phosphate formed, the more basic and nucleophilic salt ditetramethylammonium phenyl phosphate was substituted for **10** in a similar reaction. Still, none of the desired product was observed. The methyl group at the 5 position provides a convenient means for decomposition of such phosphates, by elimination. It therefore seems possible that model studies on a suitable unmethylated system might be to more avail.

Experimental Section

Melting points were determined without correction using a Mel-Temp apparatus. Infrared spectral measurements utilized a Beckman IR-5, nmr spectra a Varian A-60 spectrometer, unless otherwise specified. A consolidated Electrodynamics 21-102 spectrometer was used for obtaining mass spectra.

6,11-Dihydro-11-hydroxy-6-oxo-2,2,5-trimethyl-2*H*-naphtho[1,2-*b*]pyran (6).—To a stirred solution of 1.7 g (6.7 mmol) of the chromenol methyl ether **5** dissolved in dioxane (77 ml) and 85% phosphoric acid (7.7 ml) was added 2.5 g (20 mmol) of argentic oxide. After stirring for 2.5 hr at room temperature, the mixture was diluted with 200 ml of water and 100 ml of ether and worked up in the usual way. The ether solvent was evaporated cold, leaving an oil, which crystallized from 10% ether–hexane. There was obtained 0.584 g (35.4% yield) of the hemiketal **6**: mp 128–130° dec; ir ($CDCl_3$) ν 3600, 3400, 1650, 1605, 1340 cm^{-1}; mass spectrum *m/e* 256 (M), 238 (M − H_2O); nmr (10% DMSO-d_6–$CDCl_3$) τ 8.68 (s, 3 H), 8.32 (s, 3 H), 8.0 (s, 3 H), 5.9 (br s, 1 H), 3.74, 3.35 (q, 2 H, J_{AB} = 10.0 Hz), 2.47 (m, 2 H), and 2.04 (m, 2 H). Analytical purity could not be achieved because of the decomposition accompanying attempted recrystallizations.

Triethylamine Experiment.—A solution of 0.194 g (0.759 mmol) of the hemiketal **6** in benzene (20 ml) and triethylamine (0.32 ml, 2.27 mmol, 3 equiv) was refluxed for 44 hr under nitrogen and cooled, and the solvent was evaporated. Crystallization of the resulting gum from 4:1 hexane–ether afforded 52 mg (26.8%) of unreacted **6**. The mother liquor was evaporated cold and chromatographed on Florisil. The combined 1:1 benzene–hexane eluates were evaporated and gave 57 mg (29.4%) of **8** as a yellow gum: ir ($CHCl_3$) ν 1700, 1650, 1600 cm^{-1}; mass spectrum *m/e* 256 (M); nmr ($CDCl_3$, HA-100) τ 8.73 (several sharp lines, 9 H, among which are two doublets at 8.83 and 8.63, J = 7.0 Hz), 6.85 (sextet representing two overlapped quartets, 1 H, J = 7.0 Hz), 4.74 and 4.14 (q, 1 H, J = 6.0 Hz), 4.45 and 4.12 (q, 1 H, J = 6.0 Hz), 2.39 (m, 2 H), and 2.05 (m, 2 H).

The chloroform eluate yielded another gum which crystallized from 1:1 ether–hexane, affording 20 mg (10.3%) of the ring-opened quinone alcohol **7** as a tan solid: mp 81–85°; ir (CS_2) ν 3600, 1665, 1295, 713 cm^{-1}; mass spectrum *m/e* 256 (M); nmr ($CDCl_3$, HA-100) τ 8.55 (s, 6 H), 7.74 (s, 3 H), 3.35 (s, 2 H), 2.35 (m, 2 H), and 1.95 (m, 2 H); nmr (DMSO-d_6, 500 Hz sweep) showed the 3.35 singlet to be a doublet separated by about 1 Hz. The initially formed quinone alcohol must certainly have the cis geometry, but may isomerize by reversible addition of triethylamine to the terminal end of the dienone system. Because of the spectral similarity between **7** and the previously reported trans compound,[5] the assignment of the trans geometry is made, pending further evidence.

Tetramethylammonium *O,O*-Diphenyl Phosphate (10).—To a stirring solution of 0.616 g (4.0 mmol) of tetramethylammonium bromide in 4 ml of water was added 0.927 g (4.0 mmol) of silver(I) oxide. The mixture was stirred for 3 hr, filtered, and washed three times with 1-ml portions of water. Diphenyl phosphate (1.0 g, 4.0 mmol) was added to the filtrate, and the solution was stirred for 12 hr and then evaporated to a solid. This crude product was stirred in acetone, filtered, washed (acetone), and dried. There was obtained 1.17 g (91%) of **10** as a white solid, nmr (DMSO-d_6) τ 6.90 (s, 12 H) and 2.95 (m, 10 H).

