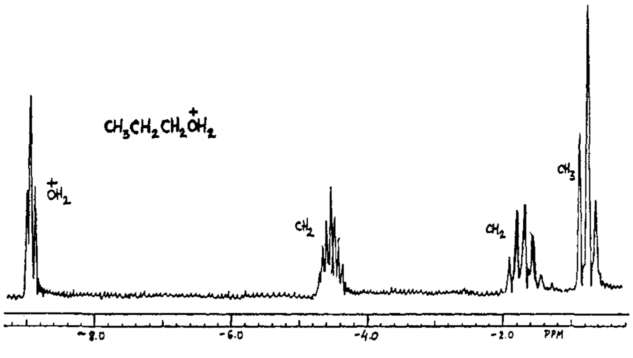

Figure 3.

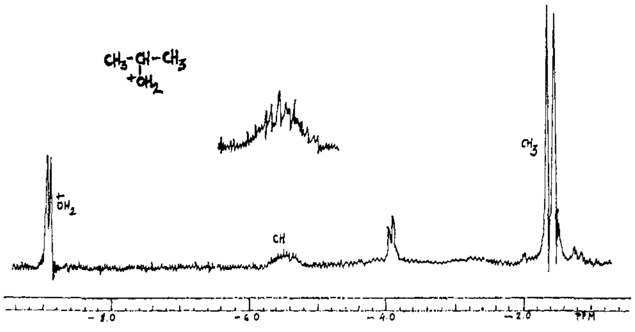

Figure 4.

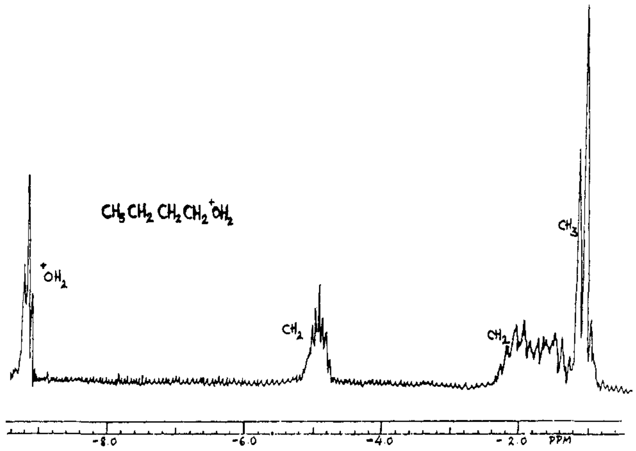

Figure 5.

Protonated 1-butanol shows the methyl triplet at -1.02 ppm ($J_{H-H} = 6.5$ cps), methylene multiplets (C_2, C_3) between -1.2 and -2 ppm, the C_1 methylene multiplet at -4.88 ppm, and the ^+OH triplet at -9.2 ppm ($J_{H-H} = 3.2$ cps.) (Figure 5).

All spectra were obtained in 1:1 molar composition of FSO_3H-SbF_5 diluted with SO $_2$and using external TMS as reference (compared to a separate sample of TMS in chloroform; if compared to capillary reference TMS all chemical shifts should be shifted by approximately 0.5 ppm to less shielding).

The nmr spectra of secondary butyl and pentyl alcohols in FSO_3H-SbF_5 solution at $-60°$ show the tertiary trimethylcarbonium ion and dimethylethylcarbonium ion, respectively. Thus, in these cases there must be an equilibrium between the protonated alcohol and the corresponding secondary carbonium ion; the secondary ions then rearrange to the more stable tertiary carbonium ions. There is no apparent return in the thermodynamically controlled strong acid system from tertiary to secondary carbonium ion. Due to this rapid shift in equilibrium the only ions observed are the tertiary carbonium ions.

The fact that the series of protonated alcohols reported in this communication are indeed exchanging slowly was further substantiated by protonation of O-deuterated alcohols. O-Deuteriomethanol, for example, in $FSO_3H-SbF_5-SO_2$ solution at $-60°$ shows an nmr spectrum of CH_3ODH^+ in which the the ^+OHD peak is a quartet and the CH_3 a doublet. This is superimposed on the spectrum of some $CH_3OH_2^+$ (and probably $CH_3OD_2^+$) formed from exchange or disproportionation. J_{HD} is apparently small, causing, however, some line broadening.

