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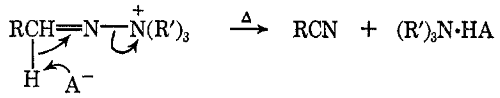
A series of aldehyde trimethylhydrazonium salts, $RCH{=}N{-}\overset{+}{N}(R')_3\ A^-$, has been pyrolyzed. This class of salts cleaved at temperatures of 240–250° to give low yields of the corresponding nitrile. Compounds prepared by replacing two of the three methyl groups with cyclic methylene substituents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



$$RCH{=}N{-}\overset{+}{N}(R')_3\ \xrightarrow{\Delta}\ RCN + (R')_3N{\cdot}HA$$

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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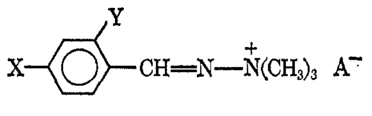
[2] R. F. Smith and L. E. Walker, *J. Org. Chem.*, **27**, 4372 (1962).

[3] B. V. Zoffee and N. L. Zelevinia, *Zh. Org. Chem.*, **4**, 1558 (1969).

[4] K. N. Zelevin and B. V. Zoffee, *Vestn. Leningrad Univ., Fiz., Khim.*, **23**, 159 (1968).

[5] P. Foley, E. Anderson, and F. Dewey, *J. Chem. Eng. Data*, **14**, 272 (1969).

(**1–3**) was cleaved at temperatures between 240 and 250° for 2 or 10 min in a small pyrolysis apparatus. At



1

X	Y	A⁻
OCH_3	H	I^-, Ot_s^-,[6] BF_4^-, Cl^-, $SnCl_6^{-2}$
H	H	
NO_2	H	
Cl	Cl	

$$CH_2[CH_2CH{=}N{-}\overset{+}{N}(CH_3)_3]_2\ A^-$$

2

$A^- = I^-, Br^-, Cl^-, SnCl_6^{-2}, Ot_s^-, ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, NO_3^-$

$$NC(CH_2)_2C(CH_3)_2CH{=}N{-}\overset{+}{N}(CH_3)_3\ A^-$$

3

$A^- = I^-, Cl^-, SnCl_6^{-2}, Ot_s^-, ClO_4^-, BF_4^-, PF_6^-, NO_3^-$

best, yields of less than 20% nitriles **4a** and **4b** were realized, with the formation of much heavy black tar. For aromatic nitriles **4a** the most product was obtained at pyrolysis times of 10 min; less time left much unchanged salt; longer times gave lower yields and more tar. For aliphatic nitriles **4b** a time of 2 min proved best. In addition to the desired nitriles **4a** and **4b** and the corresponding ammonium salt **5**, a side product from the reaction, hydrazones **6a** and **6b** (2–15%) were identified in all instances except those involving the perchlorate and nitrate salts of **2** and **3**, indicating loss of a methyl group during pyrolysis. Formation of hydrazones has been observed in the alkaline cleavage of trimethylhydrazonium salts and a mechanism involving nucleophilic attack by base on a methyl group has been proposed.[3,4]

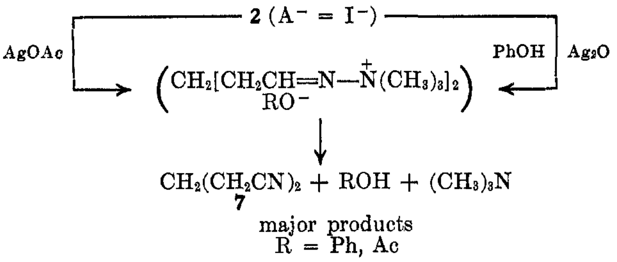
$$\mathbf{1, 2, 3} \xrightarrow{\Delta} \underset{\mathbf{4a,\ 4b}}{RCN} + \underset{\mathbf{5}}{(CH_3)_3N{\cdot}HA} + \underset{\mathbf{6a,\ 6b}}{RCH{=}N{-}N(CH_3)_2}$$

R = aromatic
R = aliphatic

Salts **1**, **2**, and **3** decomposed slowly below 200°, but the necessity for rapid reaction led to the use of 240–250° for pyrolysis. The salts darkened slightly above their melting points, then decomposed exothermically to give the desired products and much tar. The perchlorate and nitrate salts of **2** and **3** detonated at 240° to give fine black powders that were essentially inorganic. Nitriles **4b** and hydrazones **6b** were not detected (ir).

