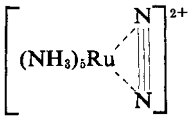
The difference in the rate of isomerization in solution compared with that in the solid finds parallels in observations made with $[Co(NH_3)_5ONO]^{2+}$ (1.7×10^{-7} sec^{-1} in $[Co(NH_3)_5ONO]I_2$ compared with 1.7×10^{-5} sec^{-1} in solution, both at 20°)[8] and with $[Rh(NH_3)_5ONO]^{2+}$ (5.5×10^{-5} sec^{-1} as the Cl^- salt at 22° compared with 9.6×10^{-4} sec^{-1} in solution at 25°).[9] As is the case for the nitrito complexes, the isomerization in $Ru(NH_3)_5N_2{}^{2+}$ is intramolecular. This conclusion follows because the half-time for dissociation of N_2 from $[Ru(NH_3)_5N_2]^{2+}$ is 96 hr,[10] which is very much longer than the half-time for isomerization.

In undergoing isomerization, the complex[11] must pass through the state



and thus the energetics of the isomerization process should provide some clues to the stability of this configuration. If it is assumed that the entropy of activation for the isomerization of $[Co(NH_3)_5ONO]^{2+}$[9] is the same as that for $[Ru(NH_3)_5N_2]^{2+}$, the measured half-time of 2 hr for the isomerization of the latter in solution corresponds to an enthalpy of activation of 21 kcal/mol. Since the enthalpy of activation for the loss of N_2[10] is 28 kcal/mol, and the rate comparisons[1] indicate that the activation process for formation of the nitrogen complex involves largely bond breaking, the N_2 in the activated complex for isomerization approaches an unbound state.

Another argument suggests that the energy profile for the isomerization of $[Ru(NH_3)_5N_2]^{2+}$ is much like that of $[Co(NH_3)_5ONO]^{2+}$. Since $HONO_2$ is a somewhat stronger acid than CH_3CO_2H, the rate of aquation of $[Co(NH_3)_5ONO]^{2+}$ by Co–O bond breaking can be taken as being somewhat faster than that of $[Co(NH_3)_5O_2CCH_3]^{2+}$ (1.2×10^{-7} sec^{-1} at 25°).[12] Thus linkage isomerization for $[Co(NH_3)_5ONO]^{2+}$, k for which[13] is 3.2×10^{-5} sec^{-1} at 25°, is perhaps a factor of 50–100 faster than aquation. For $[Ru(NH_3)_5N_2]^{2+}$ the corresponding factor is approximately 45. Thus we are led to conclude that N_2 bound to Ru(II) in an intermediate position is no more stable relative to the starting complex than is the intermediate state for the isomerization of ONO on Co(III) relative to $[Co(NH_3)_5ONO]^{2+}$. This in turn suggests that the π-bound state is not unusually stable for the ruthenium–nitrogen complex.

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(8) B. Adell, *Z. Anorg. Allg. Chem.*, **271**, 49 (1952).

(9) F. Basolo and G. S. Hammaker, *Inorg. Chem.*, **1**, 1 (1962).

(10) J. N. Armor and H. Taube, manuscript in preparation.

(11) Bimolecular mechanisms for the exchange are rejected on the basis of the following. (a) The exchange of $[Ru(NH_3)_5N^{15}N]^{2+}$ with N_2 in solution has been measured. It is very slow and fully accounted for by the aquation of the nitrogen complex and the reentry of nitrogen. (b) The ratio of the rate of isomerization of the nitrogen complex in solution compared with that of the solid is much the same as it is for the pentaamminecobalt(III) nitrito complexes (*vide infra*). The latter are known to be intramolecular processes.

(12) F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

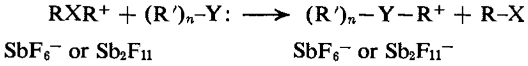
(13) R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Amer. Chem. Soc.*, **76**, 5920 (1954).

Friedel–Crafts Chemistry. VI.[1] Alkylation of Heteroorganic Compounds with Dialkylhalonium Fluoroantimonates. A New General Preparation of Onium Ion Salts

Sir:

The reaction of excess primary and secondary alkyl halides with SbF_5–SO_2 solution has recently been shown to yield quantitatively dialkylhalonium fluoroantimonate salts.[1,2] The same dialkylhalonium ions can also be prepared from excess alkyl halides with anhydrous silver hexafluoroantimonate or related complex fluoro silver salts. The properties of dialkylhalonium ions should be reflected by their chemical reactions, and the suggested[2] possibility that they play a role in Friedel–Crafts alkylation reactions stimulated our interest in their general alkylating ability.

