hydrogen and the -NCX group could be through the π orbitals of the C=X bond. However, this formulation leaves unanswered the fact that only HNCO and HNCS are detected in the products, although under the conditions of our analysis, namely, at least 25% decomposition and in a 10-cm ir gas cell, this could be accounted for if the rate constant of isomerization of these species is at least twenty times larger as that for elimination. We plan to do more work along these lines and to extend the investigation to the isoselenocyanates.

An indication of the degree of polarity of the reaction is obtained from Table VI where a similar effect of α-methylation on rate is observed for isocyanates and isothiocyanates suggesting identity of mechanism. The absolute magnitude of this effect, although comparable with that found in the acetates, is much less than in the case of alkyl halides, a reaction regarded as quasiheterolytic.[19]

Experimental Section

An all-glass apparatus of conventional design was used. The reaction vessel was a cylinder of about 380-ml capacity and fitted with a glass-diaphragm gauge which allowed the kinetics to be followed manometrically. The temperature of the furnance was kept constant within 0.2° by means of an RT5 Mk.2 temperature controller from Associated Electrical Industries, England.

Reagents.—Isopropyl and *tert*-butyl isocyanates were laboratory reagents from K & K Laboratories, Inc., that had been fractionated to give a purity better than 99.9% as established by gas chromatography using a flame ionisation detector.

Quantitative Analysis.—Method A was used for determination of the starting material by the internal standard technique. The reaction mixture was condensed, at liquid nitrogen temperature, directly in a trap containing a known amount of the standard. For this purpose, *n*-heptane and toluene were used for the determination of isopropyl and *tert*-butyl isocyanates, respectively. The factors used to convert chromatographic area ratios into pressure ratios were found to be 3.17 ± 0.15 and 1.92 ± 0.09 for the flame ionisation detector.

Method B was used for the analysis of olefins. The reaction mixture was removed from the reactor and passed through a column filled with soda-lime followed by a trap at −80°. The olefin was finally condensed at liquid nitrogen temperature in a bulb containing the standard. Isobutylene and propylene were determined in this manner with *n*-butane as a standard. The calibration factors were 0.934 ± 0.042 and 1.26 ± 0.07, respectively.

Method C was employed for the determination of propylene and was similar to method B except that the final bulb was calibrated and the amount of gas computed from P, V, and T measurements.

Instrumental Analysis.—The reaction products were identified by a combination of several physical methods of analysis which included gas chromatography with Perkin-Elmer F11 apparatus fitted with both thermal conductivity and flame ionisation detectors. For the gas chromatography–mass spectrometry technique a Perkin-Elmer 990 chromatograph coupled to a Hitachi Perkin-Elmer RMU-6H mass spectrometer was used. Ir analysis of gases were carried out in a Perkin-Elmer 337 grating spectrophotometer fitted with a 10-cm gas cell. Nmr analysis of the hydrocarbon fraction was performed at temperatures sufficiently low to keep the sample liquid in a Varian A-60 apparatus.

Registry No.—Isopropyl isocyanate, 1795-48-8; *tert*-butyl isocyanate, 1609-86-5.

(19) A. Maccoll, *Chem. Rev.*, **69**, 32 (1969).

Diquaternary Salts. I. Preparation and Characterization of the Diquaternary Salts of Some Diazines and Diazoles[1]

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By using oxonium salts as alkylating agents, diquaternary salts of pyrazines, pyrimidines, pyridazines, triazoles, and thiadiazoles have been prepared for the first time. Structures were established by a combination of spectroscopic and chemical techniques. Pyrazinium diquats were found to undergo spontaneous radical cation formation upon solution in alcohols, whereas pyrimidinium salts did not. A rationale for this in terms of HMO theory is presented.

Many monocyclic diaza aromatics, including pyrazines, pyrimidines, pyridazines, and various diazoles, possess two nitrogen atoms whose unshared electron pairs are not part of a π-electron system. While in principle, such molecules could form diquaternary salts without loss of aromaticity, in practice diquaternization has apparently never been observed.[2] Thus Bahner and Norton obtained only monoquaternary salts from the reaction of pyrazine with excess phenacyl bromide,[3] and Blood and Noller were unable to diquaternize pyridazine with *cis*-1,4-dibromo-2-butene, even though intramolecularity favored the second alkylation step.[4] Undoubtedly, these failures arise from the expected reduction in nucleophilicity of the second nitrogen attendant upon quaternization of the first. An estimate of the magnitude of this effect can be made by assuming that nucleophilicity and basicity are roughly parallel. The two K_a's of pyrazine, for example, differ by over six powers of ten.[5] A similar difference in the nucleophilicities of the dibase and of its monoquaternary salt might be expected, and therefore failure to observe diquaternization is not surprising. It seemed to us that the presence of two positive charges in a conjugated ring might be expected to lead to enhanced reactivity, and we have therefore undertaken an investigation of the preparation and properties of diquaternary salts. An additional stimulus for this work

(1) Taken in part from the Ph.D. thesis of K. S. Prasad, St. Louis University, 1970. For a preliminary communication see T. J. Curphey, *J. Amer. Chem. Soc.*, **87**, 2063 (1965).

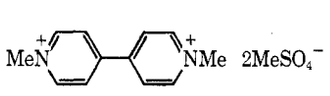
(2) For a review on quaternization of heterocycles see G. F. Duffin, *Advan. Heterocycl. Chem.*, **3**, 1 (1964).

(3) C. T. Bahner and L. L. Norton, *J. Amer. Chem. Soc.*, **72**, 2881 (1950). See also Y. T. Pratt in "Heterocyclic Compounds," Vol. 6, R. C. Elderfield, Ed., Wiley, New York, N. Y., 1957, p 400.

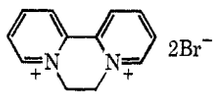
(4) A. E. Blood and C. R. Noller, *J. Org. Chem.*, **22**, 844 (1957).

(5) A. S. Chia and R. F. Trimble, Jr., *J. Chem. Phys.*, **65**, 863 (1961).

was the known herbicidal activity of the salts paraquat and diquat,[6] and of substances related to them.[7]



paraquat



diquat

Preparation of Diquats.—Previous failures to observe dialkylation with alkyl halides led us to try the more potent trialkyloxonium salts[8] as alkylating agents. Addition of pyrazine to slightly more than 2 equiv of triethyloxonium tetrafluoroborate[9] in cold 1,2-dichloroethane produced an immediate precipitate of monoquaternary salt. Upon heating this suspension to reflux, the precipitate redissolved and highly crystalline diquat **1** began to separate from the hot mixture.[10] A further brief reaction period, cooling and filtration gave **1** in virtually quantitative yield. After determining that the reaction product from pyrazine did indeed have structure **1** (*vide infra*), we proceeded to examine diquaternization of a number of diazines and diazoles, with the results shown in Table I. While

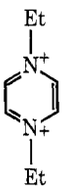
TABLE I

PREPARATION OF DIQUATERNARY SALTS[a]

