Tetraaminoethylenes. I. The Preparation and Some Reactions of Tetrapiperidino- and Tetramorpholinoethylene[1]

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(Received January 11, 1971)

The preparation of new tetraaminoethylenes was attempted by the reaction of chlorotrifluoroethylene (CTFE) with several amines. It has been found that CTFE reacted with piperidine and morpholine to give tetrapiperidino- (TPE) and tetramorpholinoethylene (TME) in moderate yields respectively, although no tetraaminoethylenes were formed in the reactions with diethylamine, pyrrolidine, aniline, *N*-alkylaniline, and diphenylamine. Also, it has been made clear that the compounds whose structures were previously assigned to the tetraaminoethylenes, obtained from 1,1-dimethoxytrimethylamine or ethyl orthoformate and secondary amines are the corresponding triaminomethanes. It has been found that TPE and TME reacted with halogens, halogen-, nitro-compounds, and aromatic carboxylic acids to form mainly the corresponding oxamidinium salts.

Tetraaminoethylenes, such as tetrakis(dimethylamino)ethylene (TDAE) and bi(1,3-diphenylimidazolidin-2-ylidene), are characterized both by their odor and by the versatility of their chemical reactivity.[2-6] Such current interest in unusually reactive tetraaminoethylenes prompted us to investigate the preparation of new tetraaminoethylenes and their chemistry.

In this paper, we wish to report the preparation of tetrapiperidino- (TPE) and tetramorpholinoethylene (TME), which are new tetraaminoethylenes, and their unusual reactions with halogens, halogen-, nitro-compounds, and aromatic carboxylic acids.

Results and Discussion

The Preparation of TPE and TME. An attempt was made to prepare new tetraaminoethylenes by the reactions of chlorotrifluoroethylene (CTFE) with aliphatic and aromatic amines according to Pruett's procedure.[7]

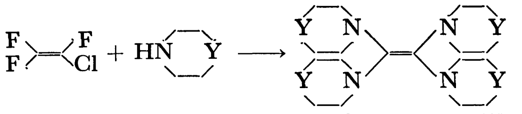
The reaction of CTFE with diethylamine gave only the compound assumed to be 1,2-bis(diethylamino)-1-chloro-2-fluoroethylene, while pyrroridine and aniline reacted with CTFE to give unidentified compounds, all in low yields. Also, no reactions of CTFE with *N*-alkylanilines and diphenylamine took place.

Although the preparation of new tetraaminoethylenes caused such difficulties, it has been found that similar reactions of CTFE with piperidine and morpholine afforded the expected tetraaminoethylenes, TPE (mp 151—152°C) and TME (mp 186—190°C), in moderate yields, accompanied by small amounts of the corresponding *N*-(diaminoacetyl)amines, whose structures were assumed on the basis of the elemental analyses and study of the IR spectra.

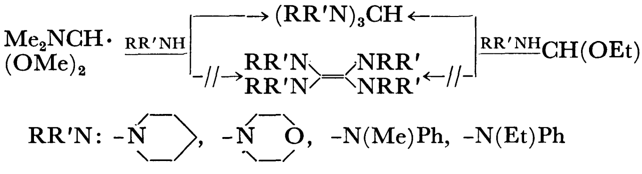
The structures of TPE and TME were confirmed by spectral studies as well as by elemental analyses; the molecular formulae of TPE and TME agreed with $C_{22}H_{40}N_4$ (M^+ m/e 360) and $C_{18}H_{32}O_4N_4$ (M^+ m/e 368) respectively.

After the completion of this work, we learned that two routes for the preparation of tetraaminoethylenes have been reported. Winberg *et al.*[8] described that tetraaminoethylenes, including TPE and TME, were obtained by the reactions of 1,1-dimethoxytrimethylamine with aliphatic secondary amines, and that TPE and TME melted at 59—61 and 170—171°C respectively. On the other hand, it has been reported by Hagedorn and Lichtel[9] that ethyl orthoformate reacted with *N*-alkylanilines to give the corresponding tetrakis(*N*-alkylanilino)ethylenes, which could not be obtained by Pruett's method, as has been mentioned above. However, it is surprising that the molecular weight (calculated value, 504.7) of tetrakis(*N*-ethylanilino)ethylene, mp 180—182°C (decomp.), was observed to be 312 or 336 by the vapor-pressure-osmometric determination.

In order to see whether or not the reported compounds are real tetraaminoethylenes, the reaction of 1,1-dimethoxytrimethylamine or ethyl orthoformate with amines was investigated. The reactions of 1,1-dimethoxytrimethylamine with piperidine and morpholine did not give any TPE and TME, but compounds which decomposed rapidly in air were obtained in low yields; these compounds were as-



CTFE TPE ($Y=CH_2$) TME ($Y=O$)



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[1] Presented at the 19th Annual Meeting (Yokohama, April, 1966) and the Kyushu Meeting (Fukuoka, October, 1966) of the Chemical Society of Japan.

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[2] N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3000 (1963).

[3] N. Wiberg and J. W. Buchler, *ibid.*, **96**, 3223 (1963).

