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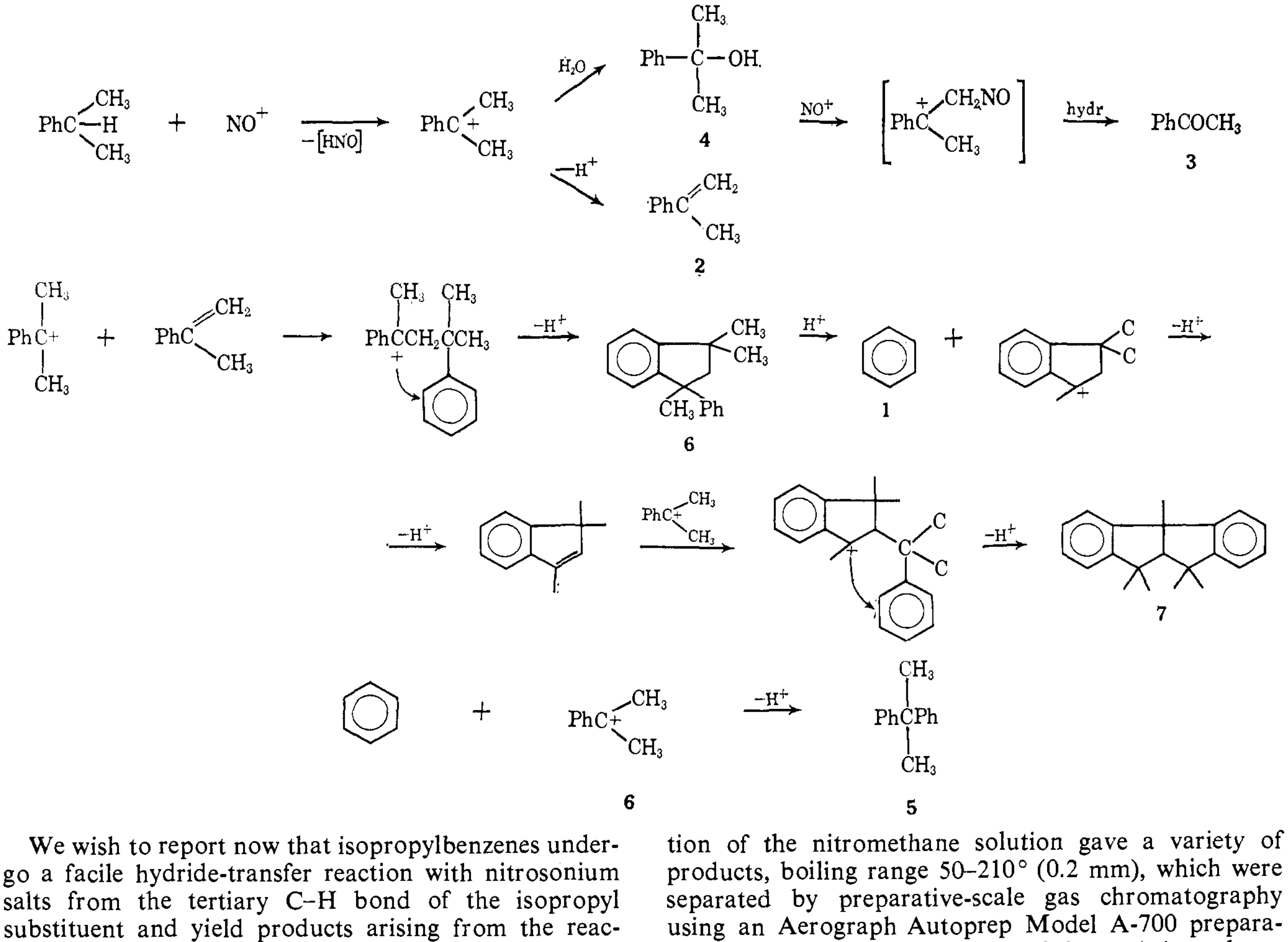
The Reaction of Isopropylbenzenes with Nitrosonium Salts. A New Hydride-Abstraction Reaction

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.

[2] J. Allan, J. Podstata, D. Snobl, and J. Jarkovsky, *Tetrahedron Letters*, **40**, 3565 (1965).

[3] G. A. Olah, N. Friedman, J. M. Bollinger, and J. Lukas, *J. Am. Chem. Soc.*, **88**, 5328 (1966).

physical data and infrared and nmr spectra. A typical product analysis is given in Table I. Although the yields of the various components may vary slightly from reaction to reaction depending on reaction time and temperature control, there is no major difference in the distribution of the products.