NBS Oxidation of 9 in the Presence of 10.—To a stirring solution of 0.24 g (1 mmol) of **9** in acetonitrile (20 ml) was added 1.14 g (3.52 mmol) of tetramethylammonium diphenyl phosphate (**10**) and then 0.18 g (1.0 mmol) of *N*-bromosuccinimide. The mixture was stirred for 0.5 hr at room temperature, filtered under nitrogen, and evaporated cold under reduced pressure to afford a solid. The latter was leached several times with carbon tetrachloride, the washes were evaporated, and the crude solid was chromatographed on Florisil. Elution with 3:1 benzene–chloroform gave a product which formed yellow crystals in 1:1 ether–hexane. There was obtained 32 mg (9.4%) of the succinimidyl derivative **11**: mp 136° (with resolidification); ir ($CHCl_3$) ν 1700, 1650, 1600, 1205 cm^{-1}; mass spectrum *m/e* 239 (M − succinimidyl); nmr (CCl_4, HA-100) τ 8.68 (s, 3 H), 8.52 (s, 3 H), 8.20 (s, 3 H), 7.36 (s, 4 H), 4.59, 4.10 (q, 2 H, J_{AB} = 10.0 Hz), and 2.0 (d, 1 H, J = 8.0 Hz).

Recrystallization from ether–hexane gave **11** as yellow crystals, mp 144–145°.

Anal. Calcd for $C_{20}H_{19}O_4N$: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.06; H, 5.81; N, 4.40.

Registry No.—**6**, 31819-55-3; **7**, 22268-05-9; **8**, 31819-57-5; **10**, 31819-58-6; **11**, 31883-40-6.

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[5] C. D. Snyder and H. Rapoport, *J. Amer. Chem. Soc.*, **91**, 731 (1969).

Neutral and Positively Charged Azonitriles. Decomposition Rates and Efficiencies of Radical Production[1]

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The uncharged azonitrile, 4,4′-azobis-4-cyano-1-methylpiperidine (ACMP), and its monopositive *N*-methyl and dipositive *N,N′*-dimethyl derivatives (MACMP and DACMP) have been synthesized. Their decomposition rates and efficiencies of radical production have been measured in the solvent DMSO and compared with the analogous data for 1,1′-azobis-1-cyanocyclohexane (ACC) and the new compound, 1,1′-azobis-1-cyano-4,4-dimethylcyclohexane (ACDC). The resulting activation parameters follow [azonitrile, ΔH^* (kcal/mol), ΔS^* (eu), ΔF^* (kcal/mol)]: ACMP, 32.6, 10.4, 28.8; MACMP, 31.7, 9.2, 28.4; DACMP, 29.8, 4.6, 28.1; ACC, 32.4, 9.7, 28.9; ACDC, 31.6, 8.6, 28.5. The efficiencies of radical production from ACC, ACDC, and DACMP are *ca.* 0.6, 0.5, and 0.4, respectively. These data are discussed in terms of electrostatic interactions between the positively charged ends of the molecules and the resultant geminate radicals. It is concluded that electrostatic effects are of minimal importance and that rate differences are largely the result of steric and/or solvation effects.

In order to determine whether positively charged geminate radicals possess a significant "cage effect," Hammond studied the thermal decomposition reactions of a pair of azobisisobutyramidines (**1a**, R = H; **1b**, R = $-CH_2-$) and their conjugate acids (**2a** and **2b**).[3] Products were consistent with radical formation (**3** and

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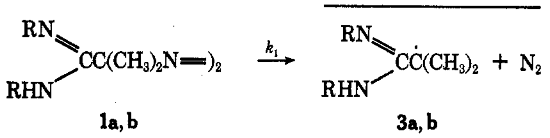
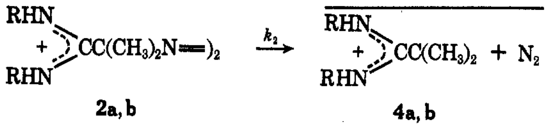
[1] Support by the National Science Foundation (GP-8670) is gratefully acknowledged.

[2] NDEA Predoctoral Fellow, 1968–1971.

[3] G. S. Hammond and R. C. Neuman, Jr., *J. Amer. Chem. Soc.*, **85**, 1501 (1963).



(1)



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4) and efficiency measurements indicated that the neutral and positively charged systems had cage effects similar to each other and to that for azobisisobutyronitrile (AIBN) (Table I).