[4] D. M. Lemal, R. A. Lovald, and K. I. Kawano, *J. Amer. Chem. Soc.*, **86**, 2518 (1964).

[5] H. W. Wanzlick, B. Lachmann, and E. Schikora, *Chem. Ber.*, **98**, 3170 (1965).

[6] H. E. Winberg and D. D. Coffman, *J. Amer. Chem. Soc.*, **87**, 2776 (1965.)

[7] R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, *ibid.*, **72**, 3649 (1950).

[8] H. E. Winberg, J. E. Carnahon, D. D. Coffman, and M. Brown, *ibid.*, **87**, 2055 (1965).

[9] I. Hagedorn and K. E. Lichtel, *Chem. Ber.*, **99**, 524 (1966).

sumed, on the basis of the results of the elemental analyses, to be tripiperidino-, mp 52—56°C, and trimorpholinomethane, mp 142—147°C, respectively. Contrary to expectation, *N*-methyl- and *N*-ethylaniline reacted with ethyl orthoformate to afford tris(*N*-methylanilino)-, mp 268—269°C (decomp.), and tris(*N*-ethylanilino)methane, mp 181—185°C (decomp.), respectively. The structures of these compounds were established by the spectral studies as well as by the elemental analyses. Also, the reaction of ethyl orthoformate with morpholine or of 1,1-dimethoxytrimethylamine with *N*-ethylaniline gave the corresponding triaminomethanes.

It may be concluded from the above facts that TPE and TME obtained in this work are valid, and that the reported compounds were previously erroneously assigned to the tetraaminoethylenes.

The Reactions of TPE and TME with Halogens. Wiberg and Buchler[3] found that TDAE was oxidized easily with halogens, especially with bromine and iodine, to give the corresponding octamethyl-oxamidinium dihalides, TDAEX$_2$, and that several periodides, TDAEI$_n$ (n=4, 5, and 7), were also formed in the oxidation with iodine.

When chlorine gas was slowly passed through a benzene solution of TPE and TME at 0°C, the dichlorides TPECl$_2$, mp 240—241°C (decomp.) and TMECl$_2$, mp 265—266°C (decomp.), were obtained in good yields. Similarly, TPE and TME reacted with equimolar amounts of bromine and iodine to give the corresponding dihalides, TPEBr$_2$, mp 247°C (decomp.), TPEI$_2$, mp 282—284°C (decomp.), TMEBr$_2$, mp 300°C (decomp.), and TMEI$_2$, mp *ca.* 190°C (decomp.), respectively, accompanied by trace amounts of the hexahalides, TPEBr$_6$ and TPEI$_6$, in the reaction of TPE:

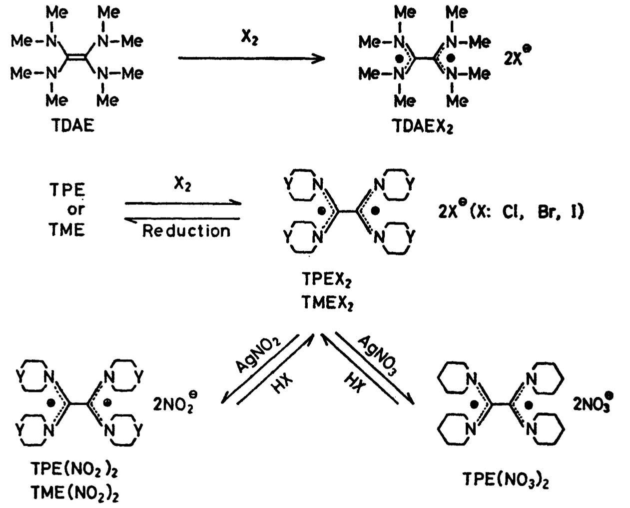
Table 1. Reactions of TPE and TME with halogens

TPE or TME	X$_2$	Reaction conditions			Products yields (%)	
		Solvent	Temp. (°C)	Time (min)	TPEX$_2$ or TMEX$_2$	TPEX$_6$
TPE	Cl$_2$	benzene	0	15	100	
TME	Cl$_2$	benzene	0	15	80	
TPE	Br$_2$	*n*-hexane	0	10	70	+[a]
TME	Br$_2$	*n*-hexane	0	10	70	
TPE	I$_2$	benzene	0	10	88	+[a]
TME	I$_2$	benzene	0	10	24	

a) A plus sign, +, indicates a trace amount.

The above hexahalides were easily formed by the further reaction of TPEBr$_2$ or TPEI$_2$ with bromine or iodine, but the dihalides, TPECl$_2$, TMECl$_2$, TMEBr$_2$, and TMEI$_2$, did not give any perhalides under similar conditions.

The structures of dihalides were confirmed, by a study of the IR spectra as well as by the chemical transformations, to be the corresponding oxamidinium dihalides. The IR spectra of all the dihalides exhibited remarkably strong absorption bands which can be ascribed to the $[\rangle N{=}C{=}N\langle]^{\oplus}$ at 1620 and 1640 cm^{-1}. Also, the ion peak which corresponded to the molecular ion of TPE or TME appeared as the ion peak of the highest mass number in the respective mass spectra of dihalides.



