N′,N′-Diphenyl-1,2-naphthylenediamine (7).—A solution of **6** (4 g, 11.8 mmol) in 200 ml of diethyl ether was added alternately with small portions of water (1 ml total) to 4 g of aluminum amalgam[27] during 1 hr at room temperature. The solution was stirred for an additional 1 hr, filtered, and dried over K_2CO_3. The product was eluted from alumina with diethyl ether and recrystallized from the same solvent to give 1.88 g (51% yield) of colorless **7**, mp 171–172°. The infrared spectrum showed NH absorptions at 3405 and 3490 cm^{-1}.

Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.84; N, 9.03. Found: C, 85.29; H, 5.90; N, 9.04.

N-(2-Naphthyl)-N′,N′-diphenyl-1,2-naphthylenediamine (8).—This compound was prepared by the copper-catalyzed reaction of 1 g (3.22 mmol) of **7** with 0.818 g (3.22 mmol) of 2-iodonaphthalene. *n*-Dodecane was used as solvent, and reaction time was 6 hr at 200°. After distillation of the solvent under a stream of nitrogen, the crude product was eluted from alumina with benzene to give 0.9 g of a pale yellow glassy solid. The thin layer chromatogram showed that only a small amount (*ca.* 5%) of diarylation had occurred. The product was reluctant to crystallize, and seed crystals were obtained by allowing the glassy solid to stand under absolute ethanol at room temperature for 6 weeks. Crystallization of the main lot from ether–alcohol yielded 0.477 (34% yield) of **8**, mp 130–130.5°. The NH absorption at 3400 cm^{-1} had the intensity required for one NH bond per molecule.[1]

Anal. Calcd for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42. Found: C, 87.97; H, 5.60; N, 6.36.

N-(2-Naphthyl)-N,N′,N′-triphenyl-1,2-naphthylenediamine (9).—The copper-catalyzed reaction of **8** (0.834 g, 1.91 mmol) with excess iodobenzene (10 ml) as solvent yielded after chromatography 0.824 g of pale yellow glassy solid, which crystallized within 1 hr upon addition of diethyl ether. Recrystallization from diethyl ether afforded 0.584 g (59% yield) of **9**, mp 205–207°. No NH absorption was observed in the infrared spectrum.

Anal. Calcd for $C_{38}H_{28}N_2$: C, 89.03; H, 5.50; N, 5.47. Found: C, 89.35; H, 5.44; N, 5.50.

Reaction of N-(2-Naphthyl)-N,N′-diphenyl-1,2-naphthylenediamine (3a) with Iodobenzene.—Under the conditions described above, **3a** (1 g, 2.3 mmol) reacted with iodobenzene to give 0.627 g (53% yield) of recrystallized **9**, mp 207–208.5°, mmp 205–208°. The infrared spectrum was identical with that of the authentic sample described above.

1,4-Diphenyl-1,4-di(2-naphthyl)-2-tetrazene (10).—A solution of potassium permanganate (2.69 g, 0.017 mol) in 500 ml of acetone was added dropwise during 3 hr to an acetone (100 ml) solution of 1-phenyl-1-(2-naphthyl)hydrazine[28] (6 g, 0.0256 mol) cooled in a Dry Ice–acetone bath under nitrogen. Stirring was continued at −78° for an additional 1 hr. The reaction was allowed to warm to 5° and filtered. The filtrate was evaporated to 60 ml at reduced pressure, stored at −18° for 16 hr, and filtered to give 3.72 g (62% yield) of tetrazene **10** as a rust-colored powder. The crude tetrazene was recrystallized with minimum decomposition by dissolving in boiling it methylene chloride (30 ml), adding absolute ethanol (25 ml) gradually, and cooling. Recovery of the pale yellow product was 70–80%. Decomposition points at several heating rates were determined with a Du Pont 900 differential thermal analyzer (deg/min, decomposition point): 2, 101; 5, 107; 10, 111; 30, 114. The decompositions of solid samples were strongly exothermic and those at fast heating rates appeared to be explosive. Thermolysis in solution was controlled and yielded 99 ± 1% of the theoretical azo nitrogen. The infrared spectrum showed a complete absence of NH bonds in the recrystallized product; uv max (2% CH_3CN–98% C_2H_5OH)[29] 350 nm (ϵ 2.22 × 10^4), 316 (1.9 × 10^4), and 274 (2.36 × 10^4).