Expt no.	Diquat	Alkylating agent	Solvent	Yield, %
1	1	$Et_3O^+BF_4^-$	$ClCH_2CH_2Cl$	97
2	1	$(EtO)_2CH^+BF_4^-$	$ClCH_2CH_2Cl$	85
3	2a	$Et_3O^+BF_4^-$	$ClCH_2CH_2Cl$	95
4	2b	$Et_3O^+BF_4^-$	$ClCH_2CH_2Cl$	46[b]
5	2c	$Et_3O^+BF_4^-$	$ClCH_2CH_2Cl$	5
6	3a	$Et_3O^+BF_4^-$	$ClCH_2CH_2Cl$	99
7	3b	$Et_3O^+BF_4^-$	$ClCH_2CH_2Cl$	98
8	4a	$Me_3O^+BF_4^-$	None	21
9	4b	$Me_3O^+BF_4^-$	None	4[c]
10	5a	$Me_3O^+BF_4^-$	$ClCH_2CH_2Cl$	67
11	5a	$Me_3O^+BF_4^-$	SO_2	35
12	5a	$Me_3O^+BF_4^-$	CH_3NO_2	2
13	5a	$Me_3O^+BF_4^-$	None	65
14	5b	$Et_3O^+BF_4^-$	$ClCH_2CH_2Cl$	35
15	5b	$(EtO)_2CH^+BF_4^-$	$ClCH_2CH_2Cl$	8
16	5c	$Me_3O^+BF_4^-$	None	53[c]
17	6a	$Me_3O^+BF_4^-$	$ClCH_2CH_2Cl$	67
18	6a	$Me_3O^+BF_4^-$	None	60
19	6b	$Me_3O^+BF_4^-$	None	45[c]
20	7a	$Me_3O^+BF_4^-$	None	52
21	7b	$Me_3O^+BF_4^-$	None	17[c]

[a] In most cases 2.5 mol of alkylating agent per mole of base was used, the reaction temperature was approximately 85°, and the reaction time varied from 15 min to 1 hr. See Experimental Section for exact details. [b] Estimated by nmr analysis of the crude product, a mixture of monoquat and diquat. [c] The starting material for this alkylation was the ethyl monoquat.

we cannot claim to have carried out an exhaustive investigation, nevertheless, several generalizations can be made as a result of these experiments. First, in common with other quaternizations, the ease of diquaternization is apparently sensitive to steric hindrance. One methyl group on an adjacent carbon had little effect (compare expt 1 to 3 and 6 to 7), but two flanking methyl groups reduced considerably the yield of diquaternary salt (compare expt 1, 4, and 5). There was also some indication that an adjacent ethyl group had an adverse effect on yield (compare expt 8 to 9 and 20 to 21). These reductions in yield are undoubtedly due in large measure to a decrease in the rate of alkylation of the more sterically hindered nitrogens, and they parallel closely the rate differences observed for quaternization of pyridines.[11] Second, in refluxing dichloroethane the effectiveness of the three alkylating agents studied was in the order $Me_3O^+BF_4^-$ > $Et_3O^+BF_4^-$ > $(EtO)_2CH^+BF_4^-$. For example,



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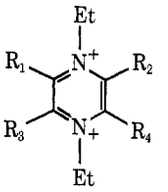
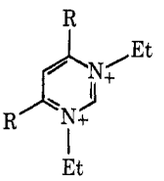
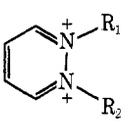


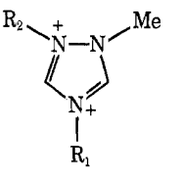
2a, $R_1 = R_4 = Me$; $R_2 = R_3 = H$
b, $R_1 = R_2 = Me$; $R_3 = R_4 = H$
c, $R_1 = R_2 = R_3 = R_4 = Me$



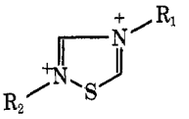
3a, R = H
b, R = Me



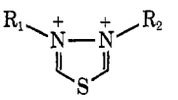
4a, $R_1 = R_2 = Me$
b, $R_1 = Et$; $R_2 = Me$



5a, $R_1 = R_2 = Me$
b, $R_1 = R_2 = Et$
c, $R_1 = Et$; $R_2 = Me$



6a, $R_1 = R_2 = Me$
b, $R_1 = Et$; $R_2 = Me$



7a, $R_1 = R_2 = Me$
b, $R_1 = Et$; $R_2 = Me$

8

diquaternization of 1-methyl-1,2,4-triazole with $Me_3O^+BF_4^-$ (expt 10) gave better results than quaternization with $Et_3O^+BF_4^-$ (expt 14), and, while 1,2,4-thiadiazole was diquaternized by $Me_3O^+BF_4^-$ (expt 17), no diquat was obtained from a similar reaction with $Et_3O^+BF_4^-$. The differences between the methyl and ethyl oxonium salts are probably primarily steric in origin and parallel similar differences noted for the alkyl halides.[11] Based on work of Kabuss[12] who had demonstrated the superior electrophilicity of dialkoxycarbonium ions toward several weak nucleophiles, we briefly examined $(EtO)_2CH^+BF_4^-$ as an ethylating agent. In the two cases tried, however, this reagent gave lower yields of diquat than $Et_3O^+BF_4^-$ (expt 1, 2, and 14, 15), and we did not study it further.

Because of the limited solubility of the oxonium salt, alkylations by $Me_3O^+BF_4^-$ in dichloroethane are heterogeneous and occur either on the surface of the suspended oxonium salt or in the bulk of the solution where the concentration of the alkylating agent is low.

(6) W. R. Boon, *Chem. Ind. (London)*, 782 (1965).

(7) A. L. Black and L. A. Summers, *J. Chem. Soc. C.*, 610 (1969), and previous papers in this series; E. C. Campbell, E. E. Glover, and G. Trenholm, *ibid.*, 1987 (1969), and previous papers in this series.

(8) H. Meerwein in "Methoden der Organischen Chemie," (Houben-Weyl), Vol. 6/3, Georg Thieme Verlag, Stuttgart, 1965, p 325.

(9) H. Meerwein, *Org. Syn.*, **46**, 113 (1966).

(10) Unless otherwise indicated, the anions throughout this paper are tetrafluoroborates.

(11) Reference 2, p 11.

(12) S. Kabuss, *Angew. Chem., Int. Ed. Engl.*, **5**, 675 (1966); K. Kimroth and P. Heinrich, *ibid.*, **5**, 676 (1966); R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).

In hopes of finding a more potent alkylating system, we investigated solutions of the trimethyloxonium salt in liquid sulfur dioxide and in nitromethane (expt 11 and 12). Both of these homogeneous systems, however, proved less effective than the heterogeneous one. We then discovered that simple fusion of a base with trimethyloxonium tetrafluoroborate was in general superior to any other alkylation procedure.[13] Utiling this method we were able to achieve two dialkylations for which other methods had previously failed, dialkylation of pyridazine (expt 8 and 9) and of 1,3,4-thiadiazole (expt 20 and 21). The fusion procedure thus allowed the preparation of diquats in which, formally at least, the two positive charges were on adjacent nitrogen atoms. While some experimentation may be necessary to discover the best conditions, we regard this procedure as the one of choice for the preparation of diquats.[14] Undoubtedly, its effectiveness is due to the very high concentration of alkylating agent (and base) in the melt and to the high polarity of the reaction mixture which greatly accelerate the rate of reaction. At the moment the only base which has resisted diquaternization by any procedure is 1,2,5-thiadiazole (**8**). The monoquaternary salt of this base appeared to be somewhat unstable, however, and our failure to obtain a diquaternary salt may be due to rapid decomposition of the monoquat or diquat rather than to any failure of the dialkylation *per se*.

Structure of Diquats.—Three lines of proof were used to secure the structures of the diquats reported in this paper. First, satisfactory analytical data were obtained for almost all diquats (see Experimental Section). Second, nmr spectra fully supported the assigned structures. For example, the spectrum of diquat **1** showed a low-field singlet for the ring hydrogens, a quartet for the methylene hydrogens, and a triplet for the methyl hydrogens. The integrated intensities of the three types of hydrogens were in the expected ratios of 2:2:3. Likewise, for diquat **3a** the hydrogen at C-2 appeared at lowest field as a singlet, strongly deshielded by the two adjacent positive nitrogens. The equivalent hydrogens at C-3 and C-5 appeared as a doublet at somewhat higher field, deshielded by the single adjacent postive nitrogen, and the C-4 hydrogen appeared as a triplet at still higher field. The equivalent ethyl groups in **3a** appeared as a quartet and triplet. Again, integrated intensities were in the expected ratios. Further details of these and other nmr spectra can be found in the Experimental Section, but in every case the spectra fully supported the assigned structures.