The dihalides in aqueous solutions were reduced with zinc dust to the original TPE or TME, although TME could not be isolated because of its instability in relation to water. Furthermore, when the dihalides were treated with silver nitrite or nitrate, the corresponding dinitrites TPE(NO$_2$)$_2$ and TME(NO$_2$)$_2$ or dinitrate TPE(NO$_3$)$_2$, whose IR spectra were similar to those of the corresponding dihalides, were obtained quantitatively.

Also, the dinitrites and dinitrate were easily transformed to the corresponding dihalides in the treatment with hydrogen halides. Incidentally, the hexahalides, TPEX$_6$, were reduced with zinc dust to give TPE.

The above observations indicate that the dihalides, dinitrites, and dinitrate are the corresponding oxamidinium salts. The results of the reactions of TPE or TME with halogens are shown in Table 1.

The Reactions of TPE and TME with Halogen-Compounds. It has been reported that TDAE reacted with cuprous chloride or carbon tetrachloride to give the dichloride, TDAECl$_2$, with the deposition of copper metal or decomposition of carbon tetrachloride.[3]

The reactions of TPE or TME with various organic halogen-compounds were also investigated. In all cases, the corresponding dihalides were obtained; the results are summarized in Table 2.

In particular, it is noteworthy that the compounds originated from the starting halogen-compounds were isolated in the reactions with benzal chloride, benzotrichloride, benzenesulfonyl chloride, phenacyl bromide, and 2,2-dichloroacenaphthenone: stilbene and 1,1,2,2-tetrachloro-1,2-diphenylethane (tolan tetrachloride), tolan tetrachloride, diphenyldisulfone, biphenacyl, and diacenaphthylidenedione were isolated respectively.

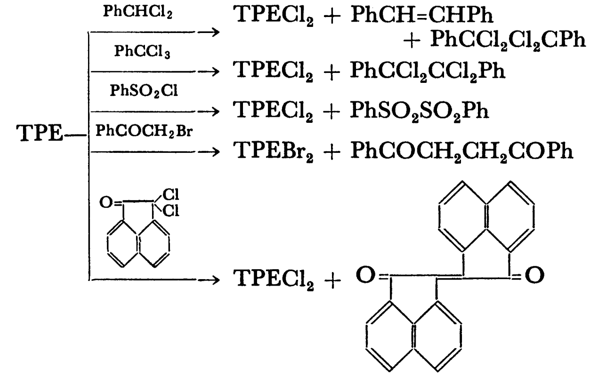
As is shown in Table 2, the yield of TPECl$_2$ in the reaction of TPE with benzyl chloride in the pres-

TABLE 2. REACTIONS OF TPE AND TME WITH HALOGEN-COMPOUNDS

TPE or TME	Halogen-compound	Reaction conditions			Products yields (%)[a]		
		Solvent	Temp. (°C)	Time (min)	$TPEX_2$ or $TMEX_2$		
TPE	$CHCl_3$	b)	reflux	180	40		
TME	$CHCl_3$	benzene	room temp.	30	+		
TPE	$CHBr_3$	benzene	room temp.	30	57		
TME	$CHBr_3$	benzene	room temp.	30	30		
TPE	CHI_3	benzene	room temp.	30	70		
TME	CHI_3	benzene	room temp.	30	47		
TPE	CCl_4	b)	0	30	66		
TME	CCl_4	b)	room temp.	120	40		
TPE	$PhCH_2Cl$	benzene	reflux	180	14		
TPE	$PhCH_2Cl$	benzene	reflux	60	9		
TPE	$PhCH_2Cl$	benzene	reflux	60	30[c]		
TPE	$PhCH_2Cl$	benzene	reflux	60	+[d]		
TME	$PhCH_2Cl$	benzene	reflux	180	10		
TPE	$PhCHCl_2$	benzene	reflux	30	83	$PhCCl_2CCl_2Ph$ $PhCH=CHPh$	10 +
TME	$PhCHCl_2$	benzene	reflux	30	40		
TPE	$PhCCl_3$	benzene	60	15	96	$PhCCl_2CCl_2Ph$	40
TME	$PhCCl_3$	benzene	60	15	51		
TPE	PhCOCl	benzene	40—50	120	86		
TME	PhCOCl	benzene	40	120	82		
TPE	$PhSO_2Cl$	benzene	room temp.	120	90	$PhSO_2SO_2Ph$	20
TME	$PhSO_2Cl$	benzene	room temp.	120	90	$PhSO_2SO_2Ph$	20
TPE	$PhCOCH_2Br$	benzene	60	30	70	$(PhCOCH_2)_2$	44
TPE	DCA[e]	benzene	room temp.	10	50	Diacenaphthylidenedione	27

a) A plus sign, +, indicates a trace amount.
b) The halogen-compound was used as the solvent respectively.
c) In the presence of benzoyl peroxide.
d) In the presence of *p*-benzoquione.
e) DCA: 2,2-Dichloroacenaphthenone.

ence of benzoyl peroxide is higher than in either the absence or presence of *p*-benzoquinone.