Table I. Reaction Products of Cumene with $NO^+PF_6^-$

Product	Yield, wt %
Benzene (**1**)	4.7
α-Methylstyrene (**2**)	2.4
Acetophenone (**3**)	2.2
2-Phenyl-2-propanol (**4**)	1.8
2,2-Diphenylpropane (**5**)	25.6
1,1,3-Trimethyl-3-phenylindan (**6**)	25.0
4b,9,9,10,10-Pentamethyl-4b,9,9a-10-tetrahydro(1,2-*a*)indan (**7**)	13.0
Residue (polymer) (**8**)	26.0

All products formed can be accounted for through the intermediate formation of the phenyldimethylcarbonium ion formed *via* hydride abstraction. Acetophenone and 2-phenyl-2-propanol are also known products from the radical decomposition of cumyl hydroperoxide, but their presence in low yield and the complete absence of any expected coupling products of the cumyl radical argue strongly against a free-radical process as a major pathway. An ionic hydride-abstraction mechanism is further supported by the observation that the nitrosonium ion reacts in a similar fashion with substituted cumenes like cymenes and halocumenes, but not with toluene or *t*-butylbenzene or their derivatives. Thus clearly the reaction is dependent on the presence of an easily abstractable tertiary hydrogen atom. This prerequisite is further supported by the observation that other substrates having easily abstractable hydrogen atoms, like tetralin, methylcyclopentane, diphenylmethane, triphenylmethane, allylbenzene, xanthene, cycloheptatriene, etc., also react readily with nitrosonium salts according to typical carbonium ion type reactions.

The general pattern of the reaction of substituted cumenes (like cymenes and halocumenes) with nitrosonium hexafluorophosphate is similar to that of cumene itself, although the reaction products are more complex.

The reaction of nitrosonium hexafluorophosphate with isopropylbenzenes is difficult to follow in a quantitative way, because carbonium ions formed in the course of the reactions and their deprotonation promote further reaction. When *p*-cymene was allowed to react, for example, with 0.25 equiv of $NO^+PF_6^-$ until the reaction ceases (1 hr), gas chromatographic analysis showed that 0.52 equiv of *p*-cymene had reacted. The reaction is thus nonstoichiometric. Competitive determinations of the over-all reactivity of cumene compared with cymenes and halocumenes shows only that methyl substitution increases the rate, whereas halogen substitution decreases the rates. The most striking observation is, however, the substantial difference in reactivity of the *meta*- and *para*-substituted cumenes compared with that of the *ortho* derivatives.

When a 1:1:1 molar mixture of *o*-, *m*-, and *p*-cymene was allowed to react with 0.33 mole equiv of $NO^+PF_6^-$ it yielded (according to capillary gas chromatography) a reaction mixture which contained only *o*-cymene, with no *p*-cymene and only traces of *m*-cymene present. The *para* and *meta* isomers react substantially faster than the *ortho* isomer. Similar observations were also made with haloisopropylbenzenes.

Reactions of mixtures of the isomeric isopropylbenzenes with NO^+ salts result in the depletion of the *meta* and *para* isomers, giving access of nearly pure *ortho* isomers. This observation explains the unusually high (>90%) yield of *o*-cymene in the isopropylation of toluene in the related alkylation work.[3] This effect is also evident, although to a lesser degree and decreasing strongly, F > Cl > Br, in the halocumene series.

The selective effect of nitrosonium salts in their reaction with isopropylbenzenes is considered to be due to their ability to abstract hydride ion without simultaneously causing electrophilic ring substitution.

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Observation of the Reactive Asymmetry of Methyl Iodide. Crossed Beam Study of the Reaction of Rubidium with Oriented Methyl Iodide Molecules

Sir:

Since the advent of crossed molecular beam kinetics,[1] dating from the work of Taylor and Datz, there has been considerable progress in the study of microscopic aspects of reactive collisions.[2] Continuing refinements of techniques have made it possible to extract more of the dynamical details of elementary reactions. As a step in this direction, the present communication reports a direct observation of the asymmetry in the reactivity of the two "ends" of a (polar) molecule; specifically, the ratio of the reactive cross sections of rubidium with methyl iodide for the two relative orientations

$$\mathrm{Rb} + \mathrm{ICH_3} \xrightarrow{\mathrm{f}} \mathrm{RbI} + \mathrm{CH_3} \quad \text{"favorable"} \qquad (1)$$

vs.

$$\mathrm{Rb} + \mathrm{H_3CI} \xrightarrow{\mathrm{u}} \mathrm{RbI} + \mathrm{CH_3} \quad \text{"unfavorable"} \qquad (2)$$

The experiment consists of crossing a Rb beam with a beam of CH_3I which has been rotational state-selected by an electric six-pole field[3] and aligned with respect to the incident Rb beam[4] by an orientation

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(1) E. H. Taylor and S. Datz, *J. Chem. Phys.*, **23**, 1711 (1955).

(2) See "Molecular Beams," J. Ross, Ed., "Advances in Chemical Physics," Vol. 10, Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1966: (a) Chapter 4 by E. F. Greene, A. L. Moursund, and J. Ross; and (b) Chapter 9 by D. R. Herschbach.

(3) K. H. Kramer and R. B. Bernstein, *J. Chem. Phys.*, **42**, 767 (1965).

(4) More properly, the alignment should be with respect to the incident relative velocity vector. This imperfection (a misalignment of *ca.* 30°) has the effect of reducing the observed asymmetry.