While analytical and spectroscopic data might perhaps have sufficed, the unique nature of the diquats led us in selected cases to pursue a third line of structure proof, conversion to substances of known structure. The first diquat prepared, the pyrazine salt **1**, was reduced catalytically in good yield to the bisfluoroborate salt of 1,4-diethylpiperazine. The reduction product was identical with material prepared from 1,4-diethylpiperazine and fluoroboric acid. This conversion ruled out, for example, the rather remote possibility that one or both of the ethyl groups in **1** was attached to carbon rather than nitrogen.[15] Three other diquats were subjected to hydrolytic degradation in order to confirm their structures. A solution of the diquat in dilute sulfuric acid was first refluxed, then basified, and the liberated organic bases were isolated by steam distillation and conversion to the hydrochlorides. For separation and analysis the hydrochlorides were converted to trifluoroacetamides,[16] and the amides, after separation and purification by gas chromatography, were compared with authentic samples. By this procedure **5b** afforded approximately equal amounts of ethylamine and 1-methyl-2-ethylhydrazine.[17] In the case of diquat **5c**, which had been synthesized from 1-methyl-1,2,4-triazole by monoalkylation with $Et_3O^+BF_4^-$ followed by methylation with $Me_3O^+BF_4^-$, degradation to ethylamine and 1,2-dimethylhydrazine established that, as expected,[18] the first alkylation had taken place at N-4 rather than at N-2. In view of the fact that thiophene can be S-alkylated,[19] we had considered it barely possible that 1,3,4-thiadiazole might alkylate on sulfur rather than on nitrogen, thereby placing the two positive charges in a more favorable 1,3 relationship on the ring.[20] In fact, however, degradation of **7b** to 1-methyl-2-ethylhydrazine established that both alkylations had occurred on nitrogen.

Two structural points remain to be disposed of. Because of the failure of 1,3,4-thiadiazole to alkylate on sulfur, we believed it highly improbable that 1,2,4-thiadiazole would do so, and have assigned structures **6a** and **6b** accordingly. Moreover the nmr spectra of **6a** and **6b** show no evidence of *S*-methyl groups. The methyl singlets in **6a** and **6b** fall near δ 4.6, whereas the methyls of *S*-thiophenium salts fall near δ 3.2.[19] The placing of alkyl groups in **6b** (prepared by an ethylation–methylation sequence) is suggested by two lines of evidence. First, in studies of nuclear alkylation in the 1,2,4-thiadiazoles,[21] it has been shown that 5-amino-1,2,4-thiadiazole and 3-phenyl-5-methylthio-1,2,4-thiadiazole alkylate at N-4. However, it is somewhat difficult in these cases to assess the effect of the 5 substituent on the relative nucleophilicities of the two ring nitrogens. Second, we might expect that the 1,2,4-thiadiazoles would resemble the 1,2,4-triazoles and oxadiazoles. As discussed above,

(13) For similar observations see A. I. Kriprianov and A. I. Tolmachev, *Zh. Obshch. Khim.*, **27**, 142 (1957); A. J. Nunn and J. T. Ralph, *J. Chem. Soc. C*, 1568 (1966).

(14) For its use elsewhere in these laboratories for alkylation of weakly basic phosphonitriles see J. N. Rapko and G. Feistel, *Inorg. Chem.*, **9**, 1401 (1970).

(15) The pyrimidine diquat **3a** has also been converted to a substance unambiguously synthesized by another route. The chemistry of diquat **3a** will be reported in detail in part II of this series, and we postpone further discussion of its structure to that paper.

(16) M. Pailer and W. J. Huebsch, *Monatsh. Chem.*, **97**, 1541 (1966).

(17) The 1-methyl-2-ethylhydrazine required for this study was at the time an unreported compound. Two attempts at a simple synthesis of this hydrazine failed, and it was finally prepared from benzalazine in four steps. Further details may be found in the Experimental Section. Recently, another synthesis has been described: N. V. Khromov-Borisov and T. N. Kononova, *Probl. Poluch. Poluprod. Prom. Org. Sin., Akad. Nauk SSR, Otd. Obshch. Tekh. Khim.*, **10** (1967); *Chem. Abstr.*, **68**, 48947 (1968). Experimental details and physical data were not reported in the abstract and the original is unavailable to us. Consequently, we have been unable to compare our preparation with that of the Russian workers.

(18) Reference 2, p 35.

(19) R. M. Acheson and D. R. Harrison, *J. Chem. Soc. C*, 1764 (1970); G. C. Brumlick, A. I. Kosak, and R. Pitcher, *J. Amer. Chem. Soc.*, **86**, 5360 (1964).

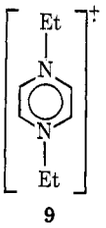
(20) Of course, this line of reasoning is somewhat naive, since one can write two entirely reasonable canonical structures for **7a** and **7b** which place a positive charge on sulfur. It is conceivable, in fact, that the sulfur atom in **7a** and **7b** carries more postive charge than either nitrogen.

(21) J. Goerdeler, A. Huppertz, and K. Weimber, *Chem. Ber.*, **87**, 68 (1954); S. Hunig and K. H. Oette, *Justus Liebigs Ann. Chem.*, **641**, 94 (1961).

the former system alkylates at N-4, and N-4 alkylation for the latter system has been demonstrated by Michelman.[22] With the structures of the alkylation products on a relatively firm basis, we turn now to observations on the properties of these diquaternary salts.

Properties of Diquats.—All of the pure diquat salts were white, usually hygroscopic, crystalline solids. However, most showed evidence of instability such as discoloration or liquefaction over a period of time. Storage at low temperature in a dry atmosphere was only partially successful in allaying this decomposition. The diquats appeared to react (heat evolution, rapid color development) with many common polar solvents, which made their purification by recrystallization difficult. For many salts solution in acetonitrile followed by immediate precipitation with dichloroethane was successful, but it was essential to work rapidly to avoid sizable losses. Acetone or methyl ethyl ketone were used for recrystallization in some cases. The only solvents in which the diquats were stable for long periods of time were trifluoroacetic acid and trifluoroacetic acid–sulfuric acid mixtures. These solvents were therefore used to obtain nmr spectra.

In examining the solubility of pyrazine diquat **1** in various solvents we observed several rather striking polychromatic displays. Addition of a small amount of **1** to water gave a transiently pink solution which almost immediately turned green, somewhat more slowly faded to violet, and then on longer standing became brown. Initially yellow solutions of **1** in methanol or ethanol turned red or violet upon standing, while yellow solutions in acetonitrile slowly developed a green coloration which eventually became a dark olive. Likewise, yellow solutions of **1** in nitromethane rapidly turned blue. Such color development led us to search for the presence of free radicals in these systems. Indeed 10^{-2} to 10^{-3} *M* solutions of **1** in methyl, ethyl, isopropyl, and *tert*-butyl alcohols gave a complex epr spectrum of over 200 lines, whose analysis[23] was consistent with the presence of the radical cation **9**. Pyrazine



9

diquats **2a–c** similarly gave radical cation epr spectra under these conditions. Alternatively, radical cations were formed by brief contact with granulated zinc of a solution of the diquat in trifluoroacetic acid. The dilute solutions employed in the epr studies were colorless or very faintly colored when first prepared but darkened somewhat upon long standing. However, provided that the radical cations were generated in the absence of oxygen, the epr spectra of such solutions changed only slightly over a period of many months. This suggests that color development is more likely associated with the decomposition of the radicals than, as we had originally thought, with their formation. Formation of **9** was also demonstrated by an nmr technique. Brief contact of a trifluoroacetic acid solution of **1** in an open tube with a small piece of zinc attached to a copper wire caused all the resonance lines of **1** to broaden to the point of unobservability. On standing, however, the spectrum of **1** gradually reappeared, until after 20 min the original spectrum had been restored in slightly diminished intensity. We attribute these spectral changes to formation of a small amount of radical cation **9** upon contact with zinc. Rapid (on the nmr time scale) electron transfer between radical cation and parent dication then induces relaxation of all hydrogen nuclei and "washes out" the spectrum.[24] Destruction of the radical cation by oxygen leads finally to reappearance of the nmr spectrum.