On the basis of the above facts, it seemed reasonable to assume that these reactions proceed through a free radical process.

The Reactions of TPE or TME with Nitro-Compounds. Previous investigations of the reactions of tetraaminoethylenes with nitro-compounds have not been extended beyond the reactions of TDAE with nitrobenzenes[10] and of bi(1,3-diphenylimidazolidin-2-ylidene) with nitromethane.[11]

The reactions of TPE or TME with several nitro-compounds were investigated.

It has been found that TPE and TME reacted with phenylnitromethane to give the respective dinitrites, $TPE(NO_2)_2$ and $TME(NO_2)_2$, which were identical with those obtained from the dihalides and silver nitrite. Surprisingly, TPE reacted with tetranitromethane to give a 1 : 2 addition product of TPE and tetranitromethane, accompanied by a small amount of the dinitrate, $TPE(NO_3)_2$. The nitrate was identified by a comparison of its IR spectrum with that obtained by the reaction of $TPEX_2$ with silver nitrate.

In the same way as in the case of TDAE,[10] TPE or TME formed charge-transfer complexes with nitrobenzene (NB), *m*-dinitro- (DNB), and 1,3,5-trinitrobenzene (TNB). Although purple-colored complexes with NB and DNB were not obtained as crystals, these complexes were established, by a spectroscopic estimation of the intensities of the absorption peaks at 514 mμ for TPE-NB, 450 mμ for TME-NB, 580 mμ for TPE-DNB, and 476.8 mμ for TME-DNB complex, to be TPE(NB), TME(NB), $TPE(DNB)_2$, and $TME(DNB)_2$ complexes respectively.

On the other hand, TPE reacted with TNB to form the charge-transfer complex $TPE(TNB)_2$, mp 122—124°C (decomp.), as a purple solid; it gradually decomposed in air.

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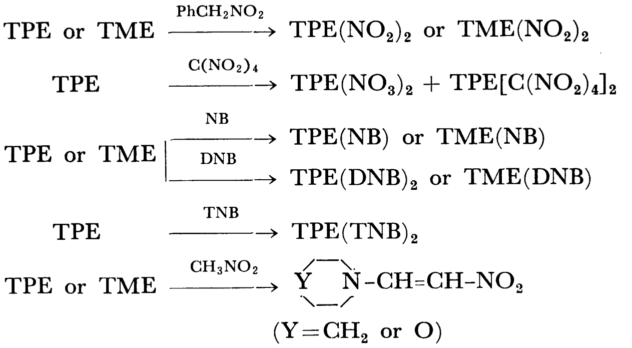
[10] N. Wiberg and J. W. Buchler, *Chem. Ber.*, **97**, 618 (1964).
[11] H. -W. Wanzlick and E. Schikora, *ibid.*, **94**, 2389 (1961).



$$\text{TPE or TME} \xrightarrow{PhCH_2NO_2} \text{TPE}(NO_2)_2 \text{ or } \text{TME}(NO_2)_2$$

$$\text{TPE} \xrightarrow{C(NO_2)_4} \text{TPE}(NO_3)_2 + \text{TPE}[C(NO_2)_4]_2$$

$$\text{TPE or TME} \xrightarrow{NB} \text{TPE(NB) or TME(NB)}; \quad \text{TPE or TME} \xrightarrow{DNB} \text{TPE}(DNB)_2 \text{ or TME(DNB)}$$

$$\text{TPE} \xrightarrow{TNB} \text{TPE}(TNB)_2$$

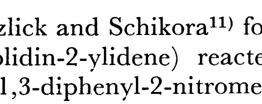
$$\text{TPE or TME} \xrightarrow{CH_3NO_2} \text{Y N-CH=CH-NO}_2 \quad (Y=CH_2 \text{ or } O)$$

Wanzlick and Schikora[11)] found that bi(1,3-diphenylimidazolidin-2-ylidene) reacted with nitromethane to give 1,3-diphenyl-2-nitromethylimidazolidine upon the cleavage of the >C=C< bond in the ethylene.

When a benzene solution of TME or TPE was heated with nitromethane under an atmosphere of nitrogen, 1-nitro-2-piperidinoethylene, mp 94—95°C, or 2-morpholino-1-nitroethylene, mp 139—140°C, was obtained respectively.[12)] The structures of the enamines were established by spectral studies as well as by elemental analyses.

The Reaction of TPE with Aromatic Carboxylic Acids. Little attention has been paid to the reactions of tetraaminoethylenes with carboxylic acids.

When a benzene solution of TPE was allowed to react with benzoic acid at room temperature, a compound, mp 104—105°C, was obtained as colorless needles. In the treatment with hydrobromic acid, the compound was easily transformed to $TPEBr_2$. The compounds was confirmed, by a study of its IR spectrum as well as by the elemental analysis, to the oxamidinium dibenzoate, $TPE(PhCO_2)_2$.