Cleavage of the iodide salts of **1**, **2**, and **3** led to the formation of an unexpected product. Tetramethylammonium iodide was isolated (45–47%) from each residue and its structure was authenticated by ir spectrum, melting point, and elemental analysis. In addition, the corresponding nitriles **4a** and **4b** and hydrazones **6a** and **6b**, in yields of 20 and 4%, respectively, were also found in the residues. After the removal of tetramethylammonium iodide and the corresponding **4a** and **4b** and **6a** and **6b**, the remaining material (tar) from each pyrolysis was subjected to ir analysis. Although the spectra were nondescript, absorptions at 2760 and 1640 cm^{-1} were assigned to trimethylammonium iodide (**5**, $A^- = I^-$). Attempts to identify other products in the residues were not made. The tetramethylammonium iodide is probably formed by the attack of trimethylamine on the iodide salts **1**, **2**, and **3**, the trimethylamine arising from pyrolyzed trimethylammonium iodide (**5**, $A^- = I^-$). Ir analysis of the residues obtained by heating equal molar amounts of hydrazone **6a** and **6b**, and trimethylammonium iodide (**5**, $A^- = I^-$) at 250° for 2 min (**6b**) and 10 min (**6a**) revealed spectra which were identical in every respect with those obtained from the individual pyrolysis residues.

Altering the basicity of the anion, A^-, did not produce a significant increase or decrease in the yields of nitriles **4a** and **4b**. A change of less than 5% was observed. Support for the mechanism of base-induced decomposition by the anion was realized by attempted preparation of the more basic acetate and phenoxide salts of **2**. Both compounds were found to eliminate *in situ* to glutaronitrile (**7**).[5] Hydrazones **6b** were not found in the reaction residues.

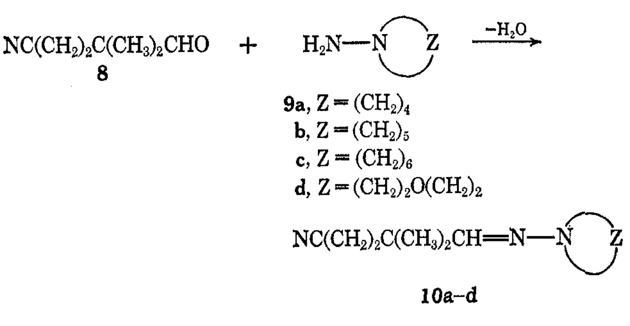


Only a small enhancement of the yield of desired nitrile **4a** from the pyrolysis of **1** ($X = NO_2$; $Y = H$) was observed, *i.e.*, a slight increase (<5%) in the yield of *p*-nitrobenzonitrile was noted. Likewise, a slight decrease (<5%) in the yield of anisonitrile was found when compounds of **1** ($X = OCH_3$; $Y = H$) were decomposed.

In summary, the aldehyde (R) or anion portions of the trimethyl salts **1**, **2**, and **3** had little effect on the yield of the desired nitrile. The cause of the low yields of nitrile was recognized as the lability of the quaternary methyl groups to nucleophilic attack.

For these reasons we concentrated our efforts on replacing the methyl groups with more sterically hindered alkyl groups to prevent dealkylation by nucleophilic attack. Likewise, we concentrated our efforts on two salts, the iodide and fluoroborate of a single aldehyde, 4-cyano-2,2-dimethylbutyraldehyde (**8**). Aldehyde **8** was chosen because of its commercial availability and because of an interest in the aliphatic dinitrile expected from the pyrolysis of its hydrazonium salts.