We did note one further interesting color phenomenon. Methanol solutions of **9** when cooled in liquid nitrogen developed a bright pink coloration. Further, it has been noted that cooled solutions of the radical cations show a marked decrease in intensity of the epr spectra.[23] These observations suggest that on cooling the pyrazinium radical cations associate reversibly to give diamagnetic species. One interesting possibility is a charge transfer complex between **1** and its neutral two-electron reduction product. Similar complexes have been postulated in other systems.[25]

The ready one-electron reduction of the pyrazine diquats by simple alcohols no doubt reflects enhanced reactivity arising from the presence of two positive charges in a single ring. Paraquat undergoes a similar reduction, but this requires photochemical initiation and does not occur in *tert*-butyl alcohol.[26a] In hopes of shedding further light on the reduction process for the diquats, decomposition of a large quantity of **1** in isopropyl alcohol was examined. No evidence was obtained for the formation of acetone, the most likely oxidation product,[26b] although acetone was shown to be stable to the reaction conditions. Gas chromatographic analysis of a distillate from the reaction mixture showed no volatile product other than isopropyl alcohol, nor could any well-defined product be isolated from the nonvolatile portion of the reaction mixture. The formation of radical cation **9** in *tert*-butyl alcohol and the failure to find acetone as an oxidation product from isopropyl alcohol make unattractive mechanisms involving hydrogen or hydride abstraction from the oxygen or α carbon of the alcohol and suggest that the alcohol solvent may in fact function as other than a reducing agent. One possibility, for example, is a mechanism in which ROH acts as a nucleophile to initiate a redox reaction.

Addition of alcohol to diquat **1** gives an intermediate **10**, which now reduces more **1**, possibly *via* the transient 8-π-electron intermediate **11**. As written, the mechanism requires that one-third of the original diquat form **12**. However, **12** may, by a similar sequence of steps, reduce two more molecules of **1** and

(22) J. S. Michelman, Ph.D. Thesis, Harvard University, 1965; *Diss. Abstr.*, **26**, 1920 (1965).

(23) M.-K. Ahn and C. S. Johnson, Jr., *Proc. Colloq. Ampere*, **14**, 253 (1966); *J. Chem. Phys.*, **50**, 632 (1969).

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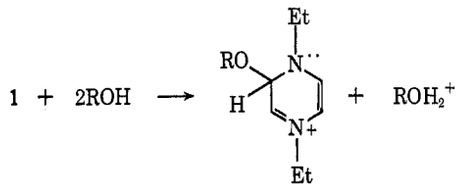

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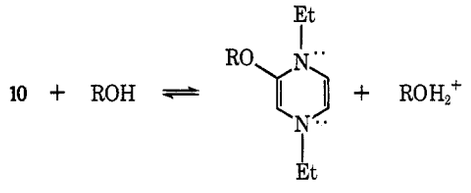

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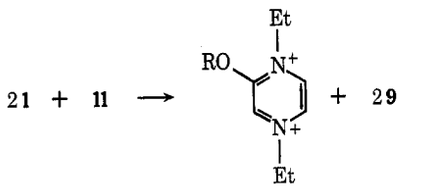

12

be oxidized to a dialkoxy diquat. Ultimately, one molecule of diquat could reduce as many as eight others to the radical cation stage. The apparent anomaly of a highly electron deficient diquat functioning as a reducing agent can perhaps be resolved by realizing that the oxidation product **12** is stabilized by delocalization of one of the positive charges onto oxygen. Consequently, the overall redox reaction is energetically favorable.

We have so far been unable to observe formation of stable radical cations from alcoholic solutions of the pyrimidine diquats **3a** and **3b**. Instead, addition products analogous to **10** are formed.[27] One way of rationalizing this contrasting behavior is by resorting to simple molecular orbital calculations. A standard[28] HMO treatment of diquats **1** and **3a** with $h_N = 2$ and $k_{CN} = 1$ indicates that the energy of the lowest unoccupied MO (LUMO) of the pyrazinium diquat is 0.414β units *below* the energy of the corresponding MO in the pyrimidinium diquat. While the exact magnitude of the energy difference between LUMOs for **1** and **3a** depends on the value chosen for h_N, its direction does not.

As is well known, there is often a good linear correlation between redox potentials and LUMO energy, with a change of 1 β unit leading to a change of roughly 2 V in potential.[29] We can thus estimate that **1** should be of the order of 0.8 V more reducible than **3a**, and consequently the more facile reduction of the pyrazinium diquat is readily understood. Attempts to measure directly the difference in reduction potentials for the two diquats by electrochemical techniques have so far not been successful[30] and will not be detailed here. However, recently a similar study of the monoquaternary salts has appeared,[31] and the pyrazinium monoquat was found to be 0.27 V more reducible than the pyrimidinium monoquat. Finally, we note that the MO results for the pyridazinium dication more nearly resemble those for pyrazine than for pyrimidine. Indeed, solutions of **4a** and **4b** in water do show color changes quite similar to those of the pyrazinium diquats, but the chemistry of these pyridazinium salts remains to be elucidated. Because of the negative character of the available evidence, the mechanism by which **1** is reduced to radical cation **9** cannot be specified with absolute certainty at this time. It seems likely, however, that, whatever the mechanism for this reduction, removal of the unfavorable charge interaction in **1** must supply a large measure of the driving force for the overall change. We were encouraged by this to search for further evidence of heightened reactivity in the diquats, with results to be communicated in future papers of this series.

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Experimental Section[10]

Melting points were measured in sealed evacuated capillary tubes using a Hershberg apparatus and short-range thermometers. Nmr spectra were measured on Varian Associates A-60 and HA-100 spectrometers Infrared spectra were recorded on Perkin-Elmer Model 21 and Beckman IR-5A instruments. An Aerograph 90-P3 was used for gas chromatographic analyses. Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn. Acetonitrile and DCE (1,2-dichloroethane) were dried by distillation from phosphorous pentoxide.

Preparation of Dibases.—Commercially supplied dibases were used where available. The literature synthesis of 1,2,4-thiadiazole[32] gave highly erratic results, in agreement with a report by Flexman.[33] Attempts to improve this synthesis were unrewarding. Published procedures for the preparation of 1,3,4-thiadiazole[34] and 1,2,5-thiadiazole[35] were found to be satisfactory. Reaction of methylhydrazine with the cyanuric chloride–dimethylformamide adduct, following Gold's procedure for the synthesis of 1-alkyl-1,2,4-triazoles,[36] gave 1-methyl-1,2,4-triazole in 81% yield.

Alkylation of Dibases.—Most of the diquats reported in this work were prepared by one of two general procedures, with only minor variations.