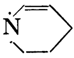
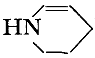
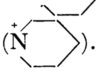
$TPE(ArCO_2)_2$ (Ar=Ph, p-MeC_6H_4, p-ClC_6H_4)

Similar reactions of TPE with *p*-methyl- and *p*-chlorobenzoic acid gave the corresponding oxamidinium salts, $TPE(p\text{-}MeC_6H_4CO_2)_2$, mp 101—103°C, and $TPE(p\text{-}ClC_6H_4CO_2)_2$, mp 109—111°C.

Experimental

All the melting and boiling points are uncorrected. The IR spectra were measured in KBr disks unless otherwise described, while the NMR spectra were determined at 60 MHz with a Hitachi R-20 spectrometer, using TMS as the internal reference. The mass spectra were obtained on a Hitachi RMS-4 spectrometer, using a direct inlet and an ionization energy of 70 eV.

The Reactions of CTFE with Amines. *i) With Piperidine*: In a 200 *ml*-autoclave cooled in a dry ice-methanol bath, 15 g (0.1 mol) of CTFE, which has been prepared from trichlorotrifluoroethane by the reported method,[13)] and 110 g (1.92 mol) of piperidine were placed as rapidly as possible. The reaction mixture was stirred at room temperature for 3 hr and then at 80°C for 8 hr; during this time, the mixture gradually solidified and became difficult to stir. After the reaction mixture had been cooled, it was extracted with 500 *ml* of petroleum ether (bp 30—45°C), leaving a mixture of insoluble piperidinium chloride and fluoride. The extract was concentrated *in vacuo* under an atmosphere of nitrogen to yield 30 g (64%) of TPE; this, on recrystallization from ethyl acetate, afforded colorless needles, mp 151—152°C.

Found: C, 73.54; H, 11.30; N, 15.53%. Calcd for $C_{22}H_{40}N_4$: C, 73.38; H, 11.18; N, 15.55%. NMR spectrum in benzene: δ 0.86 (24H, multiplet) and 2.33 ppm (16H, multiplet). UV spectrum in *n*-hexane λ_{max} mμ (ε): 231.6 (15000), 258.4 (9900). Mass spectrum: *m/e* 360 (M^+), 275 (M^+− ), 193 (275^+− ), 110 (193^+ − ), 84 ().

Also, a trace amount of *N*-(dipiperidinoacetyl)piperidine, mp 93—94°C, was isolated from the mother liquor of recrystallization.

Found: C, 69.41; H, 10.76; N, 14.23%. Calcd for $C_{17}H_{31}ON_3$: C, 69.56; H, 10.65; N, 14.31%. IR spectrum (Nujol): 1635 cm^{-1} ($\nu_{C=O}$).

ii) With Morpholine: In the same manner as in the reaction with piperidine, a mixture of 15 g (0.1 mol) of CTFE and 110 g (1.26 mol) of morpholine was heated at 70°C for 6 hr. After the reaction mixture had then been extracted with 1 *l* of ethyl acetate, the extract was concentrated *in vacuo* under an atmosphere of nitrogen to give 22 g (47%) of crude TME. Recrystallization from ethyl acetate gave colorless prisms, mp 186—190°C.

Found: C, 58.60; H, 8.92; N, 15.19%. Calcd for $C_{18}H_{32}O_4N_4$: C, 58.67; H, 8.76; N, 15.21%. NMR spectrum in benzene: δ 2.72 (16H, multiplet) and 3.54 ppm (16H, multiplet). UV spectrum in *n*-hexane λ_{max} mμ (ε): 222.5 (15000), 275.5 (9900). Mass spectrum: *m/e* 368 (M^+).

From the mother liquor of recrystallization, *N*-(dimorpholinoacetyl)molpholine, mp 125—126°C, was obtained in a trace amount.

Found: C, 56.03; H, 8.63; N, 13.99%. Calcd for $C_{14}H_{25}O_4N_3$: C, 56.17; H, 8.42; N, 14.04%. IR spectrum: 1640 cm^{-1} ($\nu_{C=O}$).

iii) With Diethylamine: A similar reaction of 15 g (0.1 mol) of CTFE with 100 g (1.37 mol) of diethylamine at 80°C for 10 hr gave 28 g of diethylammonium halide and 25 g (89%) of a colorless liquid bp 46°C/0.5 mmHg, which was assumed to be 1,2-bis(diethylamino)-1-chloro-2-fluoroethylene.

Found: C, 53.93; H, 9.33; N, 12.23%. Calcd for $C_{10}H_{20}N_2FCl$: C, 53.92; H, 9.05; N, 12.58%.

A similar reaction of CTFE with pyrrolidine or aniline gave only a small amount of an unidentified compound as yellow crystals, mp 68.5—69.5°C (Found: C, 67.84; H, 6.69; N, 15.58%), or as red prisms, mp 209—210°C (Found: C, 80.97; H, 5.20; N, 13.61%), respectively. Also, no reactions of CTFE with *N*-alkylaniline and diphenylamine took place under similar conditions.