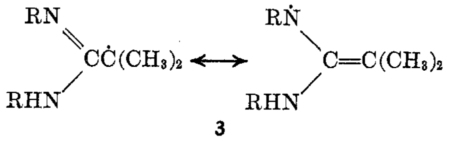
TABLE I

EFFICIENCY OF RADICAL PRODUCTION FROM 1, 2, and AIBN[a,b]

Compd	Temp, °C	Solvent	Efficiency[c]
1a	70	DMSO–cumene	0.4
1b	80	DMSO–cumene	0.4
	70	DMSO–MMA[d]	0.4
2a	70	DMSO–cumene	0.60
2b	60	DMSO–tetralin	0.66
AIBN	70	DMSO–cumene	0.58

[a] Taken from ref 3. [b] From hydrocarbon oxidation unless otherwise indicated. [c] Fraction of azo compound yielding scavengeable radicals. [d] Efficiency from methyl methacrylate (MMA) polymerization.

It was suggested that the smaller cage effects (greater efficiencies of radical production) for **2a** and **2b** could reflect electrostatic repulsion between the positively charged geminate radicals (**4**). However, it was also recognized that this difference could be due to a greater stability of the radicals **4** compared to the neutral species **3**. In both cases the conjugate acids decomposed faster than the neutral azoamidines (k_{2a}/k_{1a} *ca.* 50, and k_{2b}/k_{1b} *ca.* 20). Since decomposition rates of azo compounds (RN=NR) reflect the stabilities of the product radicals (R·),[4,5] it was suggested that the positive radicals **4** were more stable than the neutral radicals **3**. This is consistent with the contributing forms which can be written for these species (eq 3 and 4).



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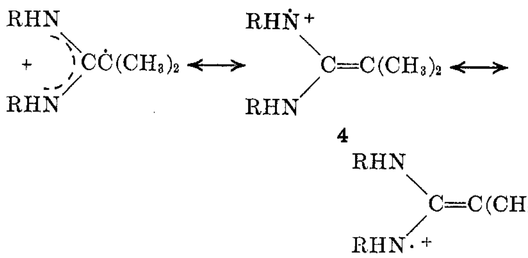

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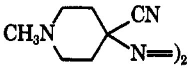
To resolve this uncertainty, it was proposed[6] that a similar study be carried out using azo compounds such as **5** and **6**. While the geminate product radicals from



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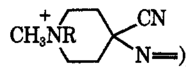
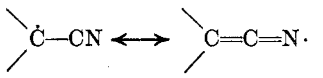


6

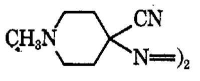
these systems would be expected to possess different electrostatic interactions, their stabilities should be essentially the same due to delocalization into the α-cyano group (**7**). Also, because of the expected simi-



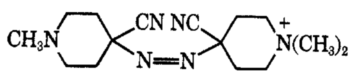
7

larities in radical stabilities, electrostatic repulsive interactions in the dipositive azo compound might be reflected in differences in the decomposition rate constants of **5** and **6**.

In this manuscript, we report such a study using the neutral, monopositive, and dipositive azo compounds **5**, **8**, and **9**. The results are compared with those for the reference compounds **10** and **11**.[7,8]



5
ACMP



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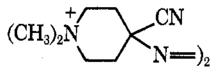
MACMP



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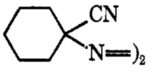
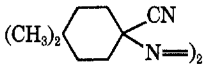
DACMP



10
ACC



11
ACDC

Results and Discussion

Decomposition Kinetics. Rates of thermal decomposition of these azo compounds in DMSO were determined at 80, 85, 90, and 95° by monitoring the evolution of molecular nitrogen. An automatic pressure-equilibrating "gas apparatus" was utilized in these studies.[9] In all cases, the kinetic plots were first order and rate constants were calculated by least-squares analysis of the data. Rate constants reported in Table II are the result of least-squares analysis of the data from several runs and errors reported are standard deviations. Activation parameters were calculated from these data (Table II).

Acid–base titration data and microanalytical results indicated that the sample of MACMP nitrate used in

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[4] For reviews see (a) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 511–516; (b) C. G. Overberger, J.-P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen-Nitrogen Bonds," Ronald Press, New York, N. Y., Chapter 4.

[5] See also R. C. Neuman, Jr., and E. S. Alhadeff, *J. Org. Chem.*, **35**, 3401 (1970).

[6] Proposition V submitted by R. C. N. in partial fulfillment of the requirements for the Ph.D. degree, California Institute of Technology, 1963; see Ph.D. dissertation of R. C. N.

[7] All kinetic data in this study were obtained using the nitrate salts of MACMP and DACMP.

[8] Compounds **5** and **10** were synthesized by W. Snider and M. Amrich, respectively.

[9] (a) T. G. Traylor and C. A. Russell, *J. Amer. Chem. Soc.*, **87**, 3698 (1965). (b) We thank Professor Traylor for his help in providing us information about construction of the gas apparatus.