We are continuing investigations, which will be reported in detail, including measurement of exchange rates by temperature-dependence studies and spin-echo investigations, as well as measurements of O_{17}–H coupling in O_{17}-labeled protonated alcohols.

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Stable Carbonium Ions. XXIX.[1] The Reaction of Alkyl (Acyl) Sulfinylamines and Isocyanates (Thioisocyanates) with Nitrosonium Salts. New Deaminative Formations of Carbonium (Oxocarbonium) Ions

Sir:

One of the classic methods of generating transient carbonium ions is the deamination of aliphatic amines.[2] Deamination of primary amines generally is achieved *via* diazotization of amines using different sources of nitrous acid such as alkali nitrites and alkyl nitrites[3] or stable nitrosonium salts.[4] Deamination of amides is similarly affected by nitrous acid or nitrosonium salt reactions.[5,6] In the diazotization reactions an equimolar amount of water is formed as by-product; the water interferes with the formation of carbonium ions. This is at least partially the reason that, in recently reported alkylation of aromatic hydrocarbons *via* diazotization of alkylamines,[4,7] the formation of alkylated aromatics is only a relatively minor reaction: *i.e.*, isopropylation of toluene produces a maximum of 2–4% of cymenes.

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[1] Part XXVIII: G. A. Olah and E. Namanworth, *J. Am. Chem. Soc.*, **88**, 5327 (1966).

[2] For a recent review see R. J. Baumgarten, *J. Chem. Educ.*, **43**, 398 (1966).

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[5] S. L. Bouveault, *Bull. Soc. Chim. France*, [3] **9**, 368 (1892).

[6] G. A. Olah and J. A. Olah, *J. Org. Chem.*, **30**, 2386 (1965).

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In view of our interest in both novel methods of generating carbonium ions[8] and in electrophilic substitution reactions, we wish to report new ways of deaminative carbonium (oxocarbonium) ion formation without forming water as a by-product of the reactions.

We observed that N-alkylsulfinylamines (readily prepared from the corresponding amines with $SOCl_2$) and alkyl isocyanates (equally readily available from the amines and phosgene) react rapidly with stable nitrosonium salts, such as $NO^+BF_4^-$, $NO^+PF_6^-$, $NO^+AsF_6^-$, $NO^+SbF_6^-$, and $NO^+HSO_4^-$, in the presence of benzene or toluene to produce a 25–45% yield of the corresponding alkylated aromatics. (No attempt was made to optimize conditions.)

$$\mathrm{ArH + RNSO + NO^+SbF_6^- \longrightarrow ArR + N_2 + SO_2 + HSbF_6}$$

$$\mathrm{ArH + RNCO + NO^+SbF_6^- \longrightarrow ArR + N_2 + CO_2 + HSbF_6}$$

In a typical experiment N-*t*-butylsulfinylamine (0.05 mole) in 25 ml of nitromethane was added dropwise to a stirred solution of $NO^+SbF_6^-$ (0.1 mole) in 50 ml of nitromethane and 50 ml of benzene. The addition was carried out over a period of 30 min and the reaction mixture was maintained at 25°. After stirring for another 15 min the reaction mixture was quenched, neutralized with sodium carbonate, and worked up in the usual manner. A 25% yield of *t*-butylbenzene was obtained (with 10% *p*-di-*t*-butylbenzene as dialkylation product).

Similar alkylation with isopropylsulfinylamine gave a 32% yield of cumene. Isopropylation of toluene gave a 42% yield of cymenes, with the unusual isomer distribution of 92.5% *ortho*, 4.0% *meta*, and 3.5% *para* isomer (see following communication[9]).