The Reaction of 1,1-Dimethoxytrimethylamine with Morpholine. After a mixture of 10 g of 1,1-dimethoxytrimethylamine[14)]

[12)] We found that various compounds having an active methyl or methylene group reacted with TPE and TME in the same manner as in the case of nitromethane, affording the corresponding enamines. The results will be reported in the near future.

[13)] H. S. Booth, P. E. Burchfield, E. M. Bixby, and J. B. McKelvey, *J. Amer. Chem. Soc.*, **55**, 2231 (1933).

[14)] H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Chem. Ber.*, **96**, 2671 (1963).

and 10 g of morpholine had been vigorously refluxed for 5 hr, the unreacted materials were distilled out *in vacuo* to leave colorless crystals. Recrystallization from ethyl acetate gave 3.1 g (10%) of trimorpholinomethane, mp 142—147°C, as colorless needles which easily decomposed in air.

Found: C, 57.24; H, 9.29; N, 15.10%. Calcd for $C_{13}H_{25}O_3N_3$: C, 57.61; H, 9.30; N, 15.51%.

A similar reaction of 1,1-dimethoxytrimethylamine with piperidine gave colorless crystals, mp 52—56°C, bp 147°C/3 mmHg. This compound was assumed to be tripiperidinomethane, but no elemental analysis could be carried out because of its instability.

The Reactions of Ethyl Orthoformate with N-*Alkylanilines.* *i) With* N-*Methylaniline*: A mixture of 7.4 g (0.05 mol) of ethyl orthoformate and 5.3 g (0.05 mol) of *N*-methylaniline was stirred with one drop of concentrated sulfuric acid at room temperature for 2 hr: during this time a suspended reaction mixture changed into a clear solution. The removal of the unreacted materials by distillation *in vacuo* gave 3 g of colorless crystals. The crystals were washed with methanol and then recrystallized from dimethylformamide to afford tris(*N*-methylanilino)methane, mp 268—269°C (decomp.), as colorless prisms.

Found: C, 79.86; H, 7.76; N, 12.74%. Calcd for $C_{22}H_{25}N_2$: C, 79.70; H, 7.60; N, 12.68%.

ii) With N-*Ethylaniline*: A mixture of 44.5 g (0.3 mol) of ethyl orthoformate and 36.4g (0.3 mol) of *N*-ethylaniline was gently refluxed for 20 hr. The reaction mixture was then concentrated *in vacuo*, leaving 0.6 g of colorless crystals. The crystals were washed with diethyl ether and then recrystallized from acetone to give tris(*N*-ethylanilino)methane, mp 181—185°C (decomp.), as colorless prisms.

Found: C, 80.76; H, 8.67; N, 11.19%. Calcd for $C_{25}H_{31}N_3$: C, 80.38; H, 8.37; N, 11.25%. NMR spectrum in deuterochloroform: δ 6.76 (15H, phenyl protons), 5.76 (1H, singlet, methine proton), 3.39 (6H, methylene protons) and 1.09 ppm (9H, methyl protons). UV spectrum in chloroform λ_{max} mμ (ε): 249.5 (28100), 295.5 (5140).

The Reactions of TPE and TME with Halogens. The reaction of TPE with bromine will be described as a representative reaction. When an equimolar amount of bromine was added to a solution of 0.5 g of TPE in 10 m*l* of *n*-hexane, an orange solid precipitated immediately. After 10 m*l* of *n*-hexane had then been added to the reaction mixture, filtration gave an orange solid. Several fractional recrystallizations from acetonitrile gave 0.54 g (70%) of $TPEBr_2 \cdot 2H_2O$, mp 247°C (decomp.), as pale yellow prisms and 0.2 g of $TPEBr_6$, mp 223°C (decomp.), as orange prisms.

The reaction conditions of TPE and TME with halogens, the yields, the physical properties, and the results of elemental analyses of the corresponding oxamidinium halides are shown in Tables 1 and 3.

The Reactions of TPE and TME with Halogen-Compounds. The reaction of TPE with benzal chloride is shown as a representative reaction. A solution of 3 g of TPE and 5.4 g of benzal chloride in 20 m*l* of benzene was refluxed for 1 hr. After the reaction mixture had been cooled, it was filtered to give 3 g (83%) of $TPECl_2 \cdot 2H_2O$. The filtrate was concentrated *in vacuo* to leave yellow crystals which, on recrystallization from a benzene-methanol mixture gave 0.5 g (19%) of 1,1,2,2-tetrachloro-1,2-diphenylethane, mp 163—164°C (lit,[15] mp 163°C), as yellow needles.

Found: C, 52.68; H, 3.13%. Calcd for $C_{14}H_{10}Cl_4$: C, 52.53; H, 3.15%.

Furthermore, a small amount of stilbene was isolated by the gas chromatography of the filtrate after the separation of tetrachlorodiphenylethane.

The reaction conditions of TPE and TME with other halogen-compounds and the yields of the products are summarized in Table 2.

In the reactions with benzenesulfonyl chloride, phenacyl bromide, and 2,2-dichloroacenaphthenone,[16] diphenylsulfone, biphenacyl, and diacenaphthylidenedione were obtained respectively besides the corresponding oxamidinium dihalide.