TABLE II

KINETIC DATA FOR THERMAL DECOMPOSITION OF ACMP, MACMP, DACMP, ACC, AND ACDC IN DMSO[a]

	$k \times 10^5$ sec^{-1}				
Temp, °C	ACMP	MACMP	DACMP	ACC	ACDC
80	0.97 ± 0.03	1.83 ± 0.02	2.84 ± 0.02	1.01 ± 0.01	1.51 ± 0.02
85	1.75 ± 0.07	3.36 ± 0.07	5.11 ± 0.05	2.01 ± 0.11	2.79 ± 0.08
90	3.64 ± 0.05	6.62 ± 0.34	9.87 ± 0.25	3.89 ± 0.05	5.40 ± 0.08
95	6.47 ± 0.06	11.80 ± 0.10	16.26 ± 0.24	6.83 ± 0.16	9.77 ± 0.04
ΔH^*	32.6 ± 0.9	31.7 ± 0.6	29.8 ± 1.0	32.4 ± 0.9	31.6 ± 0.5
ΔS^*	10.4 ± 2.6	9.2 ± 1.5	4.6 ± 2.7	9.7 ± 2.4	8.6 ± 1.3
ΔF^*	28.8	28.4	28.1	28.9	28.5

[a] Rate constants determined from nitrogen evolution.

these kinetic studies was contaminated by about 6 mol % DACMP dinitrate. Based on this and the known rate constants for decomposition of DACMP dinitrate, corrected rate constants for decomposition of MACMP nitrate were calculated from the kinetic data.[10] These and the resulting activation parameters are compared in Table III with those obtained by least-squares analysis of the uncorrected kinetic data (*i.e.*, those reported in Table II). Their similarity suggests that the contamination of MACMP nitrate can be ignored.

TABLE III

A COMPARISON OF CORRECTED AND UNCORRECTED KINETIC DATA FOR MACMP NITRATE

	$k \times 10^5$ sec^{-1}	
Temp, °C	Uncorrected[a]	Corrected[b]
80	1.83 ± 0.02	1.76 ± 0.04
85	3.36 ± 0.07	3.31 ± 0.09
90	6.62 ± 0.34	6.23 ± 0.16
95	11.80 ± 0.10	11.56 ± 0.12
ΔH^*	31.7 ± 0.6	31.7 ± 0.4
ΔS^*	9.2 ± 1.5	9.2 ± 1.0
ΔF^*	28.4	28.4

[a] Experimental results based on nitrogen evolution. [b] Calculated from experimental data assuming 6 mol % contamination by DACMP dinitrate.

The differences in rate constants between the dipositive (DACMP) and neutral compound (ACMP) are substantially smaller than those found between the compounds **1** and their conjugate acids **2**. This supports the arguments presented relative to radical stability in the azoamidine series (*vide supra*) and suggests that only a small fraction of the rate difference observed by Hammond could have been due to electrostatic repulsion between the positively charged ends of the azobisamidinium molecules.[3] That electrostatic repulsion is probably not responsible for even the small differences between ACMP and DACMP is indicated by the intermediate values of the decomposition rate constants for the monopositive compound MACMP.

The regular trend in rate constants and ΔF^* values for ACMP, MACMP, and DACMP suggests that their differences are the result of steric and/or specific solvation effects. A comparison of the rate data for ACC and ACDC shows that dimethyl substitution in the 4 positions increases the decomposition rate constants. Molecular models indicate that rehybridization of the ring carbon bearing the cyano group from sp^3 to sp^2 decreases steric interactions between the axial methyl in the 4 position and the *ring methylene groups in the 2 positions*. Since such rehybridization should occur to some extent in the transition state for decomposition of the azo compounds, the observed rate (and ΔF^*) differences between ACC and ACDC are reasonably explained on this basis.

In terms of these 1,3-steric interactions and their rate effects, it seems proper to compare the difference between ACDC and ACC with that between DACMP and ACMP. While the latter already has one methyl group on each ring nitrogen, these should be in equatorial positions[11] and this is supported by the similar rates and ΔF^* values for ACC and ACMP. Addition of the two methyl groups to form DACMP might then be expected to lead to the same rate enhancement as observed on going from ACC to ACDC. The effect is bigger, however, suggesting that other factors may be involved. Since DMSO is a good cation solvator, perhaps the increase in bulk around the positive ring nitrogens increases steric interactions in the ground state which are relieved somewhat in the decomposition transition state.

Examination of the values of ΔH^* and ΔS^* suggests that the rate variations are enthalpic and this does not conflict with the explanations proposed. While the value of ΔS^* for DACMP appears to be lower than those for the other systems, the magnitude of the difference does not seem to warrant special consideration.

