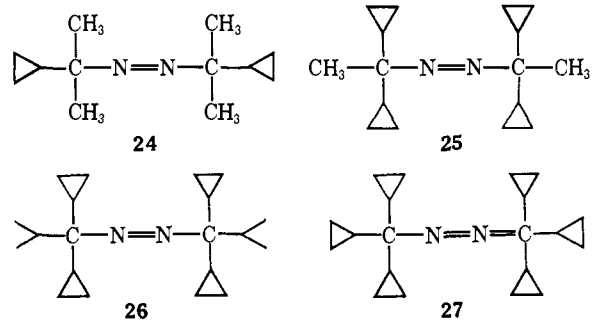
Table I. Rate Constants and Activation Parameters for Decomposition of Azo Compounds[a]

Compd	Concn, *M*	Temp, °C	$k \times 10^4$, sec^{-1}	Relative rates, 135°	ΔH^*, kcal/mol	ΔS^*, eu	ΔG^*, kcal/mol, 135°
23	0.0394	165.00	0.2782 ± 0.0006	1.00	42.2 ± 0.3	16.2 ± 0.6	36.5
	0.0414	175.00	0.874 ± 0.004				
	0.0394	185.00	2.513 ± 0.005				
	0.0359	190.00	4.143 ± 0.005				
	0.0355	195.00	6.731 ± 0.009				
	0.0348	200.00	10.93 ± 0.02				
24	0.0399	145.00	0.756 ± 0.003	26.8	37.8 ± 0.3	12.4 ± 0.6	32.7
	0.0426	150.00	1.273 ± 0.003				
	0.0396	155.00	2.147 ± 0.004				
	0.0400	160.00	3.771 ± 0.006				
	0.0399	165.00	6.07 ± 0.01				
	0.0389	170.00	10.33 ± 0.02				
25	0.0382	120.00	0.6324 ± 0.0008	362	35.6 ± 0.2	12.1 ± 0.6	30.6
	0.0406	120.00	0.634 ± 0.001				
	0.0374	130.00	2.03 ± 0.02				
	0.0374	135.00	3.41 ± 0.01				
	0.0389	140.00	6.07 ± 0.01				
	0.0390	145.00	10.37 ± 0.02				
	0.0382	150.00	16.95 ± 0.04				
26	0.0313	120.00	0.426 ± 0.001	286	38.0 ± 0.2	17.6 ± 0.6	30.8
	0.0326	125.00	0.794 ± 0.002				
	0.0358	130.00	1.491 ± 0.003				
	0.0333	135.00	2.697 ± 0.005				
	0.0327	140.00	4.774 ± 0.009				
	0.0351	145.00	8.14 ± 0.01				
	0.0338	147.00	10.55 ± 0.02				
27	0.0343	105.00	0.793 ± 0.002	2540	34.3 ± 0.3	12.8 ± 0.8	29.1
	0.0348	105.00	0.784 ± 0.001				
	0.0348	110.00	1.365 ± 0.006				
	0.0344	110.00	1.383 ± 0.003				
	0.0353	115.00	2.36 ± 0.01				
	0.0345	118.50	3.77 ± 0.01				
	0.0359	120.00	4.58 ± 0.01				
	0.0316	125.00	7.70 ± 0.02				
	0.0355	125.00	7.83 ± 0.04				
	0.0350	130.00	13.81 ± 0.03				
	0.0346	130.00	13.80 ± 0.04				
	0.0349	135.00	23.8 ± 0.10				
	0.0339	135.00	24.0 ± 0.08				

[a] All uncertainties are expressed as standard deviations.

convincing evidence[18-21] that, for symmetrical azomethanes such as **22**, decomposition occurs by a concerted, two-bond cleavage without any intermediate diazoalkyl radical formation.