When *t*-butylation of benzene was attempted using acetonitrile as solvent, N-alkylation of the solvent instead of benzene alkylation was observed by the incipient *t*-butyl cation, giving 72% yield of N-*t*-butylacetamide after hydrolysis.

$$\begin{array}{l}\mathrm{CH_3CN + (CH_3)_3CNSO + NO^+SbF_6 \longrightarrow}\\ \qquad\qquad \mathrm{[CH_3C\overset{+}{N}C(CH_3)_3]SbF_6^- + N_2 + SO_2}\\ \qquad\qquad \Big\downarrow \mathrm{H_2O}\\ \qquad\qquad \mathrm{CH_3CONHC(CH_3)_3 + HSbF_6}\end{array}$$

The alkylating ability of alkyl sulfinylamines and isocyanates in their interactions with aromatics through reaction with NO^+ does not necessarily in itself prove the formation of free carbonium ions. A concerted mechanism involving attack of NO^+ on sulfinylamines or isocyanates followed by interaction of the polarized intermediate with the substrate to be alkylated could equally well explain the observed reactions as the formation of a carbonium ion intermediate.

In order to prove that the reaction of alkyl sulfinylamines and isocyanates with nitrosonium salts indeed can yield carbonium ions, we investigated the reaction of N-triphenylmethylsulfinylamines and triphenylmethyl isocyanate with $NO^+SbF_6^-$ and related nitrosonium salts ($NO^+BF_4^-$, $NO^+AsF_6^-$, $NO^+HSO_4^-$, $NO^+PF_6^-$). Even in acetonitrile solution a practically quantitative yield of the corresponding triphenylcarbonium salts was obtained.[10] They were identified by their physical data (melting point and infrared, ultraviolet, and nmr spectra) and analysis.

$$\mathrm{(C_6H_5)_3CNSO + NO^+X^- \longrightarrow (C_6H_5)_3C^+X^- + N_2 + SO_2}$$

$$\mathrm{(C_6H_5)_3CNCO + NO^+X^- \longrightarrow (C_6H_5)_3C^+X^- + N_2 + CO_2}$$

Carbonium ions of lesser stability, which cannot be isolated as crystalline salts but can be observed in solution, can also be formed by the above methods. When, for example, *t*-butylsulfinylamine or *t*-butyl isocyanate was allowed to react with $NO^+SbF_6^-$ in SO_2 containing some SbF_5 at −60°, the reaction proceeded to the formation of the trimethylcarbonium ion[11] which was observed by its known nmr spectra ($\delta_{\text{methyl}} = -4.25$ ppm).

$$\mathrm{(CH_3)_3CNSO + NO^+SbF_6^- \longrightarrow (CH_3)_3C^+SbF_6^- + N_2 + SO_2}$$

$$\mathrm{(CH_3)_3CNCO + NO^+SbF_6^- \longrightarrow (CH_3)_3C^+SbF_6^- + N_2 + CO_2}$$

Acyl sulfinylamines and isocyanates react in a similar manner with nitrosonium salts, giving oxocarbonium ions and providing effective acylating systems (solvents as nitromethane, nitrobenzene, or sulfolane can be advantageously used for the acylation reactions).

$$\mathrm{C_6H_5CONSO + NO^+SbF_6^- \longrightarrow C_6H_5CO^+SbF_6^- + N_2 + SO_2}$$

$$\begin{array}{l}\mathrm{C_6H_5CONCO + NO^+SbF_6^- \longrightarrow C_6H_5CO^+SbF_6^- + N_2 + CO_2}\\ \qquad\qquad\qquad\qquad\qquad\quad \Big\downarrow \mathrm{C_6H_6}\\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{C_6H_5COC_6H_5}\end{array}$$

The benzylation of toluene, for example, with benzoyl isocyanate and $NO^+SbF_6^-$ in nitrobenzene solution gave a 32% yield with an isomer distribution of 10.5% *o*-, 0.7% *m*-, and 88.8% *p*-methylbenzophenone, a typical electrophilic isomer distribution. Similar benzoylation with benzoylsulfinylamine gave a 36% yield with an isomer distribution of 9.0% *ortho*, 0.7% *meta*, and 90.3% *para* isomer.