Presently we wish to report the alkylation of a variety of heteroorganic compound with dialkylhalonium ions **1** and **2** as an indication of the general nature of alkylation with this new class of alkylating agent. Table I shows the onium cations **3–38** obtained from alkylation of ethers, alcohols (water), ketones, aldehydes, carboxylic acids and nitro, sulfur, and amino compounds with halonium ions **1–2**. Only alkylation reactions of dimethyl- and diethylhalonium ions are reported. Other dialkylhalonium ions such as diisopropylbromonium and -chloronium ions[2] react in a similar fashion. In general, reactions were performed by addition of an aliquot portion of halonium ion in SO_2 at *ca.* −60° to a calculated amount of the heteroorganic n-base substrate at −78°. At least two runs with each system, one with alkylating agent in excess and one with n-base substrate in excess, were carried out. Alkylation of n-donor bases by dialkylchloronium and dialkylbromonium ions **1a,b** and **2a,b** appears to be indiscriminative but mild. Dialkyliodonium ions **1c** and **2c** do not react with n-donor bases in SO_2 or SO_2ClF solution at temperatures varied from −78 to 0°.



$$\underset{SbF_6^- \text{ or } Sb_2F_{11}}{RXR^+} + (R')_n\text{–}Y: \longrightarrow \underset{SbF_6^- \text{ or } Sb_2F_{11}^-}{(R')_n\text{–}Y\text{–}R^+} + R\text{–}X$$

1, R = Me
a, X = Cl
b, X = Br
c, X = I

2, R = Et
a, X = Cl
b, X = Br
c, X = I

$R' =$ alkyl or aryl; $Y = -\ddot{\underset{\cdot\cdot}{O}}-, -\ddot{\underset{\cdot\cdot}{S}}-, -\ddot{N}-$; $n = 1, 2, 3$

Pmr spectra obtained for solutions prepared by addition of ions **1a,b** and **2a,b** in SO_2 to alcohols (water) and ethers are identical with spectra reported for the protonation of the corresponding ethers[3] (methanol[4])

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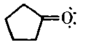
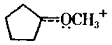
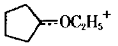
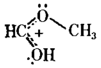
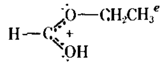
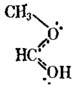
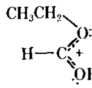
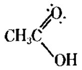
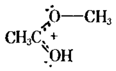
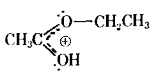
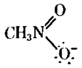
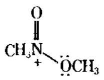
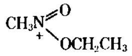
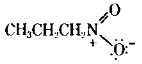
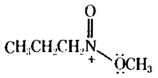
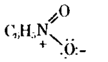
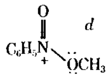
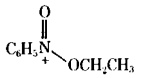
(1) Part V: G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 718 (1970).

(2) G. A. Olah and J. R. DeMember, *ibid.*, **91**, 2113 (1969).

(3) G. A. Olah and D. H. O'Brien, *ibid.*, **89**, 1725 (1967).

(4) G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

Table I. Pmr[a] Chemical Shifts of Onium Ions[b] Obtained by Alkylation of Heteroatom n-Donor Bases[c–f]