2,2′-Azoisobutane (**23**),[21,28-30] 2,2′-dicyclopropyl-2,2′-azopropane (**24**), 1,1,1′,1′-tetracyclopropyl-1,1′-azoethane (**25**), 1,1,1′,1′-tetracyclopropyl-1,1′-azoisobutane (**26**), and 1,1,1,1′,1′,1′-hexacyclopropylazomethane (**27**) were prepared by oxidative coupling of the corresponding amines with iodine pentafluoride and their complete syntheses have been described in an earlier publication.[30]



The rates of decomposition of compounds **23–27** were followed by measuring the rate of increase in pressure of evolved nitrogen at constant volume. A detailed description of the apparatus and the technique used is presented in the Experimental Section. All the decompositions were conducted in diphenyl ether–isoquinoline (90:10) solvent unless otherwise stated. The isoquinoline was introduced as a buffer. In its absence small amounts of acid, either adventitious or formed in the reaction, caused an ionic cleavage of the azo compounds. In all cases good first-order kinetics were obtained and the results gave no evidence for induced

(19) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961); **85**, 14 (1963).
(20) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967); W. A. Pryor and K. Smith, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.
(21) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137 (1966).
(22) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 143 (1966).
(23) S. Seltzer, *ibid.*, **87**, 2628 (1965).
(24) S. Seltzer and E. J. Hamilton, Jr., *ibid.*, **88**, 3775 (1966).
(25) S. G. Cohen and C. H. Wang, *ibid.*, 77, 3628 (1955).
(26) R. K. Lyon, *ibid.*, **86**, 1907 (1964).
(27) C. Steel and K. J. Leidler, *J. Chem. Phys.*, **34**, 1827 (1961).
(28) M. Procházka, O. Ryba, and D. Lím, *Collect. Czech. Chem. Commun.*, **33**, 3387 (1968).
(29) T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961).
(30) J. W. Timberlake and J. C. Martin, *ibid.*, **33**, 4054 (1968).
(31) A. V. Blackham and N. L. Eatough, *J. Am. Chem. Soc.*, **84**, 2922 (1962).
(32) J. B. Levy and B. K. W. Copeland, *ibid.*, **82**, 5314 (1960).
(33) J. R. Shelton, C. K. Liang, and P. Kovacic, *ibid.*, **90**, 354 (1968).
(34) S. A. Weiner and G. S. Hammond, *ibid.*, **91**, 986 (1969).

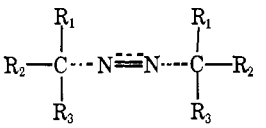
decomposition. Rate constants and activation parameters for compounds **23–27** are listed in Table I.

There is a small solvent effect on the rate of decomposition of 1,1,1,1′,1′,1′-hexacyclopropylazomethane (**27**), Table II, the reaction being 4.5% slower in decalin–isoquinoline (90:10), 12.5% slower in 100% isoquinoline, and 18% faster in cumene–isoquinoline (90:10) than in the standard solvent system diphenyl ether–isoquinoline (90:10). These results are similar in magnitude to those found by Bartlett and Nelson for the decomposition of azocumene,[21] which decomposes 21% more slowly in dodecane and 27% more rapidly in 3.9 *M* thiophenol in benzene than in pure toluene. Solvent effects of the same magnitude have also been found for the decomposition of 2,2′-azobisisobutyronitrile.[4]

Table II. Decomposition of 1,1,1,1′,1′,1′-Hexacyclopropylazomethane

Solvent system	Concn	Temp, °C	$k \times 10^4$, sec^{-1}
90% diphenyl ether–10% isoquinoline	0.0345	118.50	3.77 ± 0.01
90% decalin–10% isoquinoline	0.0347	118.50	3.60 ± 0.01
100% isoquinoline	0.0356	118.50	3.30 ± 0.01
90% cumene–10% isoquinoline	0.0357	118.50	4.45 ± 0.02
90% diphenyl ether–10% isoquinoline	0.0231	129.80	13.66 ± 0.03
90% diphenyl ether–10% isoquinoline	0.0944	129.80	13.63 ± 0.02