Anal. Calcd for $C_{32}H_{24}N_4$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.62; H, 5.24; N, 11.95.

Photolysis of **10** was conducted under nitrogen in a quartz reactor with 2537-Å light for 10 hr at 5°. Nitrogen evolution was 93% of theory.

Registry No.—**1a**, 135-88-6; **2c**, 23854-07-1; **2d**, 23854-08-2; **2e**, 23854-09-3; **2f**, 23854-10-6; **2g**, 23854-11-7; **6**, 23854-12-8; **7**, 23854-13-9; **8**, 23854-14-0; **9**, 23890-44-0; **10**, 23854-15-1.

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[27] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 20.

[28] J. Heidt, E. Gömbös, and F. Tüdös, *KFKI* (*Közp. Fiz. Kut. Intez. Közlem.*), **14**, 183 (1966).

[29] Acetonitrile was used to rapidly dissolve the tetrazene before dilution with alcohol in order to avoid decomposition from prolonged stirring.

The Oxidative Coupling Reaction of Vinylidenebisdialkylamines[1]

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A series of vinylidinebisdialkylamines, $R_2C{=}C(NMe_2)_2$, were oxidized by silver ion in acetonitrile solvent, yielding diamidinium salts *via* dimerization. Cyclization is also possible by this method, which is believed to involve radical cation intermediates.

While enamines and related compounds have been the focus of extensive research in recent years, rather limited attention has been paid to their oxidation.[2-7] We felt that vinylidenebisdialkylamines (ketene-N,N-acetals), a somewhat less common class of enamines, would be ideally suited as substrates for oxidation. It is, of course, well known that olefinic systems having electron-withdrawing substituents will reductively accept electrons, giving rise to subsequent reactions.[8] It seemed reasonable to assume that enamines would readily give up electrons to form reactive intermediates.

Results and Discussion

The observation that led to the present study was that 9-[bis(dimethylamino)methylene]fluorene (**1**) gradually turned blue on exposure to air and that the blue material was esr active. Bromine vapors caused the same transformation even more rapidly, and the oxidizing system settled on as the most convenient and free of side reactions was silver nitrate in acetonitrile.

Oxidation of **1** with silver nitrate produces a deep blue, esr active[9] solution of radical cation, which can be isolated as a copper-colored crystalline hexafluorophosphate, **2**. Although **1** and **2** can be reversibly interconverted electrochemically[9] in what appears to

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[1] Reported in part by H. Weingarten and J. S. Wager, *Tetrahedron Lett.*, No. 38, 3267 (1969).

[2] F. A. Bell, R. A. Crellin, H. Fujii, and A. Ledwith, *Chem. Commun.*, 251 (1969).

[3] M. E. Kuehne and T. J. Giacobbe, *J. Org. Chem.*, **33**, 3359 (1968).

[4] F. Bohlmann and H. Peter, *Chem. Ber.*, **99**, 3362 (1966).

[5] V. Van Rheenen, *Chem. Commun.*, 314 (1969).

[6] L. P. Vinogradova, G. A. Kogan, and S. I. Zav'yalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1061 (1964).

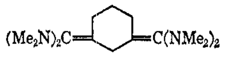
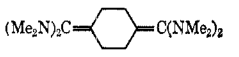
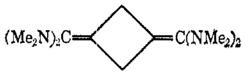
[7] C. S. Foote and J. Wei-Ping Lin, *Tetrahedron Lett.*, No. 29, 3267 (1968).

[8] M. M. Baizer, *J. Electrochem. Soc.*, **111** (2), 215 (1964).

[9] An esr study and an electrochemical study will be reported elsewhere: J. Fritsch, H. Weingarten, and J. D. Wilson, in press.