Efficiencies of Radical Production.—The efficiencies of radical production from ACC (**10**), ACDC (**11**), and DACMP dinitrate (**9**) were determined from studies of inhibition of hydrocarbon oxidation.[3,12] The solvent system was a 2:1 v/v mixture of dimethyl sulfoxide and cumene;[3] the inhibitor was di-*tert*-butyl-*p*-cresol (DBPC). The neutral azo compound ACMP functioned as an oxidation inhibitor, and data could not be obtained for this system.[13] The efficiencies were cal-

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[10] (a) The best values of the rate constant for decomposition of MACMP (k_1) were calculated from the known values (Table II) for DACMP (k_2) using the equation[10b] $V_\infty - V_t = V_{\infty 1}e^{-k_1 t} + V_{\infty 2}e^{-k_2 t}$, where V_∞ and V_t are the experimental volumes of nitrogen at infinite time and time t, and $V_{\infty 1}$ and $V_{\infty 2}$ are infinite time volumes from MACMP and DACMP, respectively; it was assumed that $V_\infty = V_{\infty 1} + V_{\infty 2}$ and that $V_{\infty 1} = 0.94\ V_\infty$. (b) See, *e.g.*, I. Amdur and G. G. Hammes, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1966, pp 15–16.

[11] While the relative "sizes" of the NH hydrogen and the nitrogen lone pair in piperidine are not certain [G. A. Yousif and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 6428 (1968)] it seems accepted that the methyl group on nitrogen in *N*-methylpiperidine should occupy an equatorial position [J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *ibid.*, **89**, 3761 (1967); J. L. Sudmeier and G. Occupati, *ibid.*, **90**, 154 (1968)].

[12] (a) C.-H. S. Wu, G. S. Hammond, and J. M. Wright, *ibid.*, **82**, 5386 (1960). (b) Inhibition times (t_i) were sufficiently short to preclude complications from ketenimine formation.

[13] The tertiary amino groups must be acting as the inhibitors. Similar results were observed in attempts to study neutral azoamidines.[3]

TABLE IV

EFFICIENCIES OF RADICAL PRODUCTION FROM ACC, ACDC, AND DACMP DINITRATE IN 2:1 DMSO–CUMENE BY INHIBITION OF CUMENE AUTOXIDATION (80°)

RN_2R	$k \times 10^5$,[a] sec^{-1}	$(RN_2R)_0$, $M \times 10^2$	$(DBPC)_0$, $M \times 10^3$	t_i, min	Efficiency[a]
ACC	1.03	6.57	5.20	215.8	0.64
		6.40	1.40	58.2	0.62
		6.85	1.40	54.0	0.63
ACDC	1.40	6.44	1.40	51.6	0.51
		6.04	0.866	33.7	0.51
		5.13	0.866	37.9	0.54
DACMP·	3.28	1.10	0.253	31.7	0.38
$2NO_3$		0.87	0.174	26.3	0.40

[a] Rate constant for decomposition of RN_2R in DMSO–cumene solvent system; determined from nitrogen evolution.

culated (Table IV) using eq 5 in which $(DBPC)_0$ and $(RN_2R)_0$ are the initial concentrations of inhibitor and

$$a = (DBPC)_0/(RN_2R)_0(1 - e^{-kt_i}) \quad (5)$$

initiator, respectively; k is the rate constant for decomposition of RN_2R in 2:1 DMSO–cumene (Table IV),[14] and t_i is the duration of the inhibition period.[3,12]

The a values for ACC (Table IV) are in reasonable agreement with those reported by Hammond (0.61).[12] In comparison, the values of a for ACDC are smaller than those for ACC, while those for the dipositive azo compound, DACMP nitrate, are the *smallest* of the three. These data imply that any electrostatic repulsion between the positively charged geminate neighbors must be balanced by contributions which tend to decrease k_d. We suggest that among such factors, the mass of the radicals is of substantial importance. Increasing radical mass should lead to lower values of k_d, and a decrease in the efficiency of radical production. If it is assumed that the nitrate anions contribute to the mass of the product radicals from DACMP dinitrate, the data in Table IV follow the expected trend. These results indicate that the variation in the data in Table I is largely due to relative radical stability.

Experimental Section

Syntheses. 4,4′-Hydrazobis-4-cyano-1-methylpiperidine.—A 64.3-g (0.569 mol) sample of *N*-methyl-4-piperidone (Aldrich) was dissolved in 283 ml of water containing 56 g of concentrated hydrochloric acid. To this solution was carefully added with stirring 45.7 g of hydrazine sulfate followed by 31.3 g of sodium cyanide. After stirring for 24 hr, sufficient concentrated aqueous sodium hydroxide was added to bring the pH of the solution above 10. The resultant white precipitate was collected, washed with three portions of water, and dried *in vacuo* over P_2O_5, yield 57.0 g (72.6%).