It is interesting that our results for 2,2′-azoisobutane (**23**, $\Delta H^* = 42.2$ kcal/mol, $\Delta S^* = 16.2$ eu) are, within experimental error, the same as those found by other workers for its decomposition in the gas phase.[31,32] Values of 42.3 ± 0.8 kcal/mol for ΔH^* and 17.5 ± 1.5 eu for ΔS^* were obtained from calculations using the gas-phase rate constants determined by Blackham and Eatough.[31] This close agreement with our values for the decomposition of **23** in diphenyl ether, and with those found by Procházka, Ryba, and Lim,[28] suggests that solvation effects are relatively unimportant for this azo compound and, by extrapolation, for compounds **24–27**. This is in contrast with the results of Leffler and Alder[35] on the decomposition of phenylazotriphenylmethane (PAT). They found that changes in solvent polarity had no effect on the decomposition rate of this compound because of compensatory changes in ΔH^* and ΔS^*. The enthalpy of activation changed from 29.0 to 24.5 kcal/mol on going from benzonitrile to cyclohexane, however, while ΔS^* varied from 13.4 to −1.2 eu. These changes in activation parameters were postulated to result from preferential ground-state solvation of PAT, which probably decomposes by a single-bond cleavage mechanism. The two-bond cleavage mechanism operative for **23**, however, apparently proceeds through a transition state **28** with solvation similar to that in the ground state. This suggests that polarization of the transition state to introduce positive charge on the azomethane carbons, as in resonance structure **29**, is no more important than in the ground state. Substituent effects in **28** would therefore parallel



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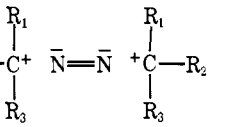

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substituent effects on radical stability rather than on carbonium ion stability.

The data for decomposition of the azo compounds in Table I clearly show that the replacement of a pair of methyl groups with a pair of cyclopropyl groups markedly increases the rate of decomposition. At 135° hexacyclopropyl azomethane **27** decomposes 2540 times more rapidly than the hexamethyl analog **23**. The addition of each pair of cyclopropyl substituents produces an approximately additive change (Table I) in the free energy of activation. The $\Delta\Delta G^*$ for progression from **23** to **24** is 2.9 kcal/mol; from **24** to **25**, 2.1 kcal/mol; and from **25** to **27**, 1.5 kcal/mol. These results are consistent with the postulate that the transition states for the decomposition of azo compounds **24–27**, which resemble cyclopropylcarbinyl radicals, are stabilized by resonance interaction between the cyclopropyl groups and the adjacent free-radical center.

It might be argued that the increase in rate of decomposition in the series of compounds **23–27** is not due to resonance stabilization of the radical, but rather to an increased steric interaction in the ground state which is relieved by going to a trigonal transition state. The isopropyl group is certainly more sterically demanding than a methyl group. However, $\Delta\Delta G^*$ between **25** and **26** is only 0.2 kcal/mol, with the methyl analog actually showing the faster decomposition rate. If steric factors were solely responsible for the rate differences, 1,1,1′,-1′-tetracyclopropyl-1,1′-azoisobutane (**26**) should be faster than 1,1,1,1′,1′,1′-hexacyclopropylazomethane (**27**). The reverse is true. Compound **27** decomposes 9 times more rapidly than **26** at 135.0°.

The deviation from a strict linear free-energy relationship for compounds **23–27** could be the result of a saturation effect or, more likely, an increasing steric inhibition of resonance as the number of cyclopropyl groups is increased. This argument is reinforced if it is assumed that there is a preferred conformation for delocalization of the free electron in the radical.[36] Such a conformational preference is well established for cyclopropylcarbonium ions.[37,38]

The close similarity in the $\Delta\Delta G^*$ values in Table I and the $\Delta\Delta G^*$ values for AIBN (**15**) and 2,2′-azobis-2-cyclopropylpropionitrile (**16**),[2] 2.3 kcal/mol, and for **16** and α,α′-azobis-(dicyclopropylacetonitrile) (**17**), 1.5 kcal/mol,[12,13] indicates that polar effects in the transition state for the decomposition of azobisnitriles are also unimportant in accounting for the rate enhancement.