TABLE I

PHYSICAL CONSTANTS AND ELEMENTAL ANALYSES OF DIENETETRAMINES

Compd no.	Compd[a]	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Nmr, τ	Mp or bp, °C (mm)
12	$CH_2[CH{=}C(NMe_2)_2]_2$	52	65.1	11.6	23.3	64.9	11.5	23.6	(C_6H_6) 6.28 (t, 1, J = 7 Hz), 7.17 (t, 1, J = 7 Hz), 7.31 (s, 6), 7.61 (s, 6)	73 (0.1)
14	$+CH_2CH{=}C(NMe_2)_2]_2$	40	66.1	11.8		66.4	11.6		(C_6H_6) 6.25 (m, 1), 7.32 (s, 6), 7.58 (s, 6), 7.70 (m, 2)	85 (0.1)
15	$CH_2[CH_2CH{=}C(NMe_2)_2]_2$	74				. . .[b]			(C_6H_6) 6.30 (t, 1) 7,35 (s, 6), 7.61 (s, 6), 7.89 (m, 2), 8.44 (m, 1)	87 (0.1)
17		61	68.5	11.5	20.0	68.4	11.4	19.6	(CD_3CN) 7.34 (s, 1), 7.42 (s, 6), 7.44 (s, 6), 7.90 (m, 2), 8.45 (m, 1)	100 (0.15)
19		65	68.5	11.5	20.0	68.6	11.8	19.7	(C_6H_6) 7.38 (s, 3), 7.69 (s, 1)	83–85
21		73	66.6	11.2		66.9	10.9		(CD_3CN) 6.47 (s, 1), 7.46 (s, 1)	100 (0.2)
22		68				. . .[b]			(CD_3CN) 7.13 (m, 1), 7.42 (s, 12), 7.75 (m, 2)	98 (0.15)

[a] See ref 10. [b] These compounds are very atmosphere sensitive and in some cases we were not able to obtain satisfactory elemental analyses.

be a one-electron process, we have not been able to determine if the radical cation is dimerized to any extent. If the dimer exists, it must be in dynamic equilibrium with the radical cation.

The result of silver-ion oxidation of 2-methylpropenylidenebisdimethylamine [$(CH_3)_2C{=}C(NMe_2)_2$, **3**], although varying from the oxidation of **1**, is consistent with the formation of a radical cation intermediate. The only observable reaction is disproportionation, yielding an equal mixture of 1,1-bis(dimethylamino)isobutylium nitrate [$(CH_3)_2CH\overset{+}{C}(NMe_2)_2NO_3^-$, **4**] and 1,1-bis(dimethylamino)methylallylium nitrate [$CH_2{=}C(CH_3)\overset{+}{C}(NMe_2)_2NO_3^-$, **5**].

Vinylidenebisdialkylamine (**6**), the parent enediamine of the series, yields yet a different result on oxidation. Dimerization takes place and the ultimate product

$$\begin{array}{c} \underset{\mathbf{6}}{2CH_2{=}C(NMe_2)_2} + 2Ag^+ \\ \downarrow \\ \underset{\mathbf{7}}{(Me_2N)_2\overset{+}{C}CH_2CH_2\overset{+}{C}(NMe_2)_2} + 2Ag \\ \downarrow{\scriptstyle 2\ (6)} \\ \underset{\mathbf{8}}{(Me_2N)_2C{=}CHCH{=}C(NMe_2)_2} + 2CH_3\overset{+}{C}(NMe_2)_2 \\ \downarrow{\scriptstyle 2Ag^+} \\ \underset{\mathbf{9}}{(Me_2N)_2\overset{+}{C}CH{=}CH\overset{+}{C}(NMe_2)_2} + 2Ag \end{array}$$

is 1,1,4,4-tetrakis(dimethylamino)-2-butene-1,4-diylium nitrate (**9**). The intermediate **7** is no doubt first formed and converted into 1,1,4,4-tetrakis(dimethylamino)butadiene (**8**) by reaction with additional **6**, and **8** is then rapidly oxidized to **9**. The compound **8** was prepared independently[10] and shown to be readily oxidized to **9**. A mixture of **8** and **9** in acetonitrile solvent is strongly esr active and the activity persists indefinitely.

The results of the oxidation of propenylidenebisdimethylamine [$CH_3CH{=}C(NMe_2)_2$, **10**] further wakened our interest in the reaction for its possible synthetic utility as a carbon–carbon bond-forming process. When **10** is oxidized under the reaction conditions, the primary product is a *dl* and *meso* mixture of 1,1,4,4-tetrakis(dimethylamino)-2,3-dimethylbutane-1,4-diylium nitrate [$(Me_2N)_2\overset{+}{C}CH(CH_3)CH(CH_3)\overset{+}{C}(NMe_2)_2\text{-}2NO_3^-$, **11**], corresponding to **7** above. Loss of protons to starting product **10** does not occur to any great extent, indicating that it may not be necessary to sacrifice half of a rather esoteric starting material in the process. The structural assignment of **11** was confirmed by independent synthesis.