General Procedure. Method A.—A solution or suspension of 0.05 mol of alkylating agent in 20 ml of DCE was stirred under nitrogen while 0.02 mol of dibase in 5 ml of DCE was added over a 5-min period. The reaction mixture was then heated rapidly to reflux and stirred at reflux for the requisite time. Cooling to room temperature generally produced the crystalline diquat, which was filtered with miniumum exposure to moisture and recrystallized as indicated.

General Procedure. Method B.—A solid mixture consisting of 2.5 mol of alkylating agent per mole of dibase was prepared in a drybox, attached to a nitrogen manifold, and heated at 85–90° (bath temperature) until it ceased evolving gas. Direct crystallization of the melt then yielded the diquat.

1,4-Diethylpyrazinium Diquat (1).—Reaction of pyrazine with triethyloxonium tetrafluoroborate by method A (35-min reflux), followed by filtration of the reaction mixture gave 1 (6.06 g, 97%), mp 204–209° dec. Solution of this material in acetonitrile, followed by slow addition with stirring of 2 volumes of DCE, led to 70% recovery of material melting at 208–210°: nmr (CF_3CO_2H, internal TMS) δ 1.92 (t, 6), 5.22 (q, 4), 9.86 ppm (s, 4).

Anal. Calcd for $C_8H_{14}N_2B_2F_8$: C, 30.82; H, 4.53; N, 8.98. Found: C, 30.55; H, 4.42; N, 8.78.

Replacing triethyloxonium tetrafluoroborate in this procedure by diethoxycarbonium tetrafluoroborate[12] lowered the yield to 85%.

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1,4-Diethyl-2,5-dimethylpyrazinium Diquat (2a).—Reaction of 2,5-dimethylpyrazine with triethyloxonium tetrafluoroborate by method A (15-min reflux) produced **2a** as a pinkish solid, mp 205–206° dec, in 95% yield. Two recrystallizations by solution in warm acetonitrile and addition of an equal volume of DCE gave pure material: mp 215–218° dec; nmr (CF_3CO_2D, external TMS) δ 1.88 (t, 6), 3.23 (s, 6), 5.05 (q, 4), 9.60 ppm (s, 2).

Anal. Calcd for $C_{10}H_{18}N_2B_2F_8$: C, 35.33; H, 5.34; N, 8.24. Found: C, 35.19; H, 5.22; N, 8.44.

1,4-Diethyl-2,6-dimethylpyrazinium Diquat (2b).—Reaction by method A of 38 g (0.2 mol) of triethyloxonium tetrafluoroborate and 2.18 g (0.02 mol) of 2,6-dimethylpyrazine in 30 ml of DCE with overnight refluxing gave an oil which solidified to a dark solid (4.50 g) upon trituration with a mixture of DCE and dry tetrahydrofuran. Nmr spectroscopy suggested that this material consisted of 60 ± 4 mol % of **2b** and 40 ± 4 mol % of monoquat (presumably the 4-ethyl isomer in which the less hindered nitrogen had been alkylated). On this basis the yield of dialkylated product was calculated to be 46%. To obtain pure **2b**, the crude salt mixture was resubmitted to alkylation exactly as described above. Now, however, the reaction mixture deposited a solid upon cooling to room temperature. The solid was precipitated three times from 1:2 acetonitrile–tetrahydrofuran to give **2b**: 1.20 g (18%); mp 153–155° dec; nmr (CF_3CO_2H, external TMS) δ 2.00 (t, 6), 3.44 (s, 6), 5.20 (q, 4), 9.65 ppm (s, 2).

Anal. Calcd for $C_{10}H_{18}N_2B_2F_8$: C, 35.33; H, 5.34; N, 8.24. Found: C, 35.20; H, 5.15; N, 8.29.

1,4-Diethyl-2,3,5,6-tetramethylpyrazinium Diquat (2c).—Alkylation of 2,3,5,6-tetramethylpyrazine with triethyloxonium tetrafluoroborate by method A (2-hr reflux) yielded 0.40 g (5%) of DCE-insoluble diquat, mp 221–226° dec. Two precipitations from acetonitrile–DCE (1:1) gave a pure sample of **2c**: mp 247–248° dec; nmr (CF_3CO_2H, internal TMS) δ 1.73 (t, 6), 3.16 (s, 12), 4.98 ppm (q, 4).

Anal. Calcd for $C_{12}H_{22}N_2B_2F_8$: C, 39.16; H, 6.03; N, 7.62. Found: C, 39.20; H, 6.18; N, 7.68.

1,3-Diethylpyrimidinium Diquat (3a).—Alkylation of pyrimidine with triethyloxonium tetrafluoroborate by method A (30-min reflux) gave 6.2 g (99%) of diquat **3a**, mp 167–172° dec. Pure material was obtained by two precipitations from 1:2 acetonitrile–DCE: mp 186–188° dec; nmr (CF_3CO_2D, internal TMS) δ 1.93 (t, 6), 5.20 (q, 4), 9.02 (t, 1), 9.93 (d, 2), 10.54 ppm (s, 1).

Anal. Calcd for $C_8H_{14}N_2B_2F_8$: C, 30.81; H, 4.52; N, 8.99. Found: C, 30.90; H, 4.67; N, 8.77.

1,3-Diethyl-4,6-dimethylpyrimidinium Diquat (3b).—Alkylation of 4,6-dimethylpyrimidine with triethyloxonium tetrafluoroborate by method A (45 minute reflux) yielded 6.60 g (98%) of **3b** as a pink solid, mp 202–207°. Two precipitations from 1:2 acetonitrile–DCE gave nearly colorless diquat: mp 212–214° dec (turns bright scarlet before melting!); nmr (CF_3CO_2D, external TMS) δ 1.75 (t, 6), 3.15 (s, 6), 4.88 (q, 4), 8.45 (s, 1), 10.10 (s, 1).

Anal. Calcd for $C_{10}H_{18}N_2B_2F_8$: C, 35.33; H, 5.34; N, 8.24. Found: C, 35.06; H, 5.28; N, 8.29.

1,2-Dimethylpyridazinium diquat (4a) was prepared by method B. A mixture of 0.77 g (5.2 mmol) of trimethyloxonium tetrafluoroborate[37] and 0.16 g (2.0 mmol) of pyridazine was held at 85–90° for 30 min. The resulting dark solid was soluble only in sulfuric acid and sulfuric–trifluoroacetic acid mixtures. It was therefore purified by several treatments with refluxing trifluoroacetic acid, leaving **4a** as a nearly white solid: 0.12 g (21%); mp 171–172° dec; nmr (3:1 CF_3CO_2D–D_2SO_4, external TMS) δ 5.10 (s, 6), 9.15 (t, 2, H-4 and H-5(?)], 10.16 ppm [t, 2, H-3 and H-6(?)].

Anal. Calcd for $C_6H_{10}N_2B_2F_8$: C, 25.40; H, 3.55; H, 9.87. Found: C, 25.28; H, 3.48; N, 9.82.

1-Ethyl-2-methylpyridazinium Diquat (4b).—Alkylation of 1.6 g (0.02 mol) of pyridazine by 3.8 g (0.02 mol) of triethyloxonium tetrafluoroborate using method A (15-min reflux) produced an oil which crystallized upon cooling to −78°. Removal of DCE solvent at −10° gave **1-ethylpyridazinium tetrafluoroborate**: 2.7 g (69%); mp 26–28°; nmr (CF_3CO_2H, internal TMS) δ 1.78 (t, 3), 4.96 (q, 2), 8.55 (m, 2), 9.50 ppm (m, 2).