It is interesting to compare our results for 2,2′-dicyclopropyl-2,2′-azopropane **24** with rate data for azocumene. Bartlett and Nelsen[21] found activation

(35) M. G. Alder and J. E. Leffler, *J. Amer. Chem. Soc.*, 76, 1425 (1954).

(36) G. A. Russell and H. Malkus, *ibid.*, 89, 160 (1967); N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *ibid.*, 89, 3948 (1967); J. K. Kochi, P. J. Krusic, and P. R. Eaton, *ibid.*, 91, 1877, 1879 (1969).

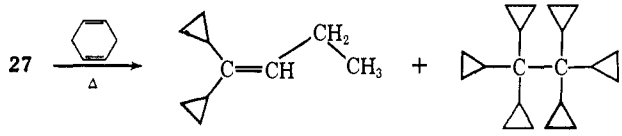
(37) C. U. Pittman and G. A. Olah, *ibid.*, 87, 2998, 5123 (1965); H. G. Richey, Jr., and J. M. Richey, *ibid.*, 88, 4971 (1966); T. Sharpe and J. C. Martin, *ibid.*, 88, 1815 (1966); H. C. Brown and J. D. Cleveland, *ibid.*, 88, 2015 (1966).

(38) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, 87, 4533 (1965).

parameters of $\Delta H^* = 29.0$ kcal/mol and $\Delta S^* = 11.0$ eu for the decomposition of azocumene in toluene. This corresponds to a ΔG^* of 25.5 kcal/mol at 135.0°. 2,2′-Dicyclopropyl-2,2-azopropane (**24**), Table I, has a ΔG^* of 32.7 kcal/mol at this temperature. Neglecting differences in ground-state energies, the difference, 7.2 kcal/mol, reflects a much greater stability of the benzyl free radicals. The difference in $\Delta\Delta G^*$ between 2,2′-azoisobutane (**23**) and 1,1′-dicyclopropyl-2,2′-azopropane (**24**), while significant, 2.9 kcal/mol, is much less than this 7.2 kcal/mol and indicates the order of increasing stabilizing ability to be alkyl < cyclopropyl << phenyl. In the carbonium ion series a cyclopropyl group has been found to provide more stabilization than a phenyl group.[38]

A complete product study was carried out for the decomposition of 1,1,1,1′,1′,1′-hexacyclopropylazomethane (**27**). A solution of the azo compound in 1,4-cyclohexadiene (0.17 *M*), buffered with a small amount of isoquinoline, was heated at 105° for 65 hr. The decomposition yielded 86% of 1,1-dicyclopropyl-1-butene (**30**) and 2% of hexacyclopropylethane (**31**). No tricyclopropylmethane, within the limits of detection by glpc (0.25%), was produced. Hexacyclopropyl ethane is stable under the reaction conditions.

Compound **30** was identified from its elemental analysis and nmr, infrared, and mass spectral data.



30 31

Compound **31** was also obtained by photolysis of a sample of **27** at 0°. It was identified from its elemental analysis and nmr, infrared, and mass spectral data.

The low yield of hexacyclopropylethane in the pyrolysis (2%) implies either that: (1) ring opening is a concerted process, (2) there is only a 2% cage effect in recombination of tricyclopropylmethyl radicals, and ring opening occurs outside the cage before trapping by hydrogen transfer from cyclohexadiene, or (3) that ring opening is occurring within the solvent cage. Evidence from our rate studies on azo compounds makes a concerted process seem unlikely. The fact that irradiation of 1,1,1,1′,1′,1′-hexacyclopropylazomethane at 0° gives only hexacyclopropylethane and no detectable ring-opened products shows that concerted ring opening does not occur under these conditions. At, or above, room temperature irradiation of **27** gives olefinic products. Several azo compounds show cage recombination to the extent of about 20%.[12,21,22,34,39,40] The greater stability of the tricyclopropylcarbinyl radical may slow the geminate radical cage reactions sufficiently to allow diffusion from the cage to be more important. Failure to trap these radicals with cyclohexadiene before ring cleavage suggests that the lifetime of the tricyclopropylcarbinyl radical is short, however.