To explore the possible generality of the process we turned our attention to the interesting prospect of ring-forming reactions. A series of dienetetramines were prepared by methods already described[10] (see Table I) and subjected to oxidation. N,N,N′,N′,N″,N″,N‴,N‴-Octamethyl-1,4-pentadiene-1,1,5,5-tetramine (**12**), on oxidation with silver nitrate, affords a high yield of a mixture of *cis*- and *trans*-cyclopropylenebis(dimethylaminomethylium) nitrate (**13**). The structural assignment was made by hydrolysis of **13** to the corresponding diamide and comparison with authentic diamide.[11] The *cis/trans* ratio in **13** is about 2:3, whereas the *cis/trans* ratio in the corresponding diamide is about 1:5. It is almost certain that **13** is isomerized in the hydrolysis media, since addition of trace amounts of **6**, a strong base, to an acetonitrile solution of **13** causes the nmr peaks attributed to the *cis* isomer to disappear while the *cis* diamide is stable to base. N,N,N′,N′,N″,N″,N‴,N‴-Octamethyl-1,5-hexadiene-1,1,6,6-tetramine (**14**), however, on oxidation gave only a complex mixture which included polymeric substances. Comparison of nmr spectra of this mixture with those of the expected authentic cyclobutane derivatives suggested that 1,2-cyclobutanes may be present, but in yields below 15%. No cyclobutane derivative was actually isolated.

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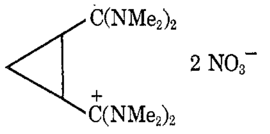
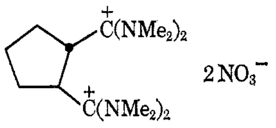
[10] H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 2874 (1966).

[11] A. T. Blomquist and D. T. Longone, *J. Amer. Chem. Soc.*, **81**, 2012 (1959). The *cis* isomer was supplied by C. F. Hobbs, Monsanto Co., St. Louis, Mo.

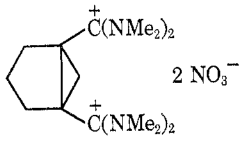
As might be expected, five-membered rings are formed quite readily. N,N,N′,N′,N″,N″,N‴,N‴-Octamethyl-1,6-heptadiene-1,1,7,7-tetramine (**15**) is oxidized in high yield to 1,2-cyclopentylenebis(dimethylaminomethylium) nitrate (**16**). The structural assignment of **16** is based on its hydrolysis to diamide and comparison with authentic sample (only *trans* diamide is observed). The above three examples indicate that the normal order of ease of ring closure applies in this reaction.



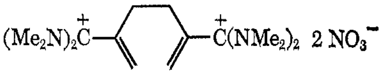
13 (*cis* and *trans*)



16



18



20

We next turned our attention to bicyclic synthesis. 1,3-Bis[bis(dimethylamino)methylene]cyclohexane (**17**) is smoothly and in high yield converted into bicyclo[3.1.0]cyclohexan-1,5-ylenebis(dimethylaminomethylium) nitrate (**18**). The structural assignment of **18** rests on its hydrolysis to diamide and comparison with authentic diamide.[12] The 1,4 isomer of **17**, 1,4-bis[bis(dimethylamino)methylene]cyclohexane (**19**), is converted not into the hoped for [2.2.0] system but into the expected open-chain 1,1,6,6-tetrakis(dimethylamino)-2,5-bis(methylene)hexane-1,6-diylium nitrate (**20**).

Attempts were also made to convert 1,3-bis[bis(dimethylamino)methylene]cyclobutane (**21**) and 1,3-bis[bis(dimethylamino)methylene]cyclopentane (**22**) into the corresponding bicyclo derivatives, but all attempts, even at low temperatures, failed to yield the desired products. It is possible, of course, that the bicyclic systems are formed but that the amidinium substituents considerably lower the barrier to the opening of the strained rings.

While no mechanistic studies, as such, have been carried out, a reasonable mechanistic model can be constructed based on the information at hand. If we accept the electrochemical evidence (esr, cyclic voltammetry, and coulometry) which suggests radical cations as the first intermediates, the chief remaining question is whether two radical cations dimerize or whether the radical cation reacts with starting enediamine. Two facts bear on this question: (1) we have not been able to induce free-radical polymerization of styrene or isoprene under conditions where the radical cation is believed to be generated (oxidation of **6**); (2) enediamine **6** is not incorporated into polyethylene formed by free-radical polymerization nor does it inhibit the ethylene polymerization. These experiments suggest the radical to be reasonably stable and a poor free-radical initiator, and the enediamine to be a poor radical sink. Therefore, we believe that the most plausible mechanistic model involves dimerization of two radical cations.