Reaction of 0.95 g (5 mmol) of the above 1-ethylpyridazinium tetrafluoroborate with 0.96 g (6.5 mmol) of trimethyloxonium tetrafluoroborate by method B (45 min at 90–100°) gave **4b** as a dark solid, purified by solution in acetonitrile and precipitation with DCE: 0.06 g (4%); mp 153–154° dec; nmr (CF_3CO_2D, internal TMS) δ 1.82 (t, 3), 4.90 (s, 3), 5.22 (q, 2), 9.10 (m, 2), 10.00 (m, 2).

Anal. Calcd for $C_7H_{12}N_2B_2F_8$: C, 28.24; H, 4.03; N, 9.41. Found: C, 28.33; H, 4.10; N, 9.34.

1,2,4-Trimethyl-1,2,4-triazolium diquat (5a) was prepared by method A from 14.8 g (0.1 mol) of trimethyloxonium tetrafluoroborate and 4.15 g (0.05 mol) of 1-methyl-1,2,4-triazole in 30 ml of DCE (30 min reflux). Filtration produced nearly pure **5a**, 9.3 g (65%), mp 188–190° dec. Crystallization from acetonitrile gave pure material: mp 190–192° dec; nmr (3:1 CF_3CO_2H–H_2SO_4, external TMS) δ 4.38 (s, 3), 4.56 (s, 6), 9.98 ppm (s, 2).

Anal. Calcd for $C_5H_{11}N_3B_2F_8$: C, 20.93; H, 3.87; N, 14.65. Found: C, 21.25; H, 3.92; N, 14.66.

Replacing DCE by dry nitromethane lowered the yield to 2%.

Reaction of 1.9 g (13 mmol) of oxonium salt and 0.5 g (6 mmol) of 1-methyltriazole in 3 ml of liquid SO_2 (sealed tube) for 30 min at 80–85° followed by removal of SO_2 and trituration with acetonitrile gave 0.6 g (35%) of **5a**, mp 188–190° dec.

Fusion of the oxonium salt and the triazole by method B (80–85° for 30 min) gave **5a** in 70% yield after purification by trituration with acetonitrile.

1-Methyl-2,4-diethyl-1,2,4-triazolium Diquat (5b).—Reaction of 4.15 g (0.05 mol) of 1-methyl-1,2,4-triazole with 47.5 g (0.25 mol) of triethyloxonium salt by method A for 1 hr produced a two-phase mixture. The bottom phase was separated, washed with DCE, and dissolved in 50 ml of dry methyl ethyl ketone. Scratching this solution induced crystallization of **5b**, 5.5 g (35%), mp 94–95°. Recrystallization from 1:1 acetonitrile–methyl ethyl ketone gave the pure diquat: mp 95–96°; nmr (CF_3CO_2H–internal TMS) δ 1.75 (t, 3), 1.85 (t, 3), 4.50 (s, 3), 4.8 (apparent hextuplet arising from two overlapping quartets, 4), 10.07 ppm (s, 2).

Anal. Calcd for $C_7H_{15}N_3B_2F_8$: C, 26.71; H, 4.80; N, 13.35. Found: C, 26.74; H, 4.85; N, 13.18.

Substituting diethoxycarbonium tetrafluoroborate[12] for the triethyloxonium salt lowered the yield to 10%.

1,2-Dimethyl-4-ethyl-1,2,4-triazolium Diquat (5c).—A solution of 4.75 g (25 mmol) of triethyloxonium tetrafluoroborate and 2.1 g (25 mmol) of 1-methyl-1,2,4-triazole in 14 ml of dry dichloromethane was allowed to stand overnight and diluted with 10 ml of ether, and the precipitated **1-methyl-4-ethyl-1,2,4-triazolium tetrafluoroborate** was removed by filtration: 5.0 g (100%); mp 56–57°; nmr (CF_3CO_2H–internal TMS) δ 1.66 (t, 3), 4.20 (s, 3), 4.43 (q, 2), 8.56 (s, 1), 9.36 ppm (s, 1).

Reaction of 0.2 g (1 mmol) of the above monoquat with 0.19 g (1.3 mmol) of trimethyloxonium tetrafluoroborate by method B (80–85° for 30 min) gave **5c**, recrystallized from 1:1 acetonitrile–DCE: 0.16 g (53%); mp 141–142°; nmr (CF_3CO_2D–internal TMS) δ 1.76 (t, 3), 4.56 (s, 6), 4.74 (q, 2), 10.22 ppm (s, 2).

Anal. Calcd for $C_6H_{13}N_3B_2F_8$: C, 23.96; H, 4.36; N, 13.97. Found: C, 23.71; H, 4.33; N, 13.72.

2,4-Dimethyl-1,2,4-thiadiazolium Diquat (6a).—Alkylation of 0.86 g (10 mmol) of 1,2,4-thiadiazole by 3.7 g (25 mmol) of trimethyloxonium tetrafluoroborate using method A (1-hr reflux) followed by dilution of the oily bottom phase of the reaction mixture with trifluoroacetic acid, gave the highly insoluble **6a**: 1.74 g (60%); mp 170–172° dec; nmr (3:1 CF_3CO_2H–H_2SO_4, external TMS) δ 4.58 (s, 3), 4.64 (s, 3), 10.10 ppm (s, 1). The resonance for the remaining ring proton was apparently under the solvent peak at δ 11.05. A completely satisfactory elemental analysis for **6a** could not be obtained.

Anal. Calcd for $C_4H_8N_2SB_2F_8$: C, 16.58; H, 2.79; N, 9.67. Found: C, 15.56; H, 2.89; N, 8.52.

2-Methyl-4-ethyl-1,2,4-thiadiazolium Diquat (6b).—Alkylation of 0.43 g (5 mmol) of 1,2,4-thiadiazole with triethyloxonium tetrafluoroborate (12 mmol) by method A for 1 hr at room temperature produced a two-phase system. Solution of the lower phase in acetone and addition of an equal volume of dichloromethane gave the monoquat, **4-ethyl-1,2,4-thiadiazolium tetrafluoroborate**: 0.7 g (70%); mp 68–70°; nmr (CF_3CO_2D, internal TMS) δ 1.80 (t, 3), 4.83 (q, 2), 9.26 (s, 1), 11.00 ppm (s, 1).

Reaction of 0.45 g (2.2 mmol) of the above monoquat with 0.43 g (2.9 mmol) of trimethyloxonium tetrafluoroborate by method B (30 min at 80–90°) gave a yellow semisolid. Recrystallization from 1:1 acetonitrile–DCE afforded **6b**: 0.3 g (45%); mp 143–145°; nmr (CF_3CO_2D, internal TMS) δ 1.88 (t, 3), 4.73 (s, 3), 5.05 (q, 2), 10.38 (s, 1), 11.33 ppm (s, 1).

(37) Prepared by an improved procedure: T. J. Curphey, *Org. Syn.*, **51**, 142 (1971).

Anal. Calcd for $C_6H_{10}N_2SB_2F_8$: C, 19.77; H, 3.32; N, 9.22. Found: C, 19.90; H, 3.40; N, 9.22.

3,4-Dimethyl-1,3,4-thiadiazolium Diquat (7a).—Alkylation of 0.17 g (2 mmol) of 1,3,4-thiadiazole by 0.77 g (5.2 mmol) of trimethyloxonium tetrafluoroborate according to method B (30 min at 85–90°) gave the highly insoluble **7a**, purified by trituration with trifluoroacetic acid: 0.3 g (52%); mp 149–150°; nmr (CF_3CO_2H–H_2SO_4, external TMS) δ 4.50 (s, 6), 10.45 ppm (s, 2). A completely satisfactory elemental analysis could not be obtained for this substance.