Schultz and Martin[12] were able to account for 78% of the dicyclopropylcyanomethyl radicals with the rings intact from the decomposition of α,α′-azobis(dicyclopropylacetonitrile) (**17**). The product tetracyclopropylsuccinonitrile (25%) is probably formed by recombination of the dicyclopropylcyanomethyl radicals within the solvent cage. The decomposition of **17** was studied at 30°, which is 85° below the temperatures used in the product studies for **27**. The greater extent of ring opening seen for tricyclopropylmethyl radicals probably is a reflection of this higher temperature.

Another approach to assessing the resonance stability of the tricyclopropylmethyl radical compares the bond dissociation energy of hexacyclopropylethane with suitable models.

Although hexacyclopropylethane is stable in isoquinoline at 210° for 18 hr, at 295° in decalin decomposition occurs rapidly in a first-order process with a rate constant of 1.31×10^{-3} sec^{-1} ($T_{1/2}$ = 8.9 min). This corresponds to a ΔG^* value of approximately 41.5 kcal/mol. An estimated value for ΔS^* of 13 eu, using as a model ΔS^* for 1,1,1,1′,1′,1′-hexacyclopropylazomethane (Table I) or ΔS^* for the decomposition of 2,2,3,3-tetraphenylbutane,[41] gives us an estimate for ΔH^* of 45 kcal/mol.

Setser and Rabinovitch[42] have studied the isomerization of methylcyclopropane to give butenes, and activation energies for these processes are all approximately 62 kcal/mol. Hence, it would seem unlikely that the path of decomposition for hexacyclopropylethane ($\Delta H^* = 45$ kcal/mol) involves only C–C bond fission in a cyclopropyl ring. The presumption that it involves simple central C–C bond cleavage to form two tricyclopropylmethyl radicals is rendered somewhat tenuous, however, at the high temperature, 295°, involved in this study. Ring cleavage concerted with central C–C bond cleavage may become an important mode of reaction.

The value of ΔH^* can be equated with bond dissociation energy if the energy of activation for the recombination of two tricyclopropylmethyl radicals is small. The activation energy for recombination of two cumyl radicals in the solvent cage has been found to be 1.3 kcal/mol, and it seems unlikely that recombination of two tricyclopropylmethyl radicals would differ significantly enough from this value to affect our conclusions.

Gas-phase dissociation energies for hexaphenyl ethane (hpe) and 2,2,3,3-tetramethylbutane (tmb) are reported as 15 and 67.5 kcal/mol, respectively.[43] Recent evidence[44] has suggested however, that the compound to which the hpe structure has been assigned is in fact a dimer of triphenylmethyl involving bond formation to the *para* position of one phenyl ring, rather than to the central carbon atom as in the hpe structure. The hpe structure not seen in the equilibrium mixture is presumably of higher energy. We must therefore view the 15-kcal/mol value as a probable upper limit to the bond dissociation energy of hpe. The difference in C–C bond dissociation energies for hpe and tmb, which is therefore greater than 53 kcal/mol, can be attributed in part to the greater resonance stabilization of the trityl radical and partly to the greater steric requirements of the phenyl substituents. The difference of 16 kcal/mol in the tertiary C–H bond energies for isobutane (91