Aldehyde **8** was condensed with several cyclic hydrazines **9**. Formation of hydrazones **10** was in each



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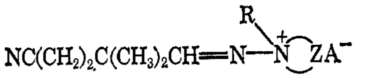
(6) Ot_s, *p*-toluenesulfonate.

TABLE I

PREPARATION AND PROPERTIES OF HYDRAZONIUM SALTS



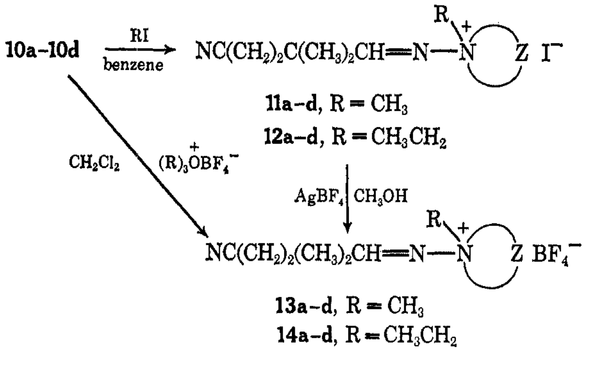
Compd	Z	R	A⁻	Yield, %	Mp, °C	S[a]	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
11a	$(CH_2)_4$	CH_3	I	90	70–75	P	$C_{12}H_{22}N_3I$	42.99	6.62	12.53	42.78	6.26	12.50
11b	$(CH_2)_5$	CH_3	I	99	114–116	P	$C_{13}H_{24}N_3I$	44.70	6.93	12.03	44.63	6.98	12.12
11c	$(CH_2)_6$	CH_3	I	76	149–150	P	$C_{14}H_{26}N_3I$	46.28	7.21	11.57	45.96	7.01	11.73
11d	$(CH_2)_2O(CH_2)_2$	CH_3	I	75	114–116	P	$C_{12}H_{22}N_3OI$	41.03	6.31	11.96	40.74	6.44	11.71
12a	$(CH_2)_4$	CH_3CH_2	I	83	84–86	P	$C_{13}H_{24}N_3I$	44.70	6.93	12.03	44.72	7.07	12.33
12b	$(CH_2)_5$	CH_3CH_2	I	80	119–120	E	$C_{14}H_{26}N_3I$	46.28	7.21	11.57	46.20	7.21	11.76
12c	$(CH_2)_6$	CH_3CH_2	I	70	136–138	E	$C_{15}H_{28}N_3I$	57.75	7.48	11.14	47.77	7.48	11.47
12d	$(CH_2)_2O(CH_2)_2$	CH_3CH_2	I	79	135–137	E	$C_{13}H_{24}N_3OI$	42.74	6.62	11.50	42.77	6.67	11.66
13b	$(CH_2)_5$	CH_3	BF_4	79 (1)[b] 89 (2)	70–72	E	$C_{13}H_{24}N_3BF_4$	50.50	7.82	13.59	50.73	7.71	13.70
13c	$(CH_2)_6$	CH_3	BF_4	75 (1) 87 (2)	70–71	P	$C_{14}H_{26}N_3BF_4$	52.03	8.11	13.00	52.00	7.84	13.08
13d	$(CH_2)_2O(CH_2)_2$	CH_3	BF_4	52 (1) 92 (2)	71–72	E	$C_{12}H_{22}N_3OBF_4$	46.32	7.13	13.51	46.34	7.15	13.49
14b	$(CH_2)_5$	CH_3CH_2	BF_4	87 (1) 91 (2)	78–79	M	$C_{14}H_{26}N_3BF_4$	52.03	8.11	13.00	52.32	8.33	12.71
14c	$(CH_2)_6$	CH_3CH_2	BF_4	80 (1) 87 (2)	91–93	E	$C_{15}H_{28}N_3BF_4$	53.42	8.37	12.46	53.68	8.21	12.27
14d	$(CH_2)_2O(CH_2)_2$	CH_3CH_2	BF_4	80 (1) 83 (2)	110–112	M	$C_{13}H_{24}N_3OBF_4$	48.02	7.44	47.91	7.58	7.58	12.72

[a] S, recrystallization solvent; P, isopropyl alcohol; E, ethanol; M, methanol. [b] Numbers in parentheses refer to the method of preparation.