Anal. Calcd for $C_4H_8N_2SB_2F_8$: C, 16.58; H, 2.78; H, 9.66. Found: C, 15.15, 15.22; H, 2.72, 2.82; N, 9.04, 9.16.

3-Ethyl-4-methyl-1,3,4-thiadiazolium Diquat (7b).—Reaction of equimolar amounts of 1,3,4-thiadiazole and triethyloxonium tetrafluoroborate by method A (30 min at room temperature) gave **3-ethyl-1,3,4-thiadiazolium tetrafluoroborate**, which crystallized directly from the reaction mixture in 88% yield: mp 92–93°; nmr (CF_3CO_2H, internal TMS) δ 1.80 (t, 3), 4.92 (q, 2), 9.68 (s, 1), 10.40 ppm (s, 1).

Treatment of the above monoquat (0.4 g, 2 mmol) with trimethyloxonium tetrafluoroborate (0.38 g, 2.6 mmol) by method B (88–90° for 30 min) gave crude **7b**, purified by crystallization from 1:1 acetonitrile–DCE: 0.1 g (17%); mp 136–137°; nmr (3:1 CF_3CO_2D–D_2SO_4, external TMS) δ 1.80 (t, 3), 4.70 (s, 3), 4.99 (q, 2), 10.74 (s, 1), 10.84 ppm (s, 1).

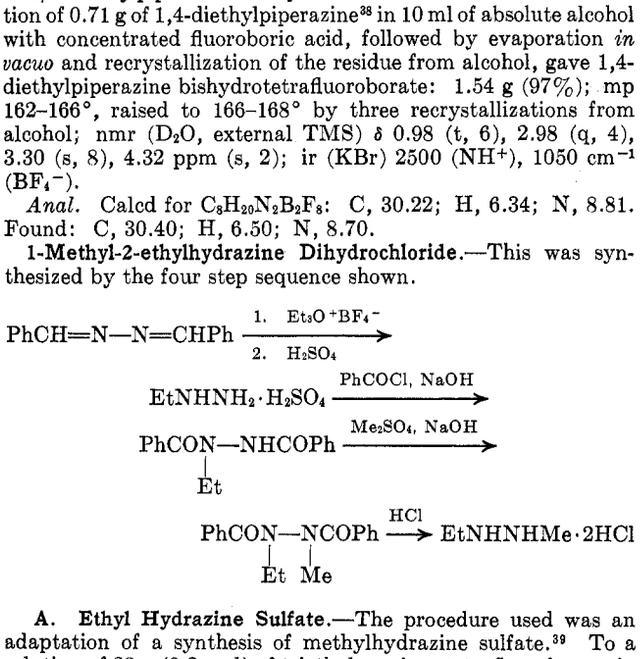
Anal. Calcd for $C_5H_{10}N_2SB_2F_8$: C, 19.73; H, 3.29; N, 9.29. Found: C, 19.72; H, 3.17; N, 9.06.

Catalytic Reduction of 1,4-Diethylpyrazine Diquat (1).—A flask containing 500 mg (0.16 mol) of **1**, 150 mg of 10% palladium on charcoal, and a Teflon-coated stirring bar was attached to a standard atmospheric hydrogenation apparatus and flushed with hydrogen. Reduction was initiated by injecting 10 ml of absolute ethanol through a serum-capped sidearm of the flask. Uptake of hydrogen amounted to 75% of theory over a 2-hr period. The reaction mixture was diluted with water and filtered, and the filtrate was evaporated. The crude product was dissolved in hot ethanol, the resulting suspension was centrifuged to remove a small amount of unidentified material, and the centrifugate was cooled to give 300 mg (59%) of 1,4-diethylpiperazine bishydrotetrafluoroborate, mp 166–168°. The ir and nmr spectra and mixture melting point of this material were identical with those of an authentic sample (*vide infra*).

1,4-Diethylpiperazine bishydrotetrafluoroborate.—Neutralization of 0.71 g of 1,4-diethylpiperazine[38] in 10 ml of absolute alcohol with concentrated fluoroboric acid, followed by evaporation *in vacuo* and recrystallization of the residue from alcohol, gave 1,4-diethylpiperazine bishydrotetrafluoroborate: 1.54 g (97%); mp 162–166°, raised to 166–168° by three recrystallizations from alcohol; nmr (D_2O, external TMS) δ 0.98 (t, 6), 2.98 (q, 4), 3.30 (s, 8), 4.32 ppm (s, 2); ir (KBr) 2500 (NH^+), 1050 cm^{-1} (BF_4^-).

Anal. Calcd for $C_8H_{20}N_2B_2F_8$: C, 30.22; H, 6.34; N, 8.81. Found: C, 30.40; H, 6.50; N, 8.70.

1-Methyl-2-ethylhydrazine Dihydrochloride.—This was synthesized by the four step sequence shown.



A. Ethyl Hydrazine Sulfate.—The procedure used was an adaptation of a synthesis of methylhydrazine sulfate.[39] To a solution of 38 g (0.2 mol) of triethyloxonium tetrafluoroborate in 70 ml of dry dichloromethane was added with stirring and exclusion of moisture 41.6 g (0.2 mol) of benzalazine in 40 ml of dry dichloromethane. After the solution was stirred for 3 hr, 21.6 ml of 9 *M* sulfuric acid was added, and the mixture was steam distilled to remove solvent and benzaldehyde. The nonvolatile residue was evaporated to dryness *in vacuo* and recrystallized from 100 ml of 80% alcohol to give ethyl hydrazine sulfate: 30 g (95%); mp 125–126° (lit.[40] mp 125–125.5°); nmr (CF_3CO_2H, internal TMS) δ 1.54 (t, 3), 3.75 ppm (q, 2).

B. 1-Ethyl-1,2-dibenzoylhydrazine.—Hatt's procedure for the preparation of dibenzoylhydrazine from benzoyl chloride and hydrazine sulfate[41] when applied to 8 g (0.05 mol) of ethylhydrazine sulfate gave 1-ethyl-1,2-dibenzoylhydrazine, recrystallized from glacial acetic acid: 13.3 g (98%); mp 95–97° (lit.[42] mp 133°); nmr ($CDCl_3$, internal TMS) δ 1.20 (t, 3), 3.78 (q, 2), 7.20–7.70 (m, 10), 8.11 ppm (s, 1).

Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.45. Found: C, 71.42; H, 5.97; N, 10.29.

C. 1-Methyl-2-ethyl-1,2-dibenzoylhydrazine.—Application of Hatt's procedure for the methylation of dibenzoylhydrazine[41] using 14 g (0.052 mol) of 1-ethyl-1,2-dibenzoylhydrazine as starting material and one-half the recommended amount of methyl sulfate gave 1-methyl-2-ethyl-1,2-dibenzoylhydrazine, recrystallized from chloroform–ether: 8 g (54%); mp 74–75°. The nmr spectrum in $CDCl_3$ (internal TMS) was temperature dependent, presumably due to hindered rotation.[43] At 58° rotation was rapid enough to approach a simple averaged spectrum: δ 1.22 (t, 3), 3.20 (s, 3), 3.6 (b, 2), 7.3 ppm (s, 10).

Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.14; H, 6.49; N, 9.90.

D. 1-Methyl-2-ethylhydrazine Dihydrochloride.—Hydrolysis of 1-methyl-2-ethyl-1,2-dibenzoylhydrazine (7 g, 0.025 mol) with hydrochloric acid was carried out in a manner identical with Hatt's procedure for the hydrolysis of dibenzoyldimethylhydrazine,[41] except that by-product benzoic acid was removed by extraction with benzene rather than by steam distillation. Crystallization from isopropyl alcohol–ether gave 1-methyl-2-ethylhydrazine dihydrochloride: 2.1 g (58%); mp 155–156°; nmr (D_2O, external TMS) δ 1.58 (t, 3), 3.14 (s, 3), 3.51 ppm (q, 2).