(39) C. G. Overberger, M. Tobkes, and A. Zweig, *J. Org. Chem.*, **28**, 620 (1963).
(40) G. S. Hammond and J. R. Fox, *J. Am. Chem. Soc.*, **86**, 1918 (1964).
(41) K. Ziegler, A. Sieb, K. Knoevenagel, P. Herte, and F. Andreas, *Ann.*, **551**, 150 (1942).
(42) D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **86**, 564 (1964).
(43) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
(44) W. Th. Nauta and C. MacLean, *Tetrahedron Lett.*, 249 (1968).

kcal/mol) and triphenylmethane (75 kcal/mol) sets a probable upper limit to the estimate of resonance stabilization of the trityl radical. (This difference of 16 kcal/mol includes a contribution from the relief of steric strain between geminal substituents accompanying the change from tetrahedral to trigonal geometry.) At any rate the steric interactions between vicinal phenyl substituents must be primarily responsible for the weakening of the central C–C bond of hpe.

The difference in dissociation energies for tmb and hexacyclopropylethane (67.5 − 45 = 22.5 kcal/mol) is also attributable to steric and electronic effects which are difficult to separate. Qualitatively, however, it is evident that hexacyclopropylethane is unusually unstable, a fact consistent with the postulate, developed in the section of this paper dealing with azoalkane decompositions, that the tricyclopropylmethyl radical is stabilized by a resonance interaction between the cyclopropyl substituents and the radical center.

Experimental Section

Product Study on the Decomposition of 1,1,1,1′,1′,1′-Hexacyclopropylazomethane (27). A Carius tube was degassed and sealed with 1.217 g (4.08 mmol) of 1,1,1,1′,1′,1′-hexacyclopropylazomethane (**27**),[30] 0.716 g (9.06 mmol) of isoquinoline, and 23.8 cc (20.2 g) of 1,4-cyclohexadiene. The tube was heated at 105° for 65 hr, opened, and the cyclohexadiene was removed *in vacuo* to give 2.21 g of material from which isoquinoline was removed by passage through a column packed with 65 g of silica gel, eluting with hexane. The colorless liquid eluate was flash distilled [30–40° (0.25 mm)] to give 880 mg of material which was purified by preparative glpc at 135° on a 3 ½-ft column of 20% SE 30 on Chromosorb W to give 850 mg of 1,1-dicyclopropyl-1-butene (lit.[45] bp 62–64° (13 mm)); nmr ($CDCl_3$) δ 4.99 (t, 0.96, J = 7.0 Hz, C=CH), 2.04 (m, 1.85, $-CH_2-CH_3$), 1.23–1.78 (m, 0.99, cyclopropyl methine *trans* to ethyl),[46,47] 0.88 (m, 3.97, CH_3 plus cyclopropyl methine *cis* to ethyl), 0.09–0.68 (m, 8.31, cyclopropyl CH_2).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.39; H, 11.95.

The 280 mg of material which remained after flash distillation was separated into three fractions, each containing several components, by preparative glpc on a 3 ½-ft SE 30 on Chromosorb W column at 202°. The first, most volatile fraction, consisted of only two major peaks and these were collected from the same column at 140°. The major component was 1,1-dicyclopropyl-1-butene (**30**), 105 mg. The total yield of **30** was 955 mg (7.02 mmol, 86%). The other component isolated (40 mg) was not identified but nmr and infrared spectra showed no absorption in the regions characteristic of cyclopropyl protons.

The second fraction from the 202° glpc run, 12 mg, was not characterized. Its infrared spectrum showed both cyclopropyl absorption and absorption at 1650 cm^{-1} characteristic of a double bond.

The third fraction was chromatographed on 6 g of silica gel and eluted with hexane to give 26 mg of a solid which was recrystallized from ether to give 23.3 mg (2.1%) of hexacyclopropylethane, mp 289–291°. A mixture melting point with an authentic sample was not depressed. The infrared spectrum and glpc retention time were identical with those of hexacyclopropylethane.