Experimental Section

Proton nmr spectra were obtained from a Varian Model A-60 spectrometer. Melting points and boiling points are uncorrected. All operations involving the ketene N,N-acetals were performed in an atmosphere of dry nitrogen.

Preparation of 9-[Bis(dimethylamino)methylene]fluorene Radical Cation Hexafluorophosphate (2).—To a solution of 0.250 g (1.47 mmol) of $AgNO_3$ in 5 ml of acetonitrile is added a solution of 0.370 g (1.40 mmol) **1** in 5 ml of acetonitrile. The reaction mixture turns deep blue immediately and a near quantitative precipitate of metallic silver appears. The solution is filtered and the filtrate is added to a 25-ml aqueous solution of $NaPF_6$ (excess). A dark precipitate of **2** is formed, collected, and dried: wt 0.43 g (75%). The precipitate is recrystallized from acetonitrile–methanol, yielding copper-colored crystals.

Anal. Calcd for $C_{18}H_{20}N_2PF_6$: C, 52.8; H, 4.9; N, 6.9. Found: C, 52.6; H, 4.9; N, 6.6.

Preparation of 1,1-Bis(dimethylamino)-2-methylallylium Tetraphenylborate (5a).[13]—To a solution of 2.4 g (0.014 mol) of $AgNO_3$ in 25 ml of acetonitrile is slowly added a solution of 2.0 g (0.0156 mol) of **3** also in 25 ml of acetonitrile. The reaction is exothermic and a black precipitate appears immediately. The solution above the precipitate is clear and colorless. The reaction mixture is filtered and an excess of ether is added, precipitating the nitrate-salt mixture. Solvent is removed from the solid, 2.5 g (90%), which is then dissolved in 20 ml of water. Sodium chloride solution is added to remove excess silver ion, the resulting mixture is filtered, and 0.5 equiv of KOH solution is slowly added with constant nmr monitoring. The resultant solution is added to a saturated solution of $NaB(C_6H_5)_4$ and a precipitate of **5a** is formed: yield 2.5 g (87%); nmr (DMSO-d_6) τ 2.75–3.26 (m, 20), 4.30 (m, 1), 4.50 (m, 1), and 6.98 (s, 12), and 9.14 (m, 3). This salt is recrystallizable from acetonitrile–water.

Anal. Calcd for $C_{32}H_{37}N_2B$: C, 83.5; H, 8.1; N, 6.1. Found: C, 83.6; H, 7.9; N, 6.1.

Preparation of 1,1,4,4-Tetrakis(dimethylamino)-2-butene-1,4-diylium Hexafluorophosphate (9a). Method I.—To a solution of 3.5 g (0.0206 mol) of $AgNO_3$ in 20 ml of acetonitrile is added slowly a solution of 2.28 g (0.0200 mol) of **6** in 10 ml of acetonitrile. The reaction is exothermic and black precipitate forms immediately. The reaction mixture is filtered and added to an excess of dry ether. A second phase oils out and is separated from the solvent layer. The second phase is dissolved in methanol and treated with $NaPF_6$, yielding a precipitate of **9a**: yield 2 g (78%);[14] nmr (CD_3CN) τ 2.86 (s, 1) and 6.78 (s, 12). This compound is recrystallizable from acetonitrile–ether.

Anal. Calcd for $C_{12}H_{26}N_4P_2F_{12}$: C, 27.9; H, 5.1; N, 10.9. Found: C, 28.2; H, 5.2; N, 10.8.

Preparation of 1,1,4,4-Tetrakis(dimethylamino)-2-butene-1,4-diylium Hexafluorophosphate (9a). Method II.—To a solution of 0.073 g (0.32 mmol) of **8** in 1 ml of acetonitrile is added slowly a solution of 0.11 g (0.65 mmol) of $AgNO_3$ also in 1 ml of acetonitrile. An exothermic reaction takes place producing a black precipitate and an amber solution which becomes colorless when the addition of silver salt is complete. The reaction mixture is filtered and the filtrate is added to excess ether. A second phase is formed which is separated from the solvent and then dissolved in methanol to which is then added $NaPF_6$. The precipitate which is formed, 0.15 g (90%), is identical in every way with that obtained by method I.