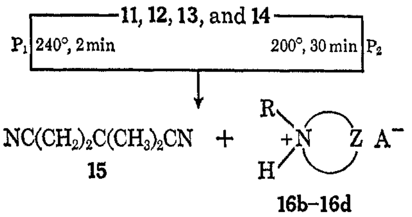
case quantitative. The methyl and ethyl quaternary salts **11** and **12** were prepared by treating hydrazones **10** with methyl and ethyl iodide respectively. Yields of **11** were 75% or better while those of the ethyl salts **12** were slightly lower (Table I).

Fluoroborate compounds **13** and **14** were prepared to compare the yields of nitrile from their cleavage with those obtained from the pyrolyses of **11** and **12**. Both salts **13** and **14** were prepared by treating **11** and **12** with a methanol solution of silver fluoroborate. Salts obtained by this method were slightly colored (gray) and were difficult to purify. Trimethyl and triethyloxonium fluoroborate[7] were found to react rapidly and smoothly with hydrazones **10** and gave excellent yields of the fluoroborate salts **13** and **14** (Scheme I). Salts **13a** and **14a** were isolated as oils and were of no further interest in our work.

SCHEME I



The series of iodide (**11** and **12**) and fluoroborate (**13** and **14**) hydrazonium salts reported in Table I were cleaved by two methods: P_1, rapid cleavage in a sealed tube at 240° for 2 min; P_2, slow pyrolysis at 200° for 30 min in an open system. Although excellent yields of 2,2-dimethylglutaronitrile (**15**) were found using rapid pyrolysis conditions (P_1), consistently higher yields of **15** were obtained when the salts were decomposed at 200° for 30 min (P_2). With iodides **11** and **12**, tar formation was negligible and higher yields of nitrile **15** were found than with fluoroborates **13** and **14**. The yields of hydrazones **10** using method P_1 were 5% and only trace amounts were detected employing method P_2 (Table II).



R = CH_3, CH_3CH_2: $A^- = I^-, BF_4^-$

TABLE II

YIELD OF PRODUCTS FROM PYROLYSIS OF QUATERNARY SALTS

Compd	% nitrile 15 P_1[a]	% nitrile 15 P_2	% hydrazones 10a–d P_1	% hydrazones 10a–d P_2
11a	90	90	2	T[b]
11b	73	80	2	T
11c	55	67	4	T
11d	95	95	T	T
12a	49	62	4	T
12b	80	91	T	T
12c	47	52	5	T
12d	78	87	T	T
13b	68	83	1	T
13c	55	78	5	T
13d	41	74	1	T
14b	19	82	5	T
14c	19	71	4	T
14d	47	76	2	T

[a] P_1 and P_2 refer to the method of pyrolysis. [b] T, trace.

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[7] H. Meerein, *Org. Syn.*, **46**, 113, 120 (1900).

Benzene was used to extract both **15** and **10** from the residues and both compounds were identified by vpc analysis. An analytical sample of **15** for comparison purposes was independently prepared in 68% yield by the alkaline decomposition of **3** ($A^- = I^-$).

