11 12

stability between 2-thianorbiphenylene[4] and the norbiphenylene anion.[17] Further studies on **6** and related systems are currently in progress.

Acknowledgments. We thank Professor H. Hellmann, Chemische Werke Hüls, for generous gifts of squaric acid, and Dr. B. P. Roberts for the esr spectrum.

(17) M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, *J. Amer. Chem. Soc.*, **91**, 2378 (1969).

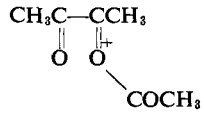
P. J. Garratt,* K. Peter C. Vollhardt
Department of Chemistry, University College London
London WC1H OAJ, England
Received November 29, 1971

Steric Inhibition of Gaseous Ionic Acetylation

Sir:

Previously we have presented evidence for steric inhibition of certain unimolecular processes of gaseous ions.[1,2] We report now the first evidence for complete removal of reactivity in gaseous ion–molecule reactions attributable to steric inhibition.

We have already reported ion cyclotron resonance studies indicating the broad ability of the *m/e* 129 ion (presumably **1**), derived by collision of the 2,3-

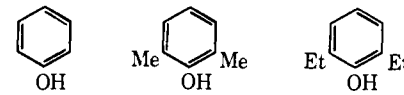


1

butanedione molecular ion with its neutral precursor, to transfer acetyl ion to a wide variety of organic compounds containing oxygen and nitrogen.[3] Lately we have observed differences in reactivity for the epimers of bicyclo[2.2.1]heptanol-2 in accepting the acetyl ion from **1**, the exo isomer producing more acetylated product than the endo isomer.[4]

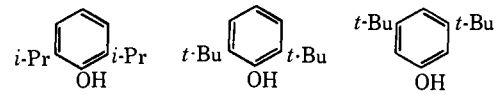
In our pursuit of substituent-effect studies on electrophilic aromatic substitution[5] reactions in the gas phase, we were distracted by consideration of multiple reaction sites, namely, the ring[5] and the substituent,[3] in compounds with electron pair donor substituents such as phenol and aniline. We find now that under conditions used for our acetylation studies (2×10^{-5} Torr $CH_3COCOCH_3$, $2\text{–}4 \times 10^{-6}$ Torr substrate, 30-eV ionizing voltage) reactions of neutral phenol with various acetylating ions from 2,3-butanedione can be reduced to below our limit of detection by increasing the size of ortho substituents. The ortho substituents chosen were alkyl groups, since the ability of alkyl groups to stabilize ions formed by attachment of protons[6] and larger groups[7] increases with increasing size of the group, as in the series methyl < ethyl < isopropyl < *tert*-butyl, so that on the basis of previously observed trends the larger substituents might be anticipated to stabilize the acetylated product.

In fact we observed that compounds **2**, **3**, and **4** are



2 3 4

acetylated by the *m/e* 129 and 43 ions. The product peak intensity decreases as the ortho group becomes larger in this series, but quantitative assignments are not possible at present since there are several competing reactions which *increase* the amount of acetylated product with respect to the amount of phenol molecular ion. The substituents introduced in compounds **5** and **6** *completely* prevent the formation of the acetylated



5 6 7

product, within the limits of detection of our instrumentation.[7a] To confirm the nature of the effect as a steric one, the acetylation of compound **7** was attempted and found successful, as would be expected since the hydroxyl group is accessible to the acetylating agent, and since in the absence of steric effects larger groups stabilize such ions.[6,7] The results incidentally indicate that the hydroxyl group rather than the ring is the site of addition of acetyl, for if the opposite were true **6** might acetylate at least as easily as **7**.

It has been our contention[3,4,7] that ion–molecule reactions with suitably large "reagent ions" will be found to be sensitive indicators of steric environment of reaction centers in organic molecules and therefore should be explored for their analytical utility. The present example is the first example of *complete* inhibition of an ion–molecule reaction by steric effects in an otherwise general reaction system. We are continuing further exploration of alteration of reactivity by steric environment in other aromatic and aliphatic systems.

Acknowledgment. We gratefully acknowledge donation of samples by the Ethyl Corporation and Burroughs-Wellcome and Co., and funds for purchase of the icr spectrometer by the Shell Companies Foundation, Hercules, Inc., the National Science Foundation (GU 2059), and the North Carolina Board of Science and Technology (159). This study was supported by the National Institute of General Medical Sciences (GM-15,994) and the National Science Foundation (GP 28,570).

(1) M. M. Bursey, *J. Amer. Chem. Soc.*, **91**, 1861 (1969).
(2) M. M. Bursey and M. K. Hoffman, *ibid.*, **91**, 5023 (1969).
(3) M. M. Bursey, T. A. Elwood, M. K. Hoffman, T. A. Lehman, and J. M. Tesarek, *Anal. Chem.*, **42**, 1370 (1970).
(4) M. M. Bursey and M. K. Hoffman, *Can. J. Chem.*, **49**, 3395 (1971).
(5) S. A. Benezra, M. K. Hoffman, and M. M. Bursey, *J. Amer. Chem. Soc.*, **92**, 7501 (1970).
(6) M. S. B. Munson, *ibid.*, **87**, 2332 (1965).
(7) W. B. Nixon and M. M. Bursey, *Tetrahedron Lett.*, 4389 (1970).

(7a) NOTE ADDED IN PROOF. Quantitative assessment of icr rate data is difficult but an upper limit on the order of 10^{-7} cm^3 molecule^{-1} sec^{-1} for the rate constants of the unobserved reactions seems reasonable. We base this on our inability to detect the product ion with more than a 100-fold excess of the precursor and trapping voltages such that the product ion would be held *ca.* 1 msec.
(8) Research Fellow of the Alfred P. Sloan Foundation.

Steven A. Benezra, Maurice M. Bursey*[8]
Venable and Kenan Chemical Laboratories
The University of North Carolina
Chapel Hill, North Carolina 27154
Received November 12, 1971