Hexacyclopropylethane 31. A sample of azoalkane **27** (2.40 g, 8.88 mmol) was irradiated with a G.E. Sunlamp from a distance of 6 in. for 50 hr in an ice-filled clear glass dewar flask. The white solid which formed was separated by pipetting away the viscous yellow liquid and washing the solid with cold ether. The compound was recrystallized twice from ether, sublimed at 90° (0.03 mm), and recrystallized again from ether to yield 300 mg of colorless needles with a very faint camphorlike odor: mp 290.5–291.5° (sealed tube), cooling and remelting gives mp 282°; nmr, δ 0.02–0.75 (m, 23.80, CH_2), 0.75–1.33 (m, 6.20, CH); uv (cyclohexane) no absorption above 200 mμ.

Anal. Calcd for $C_{20}H_{30}$: C, 88.82; H, 11.18. Found: C, 88.80; H, 11.05.

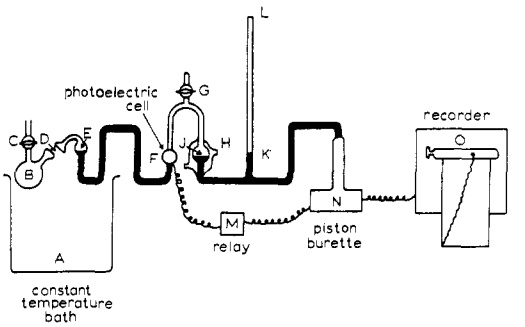


Figure 1. Apparatus for measuring pressure increase at constant volume.

Kinetic Studies. The kinetic experiments were run in the constant-volume, variable-pressure apparatus which is diagrammed in Figure 1.[48] It consists of a constant temperature bath A, a reaction flask B attached by an O-ring seal and a clamp at D, a photoelectric cell F activating a relay M to operate a motor-driven piston buret N, and a recorder O. The glass assembly is 2-mm capillary tubing except at points E and J, which are 5- and 10-ml bulbs, respectively. The black shaded areas indicate parts of the tubing which are filled with mercury. The tubing at L is open to the atmosphere and can be used as a manometer. The 5-mm bulb at J is jacketed (H), and a water-circulating bath controls the large volume of air and mercury to a constant temperature.

In a typical run, diphenyl ether (4 ml) and isoquinoline (0.5 ml) were introduced into the reaction flask and the flask attached to the assembly at D with a rubber gasket and a spring clamp. The flask contents were magnetically stirred. Stopcocks C and G were opened and the constant-temperature bath was raised to cover the reaction flask and bulb E. The flask and solvent were allowed to equilibrate. The azo compound, dissolved in 0.5 ml of diphenyl ether, was introduced through stopcock C by means of a syringe with a long needle extending into the solution and a rapid stream of prepurified nitrogen was passed through the needle into the solution for 2 min. Stopcocks C and G were then closed. As nitrogen is evolved the pressure increase is sensed by a change in the mercury level at F. The photocell at F acts through relay M and the piston buret N to deliver mercury to bulb J to equalize the pressure and restore the mercury level to its original position. A potentiometer connected to the buret drive mechanism couples the buret to the recorder.

Rate constants were calculated by a least-squares treatment, weighting pressure values in proportion to their difference from P^∞. The calculated standard deviations for the rate constants were generally ±0.2%. For any one bath setting, the reproducibility for several runs was within the limits of the calculated error.

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(45) S. K. Begidov, T. V. Domareva, and I. A. D'yakonov, *Zh. Obshch. Khim.*, 33 (10), 3426 (1963).

(46) R. B. Bates, R. H. Carnighan, R. O. Rakutis, and J. H. Schauble, *Chem. Ind.* (London), 1020 (1960).

(47) R. B. Bates and D. M. Gale, *J. Am. Chem. Soc.*, 82, 5949 (1960).

(48) We wish to thank Professor P. D. Bartlett for a description of a related apparatus, based on a somewhat different mode of operation, which was constructed in his laboratory.