4,4′-Azobis-4-cyano-1-methylpiperidine (ACMP) (5).—The 57.0-g sample of the hydrazo compound was dissolved in 347 ml of water containing 68.6 ml of concentrated hydrochloric acid in a three-necked, round-bottom flask fitted with an immersion thermometer, dropping funnel, and drying tube. While stirring this solution, 12.1 ml (35.3 g) of bromine was added dropwise over a period of 45 min. During the addition a small amount of red solid material was formed and at the end of the addition a white solid precipitated from solution. The latter was redissolved by warming the flask briefly and the red material was removed by filtration. The pH of the clear solution was raised above 10 by the addition of concentrated aqueous sodium hydroxide and the resultant white precipitate was collected by filtration, washed with water, and dried *in vacuo* over P_2O_5, yield 44.8 g (79.2%). The azo compound was recrystallized from 95% ethanol: mp 137–138° dec; uv λ_{max} (95% EtOH) 349.5 mμ (ϵ 16). *Anal.* Calcd for $C_{14}H_{22}N_6$: C, 61.29; H, 8.08; N, 30.63. Found: C, 61.30; 8.24; N, 30.20. The yield of nitrogen gas on thermal decomposition was *ca.* 99.9% of theoretical.

***N,N′*-Dimethyl-4,4′-azobis-4-cyano-1-methylpiperidine Dinitrate (DACMP Dinitrate) (9).**—A 3.4-g (0.014 mol) sample of recrystallized ACMP was dissolved in 300 ml of 95% ethanol. To this was added a solution consisting of 2 ml (*ca.* 0.032 mol) of CH_3I diluted to 30 ml with 95% ethanol. The flask was stoppered, covered with aluminum foil, and stirred at room temperature for 48 hr. The resultant white precipitate was filtered from solution, shaken with 100 ml of 95% ethanol, refiltered, and rinsed with three 10-ml portions of 95% ethanol. The 2.5 g (36.6% yield) of DACMP diiodide was dried *in vacuo* over phosphorus pentoxide: mp 187–190° dec; uv λ_{max} (50% EtOH) 349.0 mμ (ϵ 9.0). *Anal.* Calcd for $C_{16}H_{28}N_6I_2$: C, 34.42; H, 5.06; N, 15.06; I, 45.46. Found: C, 35.13; H, 5.61; N, 15.04; I, 42.70.

A 2.2-g sample of DACMP diiodide was dissolved in 50 ml of water and carefully titrated with stirring by 0.25 *M* aqueous silver nitrate until formation of silver iodide ceased. Tests on the resultant solution indicated the virtual absence of ionic iodide or silver. The solution was lyophilized, yielding 1.7 g (99%) of DACMP dinitrate: mp 183–185° dec; uv λ_{max} (H_2O) 351.2 mμ (ϵ 11.6). *Anal.* Calcd for $C_{16}H_{28}N_8O_6$: C, 44.85; H, 6.59; N, 26.15; O, 22.41. Found: C, 44.91; H, 6.91; N, 24.99. The yield of nitrogen gas on thermal decomposition was *ca.* 99.8% of theoretical.

***N*-Methyl-4,4′-azobis-4-cyano-1-methylpiperidine Nitrate (MACMP Nitrate) (8).**—A 22.3-g (0.081 mol) sample of recrystallized ACMP was dissolved in 300 ml of anhydrous methanol and to this was added a solution of 0.50 ml (0.008 mol) of methyl iodide in 25 ml of methanol. The solution was stirred for 2 days in a stoppered flask covered with aluminum foil. Subsequently, the methanol was evaporatively distilled giving white crystals with a yellowish tinge. Excess ACMP was removed using a Soxhlet extractor with ether as the solvent. The solid was continuously extracted until no more ACMP was found in the ether solvent. The remaining 2.6 g of solid material was canary yellow and tests with aqueous $AgNO_3$ showed that it contained ionic iodide. Titration with standard hydrochloric acid indicated that the solid was the iodide salt of MACMP contaminated with about 3 mol % DACMP diiodide.