When the reaction of acyl sulfinylamines or isocyanates was carried out with $NO^+BF_4^-$ at room temperature in the absence of aromatics, acyl fluorides are obtained through the decomposition of the relatively unstable oxocarbonium tetrafluoroborates.

$$\begin{array}{l}\mathrm{C_6H_5CONCO + NO^+BF_4^- \longrightarrow C_6H_5CO^+BF_4^- + N_2 + CO_2}\\ \qquad\qquad\qquad\qquad\qquad\quad \Big\downarrow\\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{C_6H_5COF + BF_3}\end{array}$$

As amines (and amides) can be readily converted into the corresponding sulfinylamines or isocyanates with thionyl chloride or phosgene, the reactions with nitrosonium salts represent a convenient new method of carbonium ion formation.

$$\mathrm{RNH_2 \xrightarrow{SOCl_2} RNSO \xrightarrow{NO^+SbF_6^-} R^+SbF_6^- + N_2 + SO_2}$$

$$\mathrm{RNH_2 \xrightarrow{COCl_2} RNCO \xrightarrow{NO^+SbF_6^-} R^+SbF_6^- + N_2 + CO_2}$$

It should be mentioned that alkyl and acyl thioisocyanates react similarly to the isocyanates in deaminative reactions with NO^+ salts.

$$\mathrm{RNH_2 + CSCl_2 \longrightarrow RNCS \xrightarrow{NO^+SbF_6^-} R^+SbF_6^- + N_2 + COS}$$

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(8) For a summary, G. A. Olah, and C. U. Pittman, Jr., *Advan. Phys. Org. Chem.*, **4**, p 303 (1966).

(9) G. A. Olah and N. Friedman, *J. Am. Chem. Soc.*, **88**, 5330 (1966).

(10) K. Bott (*Angew. Chem.*, 77, 132 (1965)) reported that the reaction of aryl sulfinylamines with nitrosonium complexes gives aryldiazonium salts in good yields.

(11) It should be noted, however, that sulfinylamines and isocyanates themselves can ionize with SbF_5, acting as pseudo-halides.

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[12] (a) National Science Foundation Postdoctoral Research Investigator, 1965–1966; (b) National Institutes of Health Postdoctoral Research Investigator, 1966.

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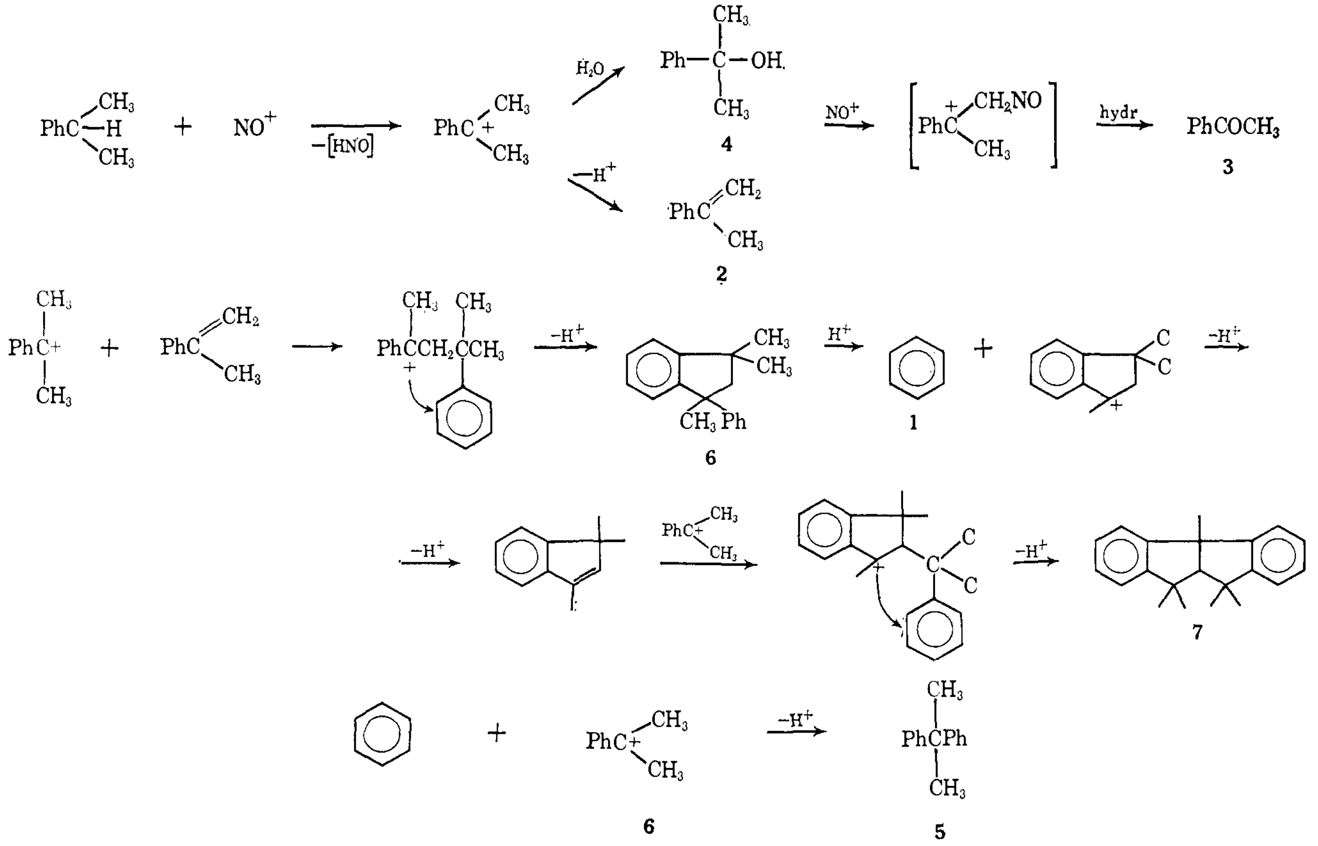
The Reaction of Isopropylbenzenes with Nitrosonium Salts. A New Hydride-Abstraction Reaction