Preparation of 1,1,4,4-Tetrakis(dimethylamino)-2,3-dimethylbutane-1,4-diylium Hexafluorophosphate (11a).—To a solution of 3.6 g (0.021 mol) of $AgNO_3$ in 30 ml of acetonitrile is added slowly a solution of 2.5 g (0.019 mol) of **10** in 20 ml of acetonitrile. An exothermic reaction takes place producing a black precipitate and a light amber solution. This solution is decanted from the silver precipitate into 100 ml of dry ether. The second phase which forms is separated, dried, and then dissolved in methanol. This methanol solution is added to a saturated solution of $NaPF_6$ also in methanol. The precipitate of **11a** which forms is dried and can be recrystallized from acetonitrile–methanol: yield 2.2 g (42%); nmr (CD_3CN) τ 6.35 (m, 1), 6.75 and 6.81 (s, 12), and 8.54 and 8.66 (m, 3) (*dl* and *meso* in a ratio of about 1:3, not assigned).

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[12] H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965).

[13] The letter **a** following a bold-face numeral signifies an anion other than nitrate.

[14] The yield is based on using one-half of compound **6** as a proton scavenger.

Anal. Calcd for $C_{14}H_{32}N_4P_2F_{12}$: C, 30.8; H, 5.9; N, 10.3. Found: C, 30.9; H, 6.0; N, 10.3.

Preparation of Cyclopropylenebis(dimethylaminomethylium) Hexafluorophosphate (13a).—To a solution of 2.0 g (0.012 mol) of $AgNO_3$ in 10 ml of acetonitrile is added slowly a solution of 1.2 g (0.0050 mol) of **12** in 15 ml of acetonitrile (1 ml of benzene added to solubilize amine). An exothermic reaction follows. The filtrate is decanted from the silver precipitate and the solvent is removed. The residue is dissolved in water and the product is precipitated by the addition of $NaPF_6$ solution. The precipitate of *cis*- and *trans*-**13a** can be recrystallized from acetonitrile–chloroform without significant fractionation: yield 2.24 g (85%); nmr (CD_3CN) τ 6.78 and 6.80 (s, 6) (*cis/trans* ratio 2:3), and 7.17–8.25 (m, 1).

Anal. Calcd for $C_{13}H_{28}N_4P_2F_{12}$: C, 29.5; G, 5.3; N, 10.6. Found: C, 29.7; H, 5.3; N, 10.3.

Hydrolysis of the above salt in dilute KOH solution yields a mixture of amides (*cis/trans* ratio, 1:5) identical with the authentic N,N,N′,N′-tetramethylcyclopropanedicarboxamides.[11]

Preparation of 1,2-Cyclopentylenebis(dimethylaminomethylium) Hexafluorophosphate (16a).—To a solution of 4.0 g (0.024 mol) of $AgNO_3$ in 40 ml of acetonitrile is added slowly a solution of 2.68 g (0.010 mol) of **15** in 20 ml of acetonitrile. The reaction is exothermic and a black precipitate is deposited. The reaction mixture is filtered, the filtrate is evaporated, and the residue is dissolved in water. This aqueous solution is treated with $NaPF_6$ yielding a precipitate of **16a**, which can be recrystallized from acetonitrile–chloroform: yield 5.1 g (91%); nmr (CD_3CN) τ 5.95–6.50 (m, 1), 6.79 (s, 12), and 7.35–8.05 (m, 3).

Anal. Calcd for $C_{15}H_{32}N_4P_2F_{12}$: C, 32.3; H, 5.8; N, 10.0. Found: C, 32.1; H, 5.6; N, 9.8.

Hydrolysis of the above salt in dilute KOH solution yielded a diamide identical with authentic *trans*-N,N,N′,N′-tetramethylcyclopentane-1,2-dicarboxamide (mass spectrum and nmr spectrum identical).