The nitrate salt was obtained by ion exchange. A 15.2-g sample of wet Dowex 1-10X anion-exchange resin (33.4 mequiv exchangeable anions) was placed in a standard 100-ml buret. The column was treated with a solution of 28.3 g of sodium nitrate in 100 ml of water and rinsed with 200 ml of water. A solution made up of 1.86 g of MACMP iodide in 50 ml of water was slowly run through the column followed by an additional 50 ml of water. The solution was lyophilized, giving white crystals. Titration with standard hydrochloric acid indicated that MACMP nitrate was contaminated by *ca.* 6 mol % (8 wt %) DACMP dinitrate. *Anal.* Calcd for $C_{15}H_{25}N_7O_3$: C, 51.27; H, 7.17; N, 27.90; O, 13.66. Found: C, 50.86; H, 7.50; N, 26.80. Calcd for 92 wt % $C_{15}H_{25}N_7O_3$ and 8 wt % $C_{16}H_{28}N_8O_6$: C, 50.76; H, 7.12; N, 27.77; O, 14.35. Based on 92 wt % MACMP nitrate in the samples used in the kinetic study, the yield of nitrogen gas on thermal decomposition was *ca.* 97% of theoretical.

4,4-Dimethyl-2-cyclohexen-1-one.[15]—A solution of 58.5 g (0.81 mol) of distilled isobutyraldehyde and 56.9 g (0.81 mol) of distilled methyl vinyl ketone in 300 ml of anhydrous methanol was placed in a 1-l. single-neck round-bottom flask fitted with a condenser, drying tube, and magnetic stirrer. A 30-ml portion of 1 *N* sodium methoxide in methanol was added and the resulting solution started to reflux immediately. After 1 hr, the solution was neutralized with 1.8 ml of glacial acetic acid, mixed with 1 l. of water, and extracted eight times with 20-ml portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, and evaporatively distilled. The resulting liquid was vacuum distilled and the desired product was collected in 37% yield over the range 84–87° (20 mm): ir 1680 cm^{-1} (C=O) (lit.[15] 1680 cm^{-1}); uv λ_{max} (95% EtOH) 318.5 mμ (ϵ 29.5) [lit.[15] λ_{max} (EtOH) 318.0 mμ (ϵ 30)]; semicarbazone mp 207–208° (lit.[15] 209°).

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[14] The rate constants for decomposition of ACC and ACDC are about the same in 2:1 DMSO–cumene as in pure DMSO (Table II); however, that for DACMP is slightly larger. It is possible that this reflects an electrostatic repulsion effect.

[15] J. M. Conia and A. Le Craz, *Bull. Soc. Chim. Fr.*, 1934 (1960).

4,4-Dimethylcyclohexanone.[15]—A mixture of 15.4 g of 4,4-dimethyl-2-cyclohexen-1-one, 50 ml of ether, and 1 g of platinum black was hydrogenated at room temperature using an initial hydrogen pressure of 24 psi. The mixture was allowed to react for 14 hr, filtered, and evaporatively distilled. The ir showed an absorption at 1710 cm^{-1} (C═O) (lit.[15] 1710 cm^{-1}). Another absorption was observed at 3390 cm^{-1} (OH) indicating that a part of the ketone had been reduced to the corresponding alcohol. To reoxidize the alcohol to the ketone, the procedure of Auwers and Lange was used.[16] A solution consisting of 10 g of potassium dichromate and 8.5 g of concentrated sulfuric acid in 50 ml of water was prepared and the crude reaction mixture containing both alcohol and ketone was added. This mixture was stirred for 0.5 hr, heated on a steam bath for 10 min, and steam distilled. The distillate was saturated with sodium chloride, extracted with ether, dried over anhydrous magnesium sulfate, and evaporatively distilled, resulting in the recovery of 12.1 g of white needle crystals: uv λ_{max} (EtOH) 281.0 mμ (ϵ 31) [lit.[15] λ_{max} (EtOH) 281.0 mμ (ϵ 32)].

1,1′-Hydrazobis-1-cyano-4,4-dimethylcyclohexane.—A solution of 19.0 g (0.15 mol) of 4,4-dimethylcyclohexanone, 7.4 g (0.15 mol) of sodium cyanide, 9.8 g (0.075 mol) of hydrazine sulfate, and 15 ml of dioxane in 100 ml of water was stirred for 50 hr at room temperature. The resulting solid was filtered and recrystallized from 95% ethanol, 2.19 g (97% yield), mp 148–149°.

1,1′-Azobis-1-cyano-4,4-dimethylcyclohexane (ACDC) (11).—A 15.1-g (0.05 mol) sample of the hydrazo compound was stirred with 25 ml of 2 *N* HCl, and bromine was added in 0.5-ml portions to the resulting slurry with cooling until the mixture retained a yellowish color. A total of 2.58 ml of bromine was added (94.5% of theoretical). The yellowish, fluffy solid was removed by filtration, recrystallized first from methanol, and then from low-boiling petroleum ether (bp 30–60°). The azo compound was obtained in 79% yield: mp 132–133° dec; uv λ_{max} (95% EtOH) 351.0 mμ (ϵ 18.3). *Anal.* Calcd for $C_{18}H_{28}N_4$: C, 71.96; H, 9.39; N, 18.65. Found: C, 71.75; H, 9.38; N, 18.24. The yield of nitrogen gas on thermal decomposition was *ca.* 100% of theoretical.