Diphenyldisulfone, mp 194—195°C (lit,[17] mp 193—194°C).

Found: C, 50.86; H, 3.53%. Calcd for $C_{12}H_{10}O_4S_2$:

Table 3. Physical properties and elemental analyses of oxamidinium halides

Compound	Appearance (Recryst. solvent)	Mp(°C)	λ_{max}^{EtOH} mμ(ε)	Analysis (%), Found (Calcd)		
				C	H	N
$TPECl_2 \cdot 2H_2O$	colorless prisms (MeCN-MeOH)	240—241 (decomp.)	213 (17400) 291.5 (12100)	56.52 (56.51)	9.57 (9.49)	11.94 (11.98)
$TMECl_2 \cdot 2H_2O$	light yellow prisms(MeCN-MeOH)	265—266 (decomp.)	214.5 (16100)[a] 295 (11100)	45.47 (45.47)	7.77 (7.63)	11.60 (11.79)
$TPEBr_2 \cdot 2H_2O$	pale yellow prisms(MeCN)	247 (decomp.)	212 (19900) 291 (13400)	47.72 (47.48)	8.02 (7.97)	9.84 (10.07)
$TMEBr_2 \cdot H_2O$	pale yellow prisms(MeOH)	300 (decomp.)	210 (14500)[a] 295 (9130)	39.49 (39.57)	6.24 (6.28)	9.95 (10.25)
$TPEI_2$	yellow prisms (MeOH)	282—284 (decomp.)	217 (45300) 291 (11100)	42.93 (43.00)	6.53 (6.57)	9.14 (9.12)
$TMEI_2$[c]	brown crystals[b]	*ca.* 190 (decomp.)		33.18 (32.83)	5.18 (5.51)	8.46 (8.51)
$TPEBr_6$[c]	orange prisms (MeCN)	223 (decomp.)		31.53 (31.45)	4.98 (4.80)	6.50 (6.66)
$TPEI_6$[c]	brown crystals (MeOH)	232—234		23.55 (23.57)	3.59 (3.65)	4.99 (5.07)

a) The UV spectra were measured in water.
b) $TMEI_2$ was analyzed without further purification because of its insolubility.
c) The IR spectra of hexahalides as well as dihalides showed characteristic bands at 1620 and 1640 cm^{-1}.

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15) C. Liebermann and J. Homeyer, *Ber.*, **12**, 1971 (1879).

16) O. Tsuge and M. Tashiro, This Bulletin, **26**, 970 (1963).

17) T. P. Hilditch, *J. Chem. Soc.*, **93**, 1526 (1908).

C, 51.06; H, 3.57%.

Biphenacyl was identified as 2,4-dinitrophenylhydrazone, mp 239—240°C (decomp.). Found: C, 56.32; H, 3.68; N, 18.79%. Calcd for $C_{28}H_{22}O_8N_8$: C, 56.18; H, 3.70; N, 18.72%.

Diacenaphthylidenedione, mp 294°C, was identified by comparison with an authentic sample prepared from acenaphthenone and acenaphthenequinone.

The Reaction of TPE with Phenylnitromethane. A solution of 1.5 g of TPE and 5 g of phenylnitromethane in 20 m*l* of xylene was stirred at 90°C for 15 min; during this time crystals precipitated gradually. After the solution had then been cooled, filtration gave 1.0 g (51%) of colorless crystals which, on recrystallization from acetonitrile afforded a dinitrile, $TPE(NO_2)_2 \cdot 2H_2O$, mp 188°C (decomp.), as pale pink prisms.

Found: C, 54.00; H, 9.19; N, 17.00%. Calcd for $C_{22}H_{40}O_4N_6 \cdot 2H_2O$: C, 54.07; H, 9.08; N, 17.20%. IR spectrum: 1620, 1640 cm^{-1}. UV spectrum in water λ_{max} mμ (ε): 216 (28000), 291.5 (13400).

This compound was also obtained by the reaction of dihalides, $TPEX_2$, with silver nitrite.

A similar reaction of TME with phenylnitromethane in benzene at 80°C gave a 30% yield of crude dinitrite, $TME(NO_2)_2$, which, on recrystallization from methanol, gave yellow prisms, mp 246—248°C (decomp.).

Found: C, 43.35; H, 7.05; N, 16.97%. Calcd for $C_{18}H_{38}O_8N_6 \cdot 2H_2O$: C, 43.54; H, 7.31; N, 16.93%. IR spectrum: 1620, 1640 cm^{-1}. UV spectrum in water λ_{max} mμ (ε): 210 (31600), 296 (14600).

This compound was also obtained by the reaction of dihalides, $TMEX_2$, with silver nitrite.

The Reaction of TPE with Tetranitromethane. When a solution of 0.7 g of TPE and 0.5 m*l* of tetranitromethane in 15 m*l* of diethyl ether was stirred at 0°C for 30 min, yellow crystals precipitated gradually. Filtration gave 1.1 g of yellow crystals which, on fractional recrystallization from acetone, afforded 0.9 g of a 1 : 2 adduct, $TPE[C(NO_2)_4]_2$, mp 112°C (decomp.), as yellow needles and a small amount of a dinitrate, $TPE(NO_3)_2$, mp 222—223°C (decomp.) as colorless crystals.