Although the benzene-insoluble residues were not of special interest, each was subjected to ir analysis. Peaks that could be attributed to $-C\equiv N$ (2240–2260 cm^{-1}) and $-C=N-$ (1620–1640 cm^{-1}) absorptions were not observed, evidencing complete extraction of nitrile **15** and hydrazones **10**. In fact, in the ir spectra of these residues no significant bands appeared which could not be assigned to the ammonium salt **16b–16d** ($-HN^+$, 2760–2763 cm^{-1}; BF_4^-, 1000–1100 cm^{-1}).[8]

Experimental Section[9]

Pyrolysis of Trimethylhydrazonium Salts (1, 2, and 3).—Samples (250 mg) of each salt were placed in a small Hickman-type microdistillation flask[10] equipped with two condenser alembics and lowered into a Wood's metal bath preheated to 240–250°. Aromatic salts **1** were pyrolyzed for 10 min and the aliphatic salts **2** and **3** for 2 min. In general, all salts cleaved with an exothermic reaction after 45 sec, except the perchlorate and nitrate salts of **2** and **3** which exploded after 30 sec.[11] The residues were extracted with benzene and the extracts were concentrated yielding anisonitrile, *p*-nitrobenzonitrile, and 2,4-dichlorobenzonitrile; each was identified by ir and melting point. The benzene extracts containing benzonitrile, glutaronitrile (**7**), and nitrile **15** were analyzed by vpc; the compounds were idenified by mixed injections with authentic samples. Yields of all nitriles were less than 20%. The corresponding hydrazones **6a** and **6b** in the benzene extracts were identified by vpc. Yields of **6a** and **6b** were 2–15%. Analysis (ir) of the benzene-insoluble residues revealed NH^+ absorption at 2700–2765 cm^{-1}.

The residues from the cleavage of the iodide salts were washed from the pyrolysis flask with acetone and filtered. Trituration of the solid with hot methanol gave pure tetramethylammonium iodide, yield 63–97 mg (45–47%), darkened at 230°, mp >300° (lit.[12] mp >230° dec). Elemental analysis and ir further substantiated its structure. The acetone extracts were evaporated to give black residues. The residues were extracted with benzene. Nitriles **4a** and **4b** (20%) and hydrazones **6a** and **6b** were identified in the extracts by vpc analysis. Analysis of the benzene-insoluble materials by ir revealed NH^+ absorption at 2763–2765 cm^{-1}.

Reaction of Hydrazones 5a and 5b with Trimethylammonium Iodide (5, $A^- = I^-$).—Trimethylammonium iodide (**5**, $A^- = I^-$), 8×10^{-4} mol, was heated at 250° with 8×10^{-4} mol of hydrazones **4a** (10 min), and with 8×10^{-4} mol of **4b** (2 min). A comparison of the ir spectra of the residues with those obtained from the pyrolysis of salts **1**, **2**, and **3** revealed negligible differences in the occurrance of absorptions.

Preparation of Hydrazones 10.—4-Cyano-2,2-dimethylbutyraldehyde (**8**, 0.1 mol) and the appropriate hydrazine **9** (0.1 mol) were heated at reflux in 150 ml of benzene under a Dean–Stark trap until the theortical amount of water was collected (4–6 hr). The benzene solution was dried ($CaCO_3$), filtered, and concentrated, giving the hydrazones **10** as oils in quantitative yield.[13]

Preparation of Iodide Salts 11 and 12.—Hydrazones **10** (0.05 mol) in 75 ml of benzene and methyl or ethyl iodide (0.05 mol) were heated at reflux for 4 hr. The methyl salts **11** separated after 10 min. Precipitation of the ethyl salts **12** occurred after 1 hr. The salts were recrystallized from alcohol and characterized (Table I): ir (Nujol) $-C\equiv N$ (2250) and $-C=N-$ (1635–1640 cm^{-1}).

Preparation of Trimethyl and Triethyloxonium Fluoroborate.—Preparation of these compounds was conducted according to published directions.[7] Yields were 85–90%. Both compounds were stored under ether at −20°.