1,1′-Azobis-1-cyanocyclohexane (ACC) (10).—This compound was synthesized by Mr. M. Amrich according to the procedure reported by Overberger (see Hammond)[12] and recrystallized from methanol: mp 113–115° dec (lit.[12] 113–114°, 114–115°); uv ϵ at 350.0 mμ (95% ethanol), 18.2 (lit.[12] 17.9, ethanol; 19.4, chlorobenzene).

Kinetic Studies.—Nitrogen evolution was monitored using a constant-pressure gas apparatus based on a design by Professor T. Traylor.[9]

Efficiency Studies.—Oxygen uptake was monitored using the gas apparatus employed in the kinetic studies.

Registry No.—**5**, 32174-90-6; **8**, 32174-91-7; **8** nitrate, 32174-92-8; **9**, 32174-93-9; **9** dinitrate, 32256-09-0; **9** diiodide, 32174-94-0; **11**, 32174-95-1; 1,1′-hydrazobis-1-cyano-4,4-dimethylcyclohexane, 32174-96-2.

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[16] K. v. Auwers and E. Lange, *Justus Liebigs Ann. Chem.*, **401**, 303 (1913).

Ion Radicals. XXIII. Some Reactions of the Perylene Cation Radical[1,2]

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Solid perylene cation radical perchlorate has been prepared (a) in admixture with perylene by anodic oxidation of perylene, and (b) in admixture with silver iodide by oxidation of perylene with iodine–silver perchlorate. Each of these preparations is usable for studying reactions of the cation radical. Reaction with water led to perylene and 3,10-perylenequinone (**3**). The stoichiometry of this reaction is $6C_{20}H_{12}\cdot^{+} + 2H_2O \rightarrow 5C_{20}H_{12} + C_{20}H_{10}O_2 + 6H^{+}$. Reaction with pyridine gave *N*-(3-perylenyl)pyridinium perchlorate (**9**), degradation of which by the Zincke method gave 3-aminoperylene. Compound **9** was also obtained easily by the direct reaction of perylene, iodine, silver perchlorate, and pyridine. Perylene cation radical was reduced quantitatively by iodide ion. Reduction by bromide ion also appeared to be quantitative. Reaction with chloride ion also led mostly to perylene. Reaction with fluoride ion did not occur; reaction with unremoved small amounts of water occurred slowly instead. Reaction with acetate and benzoate ion led to the 3-perylenyl esters. The overall picture is that nucleophilic substitution occurs where the nucleophile is not easily oxidized, and substitution occurs at the position in the cation radical which has the highest positive charge density according to simple HMO calculations.

Although the perylene cation radical has been known for some time and has been well characterized spectroscopically,[4] hardly anything is known about its chemistry. Some years ago it was found that perylene was recovered from dilution of a solution of the cation radical in 96% sulfuric acid with water.[5] Since conversion of perylene into the cation radical in 96% sulfuric acid is high,[5] the re-formation of perylene by dilution with water was, apparently, a chemical rather than physical reaction.

Cation radicals are frequently made in strong acid solutions. Chemical studies in such cases are almost impossible. Antimony pentachloride is also frequently used, both for spectroscopic, solution studies[4] and for precipitating cation radicals as antimony halide salts.[6] The composition of the perylene cation radical salt has been reported as $C_{20}H_{12}SbCl_5$, for example.[6] The use of antimony pentachloride systems for chemical studies, however, does not seem to be suitable. Complications are caused by the antimony halide, and, in reaction with nucleophiles, organoantimony compounds or complexes are formed.[7]

Recently, the perylene cation radical was prepared in the solid state by two methods which we have adapted fruitfully to chemical studies. Williams prepared a 1:1 complex of perylene and perylene perchlorate by anodic oxidation,[8] while Sato and coworkers[6] precipitated the perchlorate in admixture with silver iodide by treating perylene with iodine and silver perchlorate. We have already shown that the cation radical isolable by each of these methods can be used

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[1] Part XXII: J. J. Silber and H. J. Shine, *J. Org. Chem.*, **36**, 2923 (1971).

[2] Supported by the National Science Foundation Grant No. GP-25989X.

[3] Postdoctoral fellow.

[4] I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

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[6] Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, *Bull. Chem. Soc. Jap.*, **42**, 3051 (1969).

[7] Unpublished work in these laboratories by T. Okuyama.

[8] D. F. Williams, Abstracts, Fourth Molecular Crystal Symposium, Enschede, Holland, July 1968. We thank Dr. Williams for further details by private communications. T. C. Chiang, A. H. Reddoch, and D. F. Williams, *J. Chem. Phys.*, **54**, 2051 (1971).