Heteroorganic Substrate	Methylated onium ion	Compd no.	CH_3Y-	CH_3-	$-CH_2-$	H–C	H–Y	Aromatic	Ethylated onium ion	Compd no.	CH_3-CH_2Y-	CH_3CH_2Y-	CH_3Y	CH_3-	$-CH_2-$	H–C	H–Y	Aromatic
$(CH_3)_2\ddot{O}:$	$CH_3O(CH_3)_2^+$	**3**	4.30						$(CH_3)_2\ddot{O}C_2H_5^+$	**23**	4.12	1.27	3.68					
$(C_2H_5)_2\ddot{O}:$	$C_2H_5O(CH_3)(C_2H_5)^+$	**4**	4.23	1.58	4.62				$(C_2H_5)_3\ddot{O}^+$	**24**	4.33	1.41						
$CH_3\ddot{O}H$	$CH_3O(CH_3)H^+$	**5**	3.68				9.42		$(C_2H_5)C\ddot{O}H_3H^+$	**25**	4.27	1.39	3.88				10.75	
$H_2\ddot{O}:$	$CH_3OH_2^+$	**6**	4.13				9.50											
$(CH_3)_2C{=}\ddot{O}:$	$(CH_3)_2C\overset{\cdots}{-}OCH_3^+$	**7**	4.80	3.94					$(CH_3)_2C\overset{\cdots}{-}\ddot{O}C_2H_5^+$	**26**	5.02	2.05		2.92				
$(C_2H_5)_2C{=}\ddot{O}:$	$(C_2H_5)_2C\overset{\cdots}{-}OCH_3^+$	**8**	4.63	1.44	3.82				$(C_2H_5)_2C\overset{\cdots}{-}\ddot{O}C_2H_5)^+$	**27**	5.13	1.98		1.25	3.05			
		**9**	4.86		3.18, 2.24					**28**	5.25	1.98						
$(C_6H_5)_2C{=}\ddot{O}:$	$(C_6H_5)_2C\overset{\cdots}{-}\ddot{O}CH_3^+$[d]	**10**	3.53					6.8–7.4										
$CH_3CH{=}\ddot{O}:$	$CH_3CH\overset{\cdots}{-}\ddot{O}CH_3$	**11**	5.80	3.51		9.62			$CH_3CH\overset{\cdots}{-}\ddot{O}C_2H_5$	**29**	5.21	1.86		3.46		9.60		
$C_6H_5CH{=}\ddot{O}:$	$C_6H_5CH\overset{\cdots}{-}\ddot{O}CH_3$	**12**	4.12			9.42		6.6–7.6	$C_6H_5CHC{=}\ddot{O}C_2H_5^+$	**30**	5.58	1.92				9.95		7.6–8.0
$HC(OH){=}\ddot{O}:$		**13**	4.25			8.76	12.54		 [e]	**31**	4.54	1.92				8.62	13.06	
		**14**	4.18			8.70 (8.42)	12.54		 [e]	**32**	5.00	2.06				8.42	13.06	
		**15**	4.32	2.64			12.84			**33**	5.08	2.00		2.50			13.52	
		**16**	4.67	5.04						**34**	5.08	1.53		5.05				
		**17**	4.67	0.98	5.23, 2.18													
	 [d]	**18**	4.65					6.6–7.2		**35**	5.12	1.69						6.4–7.6
$[(CH_3)_2CH]_2\ddot{S}:$	$[(CH_3)CH]_2\ddot{S}CH_3^+$	**19**	4.28	1.83		5.00												
$(C_2H_5)_2\ddot{S}:$	$(C_2H_5)_2\ddot{S}CH_3$	**20**	3.18	1.38	3.18				$(CH_3CH_2)_3S:^+$	**36**	3.26	1.40		1.40				
t-Bu$\ddot{S}$–H	t-Bu$\ddot{S}HCH_3^+$	**21**	2.99	1.62			6.16		t-Bu$\ddot{S}HC_2H_5^+$	**37**	3.58	1.54		1.63			6.08	
$(C_2H_5)_3N:$	$(C_2H_5)_3NCH_3^+$	**22**	2.97	1.23	3.21				$(CH_3CH_2)_4N^+$	**38**	4.81	1.05						

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[a] Spectra were recorded on a Varian 56–60-MHz spectrometer and are reported from external capillary of TMS. [b] Identical spectra were obtained from alkylation with $RClR^+SbF_6^-$ and $RBrR^+SbF_6^-$. Many of the ions **3**–**22** have been prepared and observed separately by Dr. Richard H. Schlosberg in the study of the methylation reactions of CH_3FSbF_5 [*cf.* G. A. Olah, R. H. Schlosberg, and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2112 (1969)]. [c] Y = heteroatom. [d] Alkylation of the n-donor base occurs exclusively. [e] Usual multiplicities and coupling constants are observed. [f] At −40° in SO_2 solution.

and the alkylation of the corresponding ethers,[5] respectively. In each case alkylation leads to formation of oxonium ions quantitatively. No exchange between excess alkylating agents and oxonium ions **3–6** and **23–25** was observed on the nmr time scale between 0 and −78°.

The alkylation of *t*-butyl mercaptan and diethyl and diisopropyl thioethers with ions **1a,b** and **2a,b** yields sulfonium ions **19–21** and **36–37**, respectively. The pmr spectra of these sulfonium ions correlate very well with those reported previously for protonated mercaptans and thioethers.[6]

When aldehydes, ketones, and carboxylic acids are added to SO_2 solutions of ions **1a,b** and **2a,b** immediate and exclusive alkylation on oxygen occurs with formation of oxonium ions **7–15** and **26–33**. In the cases of the alkylation reactions of unsymmetrically substituted ketones, aldehydes, and carboxylic acids the formation of at least two isomeric forms of the resulting oxonium ions is observed. Except for alkylated formic acid, the spectra of only those isomers present in highest concentration are shown in Table I.