Preparation of Fluoroborate Salts 13 and 14. Method 1.—Freshly recrystallized iodide salts **11** and **12** (0.02 mol) were dissolved in 50 ml of warm methanol and added to a solution of silver fluoroborate (0.02 mol) in 20 ml of methanol. The mixture was stirred for 1 hr, filtered, and concentrated giving a crystalline product. Repeated recrystallization from alcohol gave pure **13** and **14** (Table I): ir (Nujol) $-C\equiv N$ (2250), $-C=N-$ (1635–1640), and BF_4^- (1000–1100 cm^{-1}).

Method 2.—Hydrazones **10** (0.01 mol) in 25 ml of methylene chloride were added to trimethyl or triethyloxonium fluoroborate (0.01 mol) in 50 ml of methylene chloride during 1 hr. The solution was heated at reflux temperature for 1 hr and the solvent was evaporated. Recrystallization from alcohol gave pure **13** and **14**.

Preparation 2,2-Dimethylglutaronitrile (15).—The method of Smith and Walker[2] was utilized. Recrystallized 4-cyano-2,2-dimethylbutyraldehyde trimethylhydrazonium salt (**3**, $A^- = I^-$), 276 g (0.9 mol) was dissolved in 600 ml of absolute methanol and heated at reflux with 48.6 g (0.9 mol) of sodium methoxide until the odor of trimethylamine disappeared. Addition of water (500 ml) and extraction with benzene (700 ml) gave **15**: ir (neat) $-C\equiv N$ (2250 cm^{-1}).

Anal. Calcd for $C_7H_{10}N_2$: C, 68.88; H, 8.19; N, 22.95. Found: C, 68.70; H, 8.16; N, 22.68.

Pyrolysis of Hydrazonium Salts 11–14. Method P_1.—Each quaternary salt (0.013 mol) was placed in a 6-in. glass tube (1.25-in. i.d.) and sealed. The tube was lowered into a Wood's metal bath preheated to 240°. Each sample was pyrolyzed for 2 min. The tube was cooled and broken, and the residue was extracted with benzene. Analysis by vpc revealed nitrile **15** and hydrazones **10** (Table II). The benzene-insoluble materials, under analysis by ir, revealed prominent bands at 2760–2765 ($-NH^+$) and 1000–1100 cm^{-1} for **16** ($A^- = BF_4^-$).

Method P_2.—Each salt was placed in a Hickman-type microdistillation flask equipped with two condensation alembics, heated slowly to 200° in a sand bath, and kept at that temperature for 30 min. The residues were cooled, extracted with benzene, and analyzed for **15** and **10** as in method P_1.

Registry No.—**11a,** 23649-85-6; **11b,** 23649-86-7; **11c,** 23649-87-8; **11d,** 23649-88-9; **12a,** 23674-47-7; **12b,** 23645-66-1; **12c,** 23645-67-2; **12d,** 23645-68-3; **13b,** 23645-58-1; **13c,** 23645-59-2; **13d,** 23645-60-5; **14b,** 23645-61-6; **14c,** 23645-62-7; **14d,** 23645-63-8.

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[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecule," 2nd ed' John Wiley & Sons, Inc., New York, N. Y., 1963, p 260.

[9] Melting points were determined in open capillaries and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by the National Bureau of Standards, Gaithersburg, Md. Infrared spectra were determined in mineral oil on a Beckman IR-5 spectrophotometer. Gas chromatograms were recorded on a Varian Aerograph Model 1520c with a thermal conductivity detector using a stainless steel 6 ft × 1/8 in. column packed with 5% EGP, 80–100 mesh, DMCS treated, on Chromasorb W.

[10] K. C. D. Hickman, *Chem. Rev.*, **34**, 51 (1944).

[11] The residues were analyzed by ir and appeared to be inorganic. The nitriles **4b** and hydrazones **6b** were not found (vpc).

[12] E. Chablay, *Ann. Chim.*, **1**, 469 (1914).

[13] The pyrrolidine hydrazone **10**, Z = $(CH_2)_4$, was prepared by treating N-aminopyrrolidine hydrochloride with triethylamine followed by reaction with aldehyde **8**.