Preparation of Bicyclo[3.1.0]cyclohexan-1,5-ylenebis(dimethylaminomethylium) Hexafluorophosphate (18a).—To a solution of 3.7 g (0.022 mol) of $AgNO_3$ in 50 ml of acetonitrile is added slowly a solution of 2.8 g (0.01 mol) of **17** in 30 ml of acetonitrile (plus 5 ml of benzene to solubilize the amine). An exothermic reaction occurs yielding a clear solution and a black precipitate. The reaction mixture is filtered and the filtrate is evaporated. The residue is dissolved in water and treated with $NaPF_6$, which precipitates **18a**. The salt can be recrystallized from acetonitrile–chloroform: yield 5.0 g (88%); nmr (CD_3CN) τ 6.74 (s, 3) and 7.25–8.06 (m, 1).

Anal. Calcd for $C_{16}H_{32}N_4P_2F_{12}$: C, 33.7; H, 5.7; N, 9.8. Found: C, 33.4; H, 5.5; N, 9.6.

Hydrolysis of the above salt in dilute KOH solution yielded a diamide having an nmr spectrum identical with that of authentic N,N,N′,N′-tetramethyl[3.1.0]bicyclohexane-1,5-dicarboxamide.[12]

Preparation of 1,1,6,6-Tetrakis(dimethylamino)-2,5-bis(methylene)hexane-1,6-diylium Hexafluorophosphate (20a).—To a solution of 0.40 g (2.3 mmol) of $AgNO_3$ in 5 ml of acetonitrile is added slowly a solution of 0.25 g (0.89 mmol) of **19** also in 5 ml of acetonitrile. An exothermic reaction takes place depositing a black precipitate. The supernatant liquid remains clear and colorless. The supernatant liquid is decanted and the solvent is removed. The residue is dissolved in methanol and treated with $NaPF_6$, producing a precipitate of **20a** which is recrystallizable from acetonitrile–methanol: yield 0.46 g (90%); nmr (CD_3CN) τ 4.10 (s, 1), 4.26 (s, 1), 6.85 (s, 12), and 7.56 (s, 2).

Anal. Calcd for $C_{16}H_{32}N_4P_2F_{12}$: C, 33.7; H, 5.7; N, 9.8. Found: C, 33.9; H, 5.55; N, 10.0.

Registry No.—**2**, 12408-23-0; **5a**, 23883-43-4; **9a**, 23846-95-9; *dl*-**11a**, 23846-96-0; *meso*-**11a**, 23890-42-8; **12**, 23853-17-0; *cis*-**13a**, 23942-64-5; *trans*-**13a**, 23942-65-6; **14**, 23853-19-2; **15**, 23853-18-1; **16a**, 23846-97-1; **17**, 23853-20-5; **18a**, 23890-43-9; **19**, 23853-97-6; **20a**, 23846-98-2; **21**, 23853-98-7; **22**, 23853-99-8.

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The Thermal Cleavage of Selected Aldehyde Hyrazonium Salts

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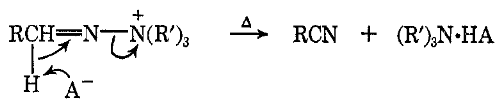
A series of aldehyde trimethylhydrazonium salts, $RCH{=}N{-}\overset{+}{N}(R')_3\ A^-$, has been pyrolyzed. This class of salts cleaved at temperatures of 240–250° to give low yields of the corresponding nitrile. Compounds prepared by replacing two of the three methyl groups with cyclic methylene substituents were found to undergo rapid cleavage at 240° to afford high yields of the desired nitrile.

A survey of the literature revealed several reports that aldehyde trimethylhydrazonium salts undergo a β elimination in alkaline solution to give good yields (51–93%) of the corresponding nitrile.[2-4] However, no study of the thermal decomposition of this class of compounds has been reported.

An interest in pyrolyzable precursors to nitriles prompted us to prepare and thermally cleave a series of aldehyde hydrazonium salts. It was proposed that a thermally induced β elimination might afford high yields of the desired nitrile and ammonium salt. It was felt that changing the basicity of the anion, A^-, as well as placing electron-withdrawing or -releasing groups on the aldehyde substituent (aromatic series), should effect the yield of nitrile. However, this approach was found to have less influence on the yield



$$\underset{\displaystyle H\quad A^-}{RCH}{=}N{-}\overset{+}{N}(R')_3 \xrightarrow{\Delta} RCN + (R')_3N{\cdot}HA$$

of nitrile than did partial replacement of the methyl groups with bulkier substituents.

Discussion and Results

As an extension of our previously reported work,[5] a series of 38 trimethyl quaternary hydrazonium salts

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