Found: C, 43.82; H, 6.10; N, 21.12%. Calcd for $C_{24}H_{40}O_{12}N_{10}$: C, 43.63; H, 6.10; N, 21.10%.

The dinitrate was easily obtained from the dihalides, $TPEX_2$, with silver nitrate.

Found: C, 50.93; H, 8.61; N, 15.85%. Calcd for $C_{22}H_{40}O_6N_6 \cdot 2H_2O$: C, 50.75; H, 8.52; N, 16.14%. IR spectrum: 1620, 1640 cm^{-1}.

The Reaction of TPE with 1,3,5-*Trinitrobenzene.* To a benzene solution of 0.5 g of TPE was added, drop by drop, a benzene solution of two equimolar amounts of 1,3,5-trinitrobenzene at room temperature, forming purple crystals. Filtration gave purple crystals, mp 122—124°C (decomp.), which easily decomposed in air. The compound was analyzed without further purification.

Found: C, 51.52; H, 6.43; N, 17.07%. Calcd for $C_{34}H_{46}O_{12}N_{10}$: C, 51.90; H, 5.90; N, 17.80%.

The Reaction of TPE with Nitromethane. After a solution of 0.8 g of TPE and 4 m*l* of nitromethane in 6 m*l* of benzene had been refluxed under an atmosphere of nitrogen for 1.5 hr, the reaction mixture was concentrated *in vacuo*. The residue was washed with petroleum ether (bp 30—45°C) to leave 0.4 g (58%) of orange crystals which, on recrystallization from carbon tetrachloride, gave 1-nitro-2-piperidinoethylene, mp 94—95°C (lit,[18] mp 95°C), as pale yellow scales.

Found: C, 53.60; H, 7.73; N, 18.07%. Calcd for $C_7H_{12}O_2N_2$: C, 53.82; H, 7.74; N, 17.94%. IR spectrum: 1635 cm^{-1} ($\nu_{C=C}$). NMR spectrum in deuterochloroform: δ 1.71 (6H, methylene protons), 3.40 (4H, methylene protons), 6.86 and 8.17 ppm (each 1H, doublet, olefinic proton). UV spectrum in ethanol λ_{max} mμ (ε): 216.9 (7250), 240 (3780), 357 (33400). Mass spectrum: *m/e* 156 (M^+).

From the washings, 0.2 g of TPE was recovered.

A similar reaction of TME with nitromethane gave a 46% yield of 2-morpholino-1-nitroethylene, mp 138—140°C (lit,[18] mp 140—141°C), as yellow prisms (from ethyl acetate).

Found: C, 45.46; H, 6.32; N, 17.78%. Calcd for $C_6H_{10}O_3N_2$: C, 45.56; H, 6.37; N, 17.71%. IR spectrum: 1630 cm^{-1} ($\nu_{C=C}$). UV spectrum in ethanol λ_{max} mμ (ε): 213 (8250), 238 (3630), 353.5 (23000). Mass spectrum: *m/e* 158 (M^+).

The Reaction of TPE with Benzoic Acid. A mixture of 0.7 g of TPE and two equimolar amounts of benzoic acid in 10 m*l* of benzene was stirred at room temperature for 4 hr. Filtration gave 0.65 g (70%) of a colorless solid which, on recrystallization from methanol - ethyl acetate, afforded the dibenzoate, $TPE(PhCO_2)_2 \cdot 2H_2O$, mp 104—105°C, as colorless needles.

Found: C, 67.43; H, 8.76; N, 8.58%. Calcd for $C_{36}H_{50}O_4N_4 \cdot 2H_2O$: C, 67.68; H, 8.52; N, 8.77%. IR spectrum: 1635, 1610, 1550 cm^{-1}.

Similar reactions of TPE with *p*-methyl- and *p*-chlorobenzoic acid gave the corresponding oxamidinium salts. $TPE(p\text{-}MeC_6H_4CO_2)_2 \cdot 2H_2O$: mp 101—103°C, colorless needles (from methanol - ethyl acetate). Yield, 52%.

Found: C, 68.13; H, 8.95; N, 8.53%. Calcd for $C_{38}H_{54}O_4N_4 \cdot 2H_2O$: C, 68.44; H, 8.77; N, 8.40%. IR spectrum: 1637, 1610, 1545 cm^{-1}.

$TPE(p\text{-}ClC_6H_4CO_2)_2 \cdot 2H_2O$: mp 109—111°C, colorless needles (from methanol - ethyl acetate). Yield, 75%.

Found: C, 60.82; H, 7.75; N, 7.77%. Calcd for $C_{36}H_{48}O_4N_4Cl_2 \cdot 2H_2O$: C, 61.09; H, 7.40; N, 7.91%. IR spectrum: 1640, 1610, 1595, 1540 cm^{-1}.

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[18] C. D. Hurd and L. T. Sherwood, Jr., *J. Org. Chem.*, **13**, 471 (1948).