Sir:

The nitrosonium ion is known for its lack of reactivity toward aromatics except in activated systems, such as phenols or N-substituted anilines.[1] It forms deeply colored solutions with aromatics such as benzene, toluene, or *t*-butylbenzene, indicative of complex formation between the nitrosonium ion and the aromatic π-electron system.[2] It is, however, in general too weak an electrophile to attack an unactivated aromatic C–H bond.



We wish to report now that isopropylbenzenes undergo a facile hydride-transfer reaction with nitrosonium salts from the tertiary C–H bond of the isopropyl substituent and yield products arising from the reactions of the dimethylphenylcarbonium ion. Furthermore, in methyl- or halo-substituted isopropylbenzenes the *meta* and *para* isomers react in preference to the *ortho* isomer, this effect apparently diminishing with the decrease of steric hindrance to attack at the C–H bond by the relatively bulky nitrosonium salt which reacts as an ion pair in nitromethane solution.

The fact that a reaction does occur between isopropylbenzenes and NO^+ became evident to us when we isopropylated toluene by the reaction of isopropylsulfinylamine (i-C_3H_7NSO) with $NO^+PF_6^-$ and found >90% *o*-cymene and <5% each of *m*- and *p*-cymene.[3]

There is no precedent for such an unusual isomer distribution in the isopropylation of toluene. Since *t*-butylation of toluene with *t*-butylsulfinylamines gives normal isomer distribution,[3] a specific secondary reaction of the isopropylated aromatic with NO^+ must be occurring. Furthermore, NO^+ must have a preference for *m*- and *p*-cymene as compared to the *ortho* isomer.

The nature of the reaction was investigated in detail for the simplest member of the series, cumene. Cumene (10.0 g, 0.085 mole) was added slowly to a stirred solution of $NO^+PF_6^-$ (0.1 mole) in 50 ml of nitromethane at room temperature and the mixture stirred for 1 hr. (The hexafluorophosphate salt was used because of its better solubility than, for example, the BF_4^- salt.) After hydrolysis and neutralization, vacuum distillation of the nitromethane solution gave a variety of products, boiling range 50–210° (0.2 mm), which were separated by preparative-scale gas chromatography using an Aerograph Autoprep Model A-700 preparative gas chromatograph with a 20 ft × $^3/_8$ in. column containing 30% SE-30 on chromosorb with He as the carrier gas. All compounds were identified by their

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(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

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