Anal. Calcd for $C_3H_{12}N_2Cl_2$: C, 24.50; H, 8.22; N, 19.05. Found: C, 24.78; H, 8.28; N, 19.25.

Amine Trifluoroacetamides.—The same general procedure was used for all amides. Trifluoroacetic anhydride (10.5 g, 0.05 mol) was added with ice cooling to a stirred mixture of amine hydrochloride or hydrazine dihydrochloride (0.01 mol), pyridine (4 g, 0.05 mol), and ether (5 ml). The mixture was allowed to warm up, stirred for 15 min at room temperature, then cooled again in an ice bath, and excess anhydride was destroyed by slow addition of water. The ether layer was washed successively with water, sodium bicarbonate solution, hydrochloric acid, and water. After drying over anhydrous sodium sulfate, the ether was removed by distillation, and the amide was purified by preparative glc on a 0.25 in. × 7 ft column of 20% Apiezon L on 60/80 mesh acid-washed and silanized Chromosorb W, operated at 70° and 80 ml/min helium carrier gas. Retention times and other pertinent data are summarized in Table II.

Hydrolytic Degradation of Diquats.—The same general procedure was employed in all three cases. A solution of 2 mmol of diquat in 10 ml of 6 *M* sulfuric acid was refluxed for 2 hr and then steam distilled to remove nonbasic volatile by-products. The acid residue was strongly basified with sodium hydroxide solution and again steam distilled. The distillate was acidified with 5 ml of 6 *M* hydrochloric acid and evaporated *in vacuo*. Residual water was removed by several evaporations with absolute alcohol, followed by drying for 1 hr *in vacuo*. The weight of the crude amine hydrochlorides was found at this stage to be 70–80% of the calculated amount in the three cases examined. The crude hydrochlorides were converted to an ether solution of the trifluoroacetamides by the procedure outlined above. The nature and amount of each amide present was determined by glc comparison with solutions of authentic amides at known concentration. Quantitation was by matching of peak heights and is probably not very accurate (±20%). The results obtained are given in Table III. To confirm the identification, the amides from the degradation were separated and purified by preparative glc and their ir and nmr spectra were compared with those of authentic samples.

(38) F. G. Menn and A. Senior, *J. Chem. Soc.*, 4476 (1954).

(39) H. H. Hatt, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 395.

(40) W. Seibert, *Chem. Ber.*, **80**, 494 (1947).

(41) H. H. Hatt, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 208.

(42) R. Stolle, *Ber.*, **34**, 3268 (1901).

(43) J. R. Fletcher and I. O. Sutherland, *Chem. Commun.*, 687 (1970), and preceding papers.

TABLE II

PROPERTIES OF AMINE TRIFLUOROACETAMIDES[a]

Amine	Registry no.	Mp (bp), °C	Retention time, min	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
$MeNH_2$	815-06-5	51–52[b]	3	28.35	3.17	11.02	28.09	3.29	10.78
$EtNH_2$	1682-66-2	14–15[c]	4	34.05	4.29	9.92	34.06	4.27	9.71
$(MeNH)_2$	34638-32-9	(180–181)	10	28.58	2.39	11.11	28.73	2.53	11.53
MeNHNHEt	34638-38-0	(205–206)	14	31.59	3.02	10.52	31.81	3.27	10.24

Amine	Nmr, δ (CCl_4, internal TMS) CH_3–C	CH_3–N	CH_2N	NH
$MeNH_2$		2.86 (d)		7.6 (b)
$EtNH_2$	1.23 (t)		3.4 (q)	8.0 (b)
$(MeNH)_2$		3.35 (s)[d,e]		
MeNHNHEt	1.20 (t)	3.3 (m)[d]	3.7 (m)[d]	

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds listed in the table. [b] Lit. mp 50–51°: E. R. Bissell and M. Finger, *J. Org. Chem.*, **24**, 1256 (1959). [c] Lit.[16] bp 90° (11 mm). [d] At 68°. [e] Multiplicity strongly temperature dependent.[43]

TABLE III

HYDROLYTIC DEGRADATION OF DIQUATS

Diquat	Yield of amines,[a] % $MeNH_2$	$EtNH_2$	$(MeNH)_2$	MeNHNHEt
5b	<1	35	<1	24
5c	<1	35	31	<1
7b	<1	<1	<1	79

[a] Per cent of trifluoroacetamide derivative formed.

Epr Studies.—The cell used was constructed from a T/S 10/30 male joint. This was sealed at one end and constricted near the ground joint, and a 4-mm side arm was sealed below the constriction. A weighed sample of diquat contained in a short melting point capillary was placed in the cell, and the cell was attached to a vacuum line and evacuated to below 1-μ pressure. A well-degassed sample of solvent was then distilled onto the diquat and the cell was sealed off at the constriction. After shaking to dissolved the diquat, the epr spectrum was observed by inserting the cell side arm into the spectrometer cavity. Solutions in methyl, ethyl, isopropyl, and *tert*-butyl alcohols gave essentially identical spectra. With *tert*-butyl alcohol the initially rather weak spectrum increased in intensity upon standing. It was observed that the diquat appeared to be only slightly soluble in this alcohol, and the increasing intensity was attributed to a slow solution with reaction. For generation of radicals in trifluoroacetic acid the cell was modified by addition of a second side arm in which was placed a few small pieces of granulated zinc. After the usual degassing and sealing off, the diquat solution was *very briefly* contacted with the zinc to generate the radicals. Too long a contact with the zinc resulted in disappearance of the epr spectrum, indicating further reduction of the radicals to nonparamagnetic species.

Decomposition of 1 in Isopropyl Alcohol.—A suspension of 0.31 g (1 mmol) of diquat 1 in 2 ml of isopropyl alcohol was stirred under nitrogen. At intervals 0.1-ml aliquots were withdrawn, and the volatiles were removed by transfer on a vacuum line. The resulting distillate was examined by glc on a Carbowax 20M column. No acetone was found in aliquots taken after 30 min, after several hours, and after stirring overnight. When 7 μl of acetone was added to the now very dark reaction mixture and an aliquot was taken 1 hr later, a large acetone peak was present in the glc. Evaporation of solvent from the remainder of the reaction mixture gave a dark oil which could not be induced to crystallize.

Registry No.—**1**, 3552-55-4; **2a**, 3552-56-5; **2b**, 3552-57-6; **2c**, 3552-58-7; **3a**, 3817-04-7; **3b**, 3552-59-8; **4a**, 34630-77-8; **4b**, 34630-78-9; **5a**, 34630-79-0; **5b**, 34630-80-3; **5c**, 34630-81-4; **6a**, 34630-82-5; **6b**, 34647-03-5; **7a**, 34630-83-6; **7b**, 34630-84-7; 1-ethylpyridazinium tetrafluoroborate, 34630-85-8; 1-methyl-4-ethyl-1,2,4-triazolium tetrafluoroborate, 34630-86-9; 4-ethyl-1,2,4-thiadiazolium tetrafluoroborate, 34630-87-0; 3-ethyl-1,3,4-thiadiazolium tetrafluoroborate, 15681-47-7; 1,4-diethylpiperazine bishydrotetrafluoroborate, 34630-89-2; ethylhydrazine sulfate, 34638-34-1; 1-ethyl-1,2-dibenzoylhydrazine, 30719-96-1; 1-methyl-2-ethyl-1,2-dibenzoylhydrazine, 30719-97-2; 1-methyl-2-ethylhydrazine 2HCl, 18247-20-6.

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