The chemical shifts, multiplicities, and coupling constants of the pmr spectra of oxonium ions **7–15** and **26–33** are very similar to those obtained from protonation of the same aldehydes,[7] ketones,[8] and carboxylic acids.[9] Particularly diagnostic in the case of aldehydes is the chemical shift of the proton on the carbonyl carbon. These range from δ 9.42–9.95 for ions **11, 12, 29,** and **30**. For ions **11** and **29** these signals appear as 1 H quartets (J = 3.5 Hz) with the corresponding 3 H methyl signals at δ 3.51 and 3.46 (J = 3.5 Hz). Similarly for alkylated carboxylic acids **13–15** and **31–33** the OH protons appear between δ 12.54 and 13.06. The chemical shifts of the CH_3Y methyl and CH_3CH_2Y ethyl groups in ions **7–15** and **26–33**, respectively, are to slightly lower field than in the oxonium ions **3–6** and **23–25**, as expected.

The reaction of diethylamine with ions **1a,b** and **2a,b** yields the corresponding tetralkylammonium ions **22** and **38**, respectively. Although alkylation was obvious from the pmr spectra of ions **22** and **38**, pronounced broadening of peaks characteristic of long-range coupling is observed.

Upon addition of nitro alkyl or aryl compounds to solutions of excess of ions **1a,b** and **2a,b** pmr spectra of the solutions obtained are consistent with the formation of ions **16–18**, **34**, and **35**, respectively. These alkylalkoxyoxonitronium cations are isoelectronic with carboxylic acid esters and are important primarily because of mechanistic implications for alkylation of nitroaromatic compounds. This subject is discussed in detail in forthcoming publications.

The alkylation data presented demonstrate the general alkylating ability and synthetic utility of dialkylhalonium ions.[10] As opposed to alkylation with Meerwein's oxonium salts[11] the synthetic advantage of alkylation with dialkylhalonium ions lies in their easy preparation and especially in their greater alkylating ability and wide range in selectivity. Many of the fluoroantimonate salts of ions **4–35** can be isolated upon evaporation of solvent, excess methyl halides, and corresponding precursor.[1] For example, isolation of the hexafluoroantimonate salt of ion **18** as a crystalline solid (90%, mp 90–91°) can be accomplished. This new preparative method makes available readily the entire scope of onium ion salts of both synthetic and theoretical interest.

The dialkylhalonium ion complexes were also found to effect C alkylations which will be reported in a following publication.[12]

Acknowledgment. Partial support of the work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[5] B. M. Ramsey and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 3058 (1966), and references therein.

[6] G. A. Olah, D. H. O'Brien, and C. U. Pittman, Jr., *ibid.*, **89**, 2996 (1967).

[7] G. A. Olah, D. H. O'Brien, and M. Calin, *ibid.*, **89**, 3582 (1967).

[8] G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).

[9] G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

[10] Similar indications have recently been reported by Peterson, Clifford, and Slama in the study of alkylation with tetramethylenehalonium ions; presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstracts, ORGN 109.

[11] H. Meerwein in Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol. 6, No. 3, D. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1965, pp 329–363.

[12] G. A. Olah, J. R. DeMember, and M. Tashiro, to be published.

[13] Postdoctoral Research Associate.

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Comparison of the Reactivity of Singlet and Triplet States of Cyclic Alkanones toward the α-Cleavage Process. An Unexpected Reactivity Difference between n,π* Singlet and Triplet[1]

Sir:

One of the more intriguing questions in organic photochemistry is whether the differences in spin multiplicity between excited singlet and triplet states will be reflected in their reactivity toward primary photochemical processes. In the case of alkyl ketones, a number of reports have recently appeared which compare the reactivity of n,π* excited singlet and triplet states in solution toward such primary photochemical processes as cycloaddition to olefins[2] and inter-[3] and intramolecular[4] hydrogen abstractions. To date, however, there have been no reports of the relative reactivities of alkyl ketone singlet and triplet states toward the primary photochemical process of α cleavage.

Yang and Feit[5] have provided evidence that α cleavage occurs from both the singlet and triplet excited states of *t*-butyl methyl ketone and have measured the quantum yields for reaction from the two states. Knowledge of the efficiency of a process, *i.e.*, the quantum yield, is, however, not sufficient to determine the reactivity toward that process.[6] Also, in a number of cyclopentanone and cyclohexanone systems,[7–9]

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[1] (a) Molecular Photochemistry. XXII. For paper XXI see N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970). (b) The authors wish to thank the Air Force Office of Scientific Research for their generous support of this work through Grant AFOSR-68-1381.

[2] N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **90**, 6863 (1968); N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970).

[3] P. J. Wagner, *ibid.*, **89**, 2503 (1967).

[4] N. C. Yang and S. P. Elliott, *ibid.*, **90**, 4194 (1968).

[5] N. C. Yang and E. D. Feit, *ibid.*, **90**, 504 (1968).

[6] The reactivity of an excited state toward a primary photochemical process is a measure of the rate constant for the process. See N. J. Turro, *J. Chem. Educ.*, **44**, 536 (1967).