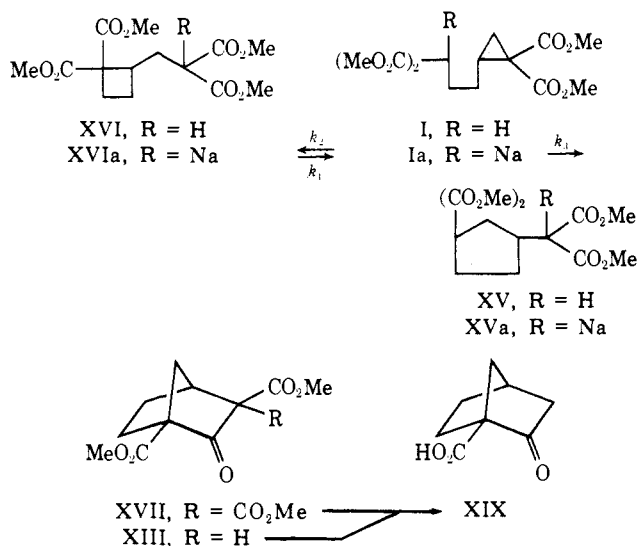


Further applications of intramolecular homoconjugate addition are under investigation.



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S. Danishefsky,\* J. Dynak, E. Hatch, M. Yamamoto  
Department of Chemistry, University of Pittsburgh  
Pittsburgh, Pennsylvania 15260  
Received July 28, 1973

### Incursion of Reversibility in Friedel-Crafts Acylations

Sir:

Friedel-Crafts acylation,<sup>1</sup> in contrast to Friedel-Crafts alkylation, is usually considered an irreversible process,<sup>2</sup> free of rearrangements.<sup>3,4</sup> This difference in behavior was attributed to the resonance stabilization existing between the acyl group and the aromatic nucleus.<sup>2</sup> However, if the acyl group is tilted out of the plane of the aromatic nucleus by ortho substituents, the acylation may become reversible<sup>2,5</sup> (e.g., the Baddeley<sup>6</sup> and the Hayashi<sup>7</sup> rearrangements). Naphthalene systems, by virtue of the dichotomy encountered in their Friedel-Crafts acylations, i.e.,  $\alpha$  vs.  $\beta$  substitution, served as an attractive testing ground for evaluating the mechanisms of these reactions.<sup>8-11</sup> Indeed, Gore's reversibility concept,<sup>8,12</sup> which states that the Friedel-Crafts acylation reaction of reactive aromatic hydrocarbons is a reversible process, was expounded with

naphthalene used as a typical example.<sup>8</sup> However, experiments designed to detect any rearrangement of  $\alpha$ -naphthyl ketones to  $\beta$ -naphthyl ketones under Friedel-Crafts acylation conditions have been mostly unsuccessful.<sup>8,13,14</sup> The recently recorded very few cases of such  $\alpha \rightarrow \beta$  rearrangements<sup>15</sup> still fall within the category of ortho substituted acyl derivatives<sup>16</sup> (*vide supra*). Their generality is further diminished by the intramolecular nature of the rearrangements. We report the incursion of reversibility in Friedel-Crafts acylations as revealed most conspicuously in the system of benzylation of naphthalene in polyphosphoric acid (PPA). We note that intramolecularity and *ortho* substitution<sup>16</sup> are not necessary conditions for violating the "pattern of irreversibility" of Friedel-Crafts acylations in the naphthalene series.

The reaction of naphthalene with benzoic acid in PPA for 8 hr at 70° afforded predominantly 1-benzoyl-naphthalene (1)<sup>17</sup> with only a small quantity of 2-benzoylnaphthalene (2)<sup>17</sup> (1:2 = 15:1).<sup>18</sup> At 120° (10 hr), the ratio of the two isomers was almost equal (1:2 = 54:46). At 140° (8 hr), however, the product distribution was inverted; 2 became the major product (1:2 = 2:3). These results indicate that in this reaction, 1 is the kinetically controlled product while 2 is the thermodynamically controlled product. This conclusion was strikingly verified by treating 1 with PPA at 140° for 10 hr; a significant, overwhelming rearrangement of 1 to 2 was achieved (1:2 = 1:12),<sup>18</sup> together with the formation of appreciable amounts of naphthalene.<sup>19</sup> The reverse isomerization could not be effected over a wide range of temperatures (70-140°), although naphthalene consistently sublimed from the reaction mixtures of 2 and PPA. Thus, the benzylation of naphthalene both at the  $\alpha$  and at the  $\beta$  position is a reversible process. The rationale for the rearrangement of 1 to 2 in PPA is probably associated with the spatial orientation of the carbonyl group *vis-à-vis* the naphthalene nucleus in each of the ketones. In 1, the *peri*-hydrogen causes a certain amount of tilting of the benzoyl complex out of the plane of the naphthalene nucleus, thus reducing the resonance stabilization in the molecule. Therefore, under thermodynamically controlled conditions (e.g., in PPA at elevated temperatures), the conjugate acid of 1 rearranges to that of 2. The rearrangement presumably involves a fission of the protonated form of 1 into the intermediate benzylium ion (or the corresponding mixed anhydride with PPA) and naphthalene, which recombine to provide the protonated form of 2. It should be noted that the benzoyl-

(13) F. R. Jensen, *J. Amer. Chem. Soc.*, **79**, 1226 (1957).

(14) See, however, R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc. C*, 181 (1966), who reported a 3% slow rearrangement of 1-acetyl-2-methoxynaphthalene to 2-acetyl-6-methoxynaphthalene.

(15) I. Agranat and D. Avnir, *J. Chem. Soc., Chem. Commun.*, 362 (1973). (The rearrangement of 7,8-dihydro-13H-benzo[5,6]cyclohepta[1,2-*a*]naphthalen-13-one to 12,13-dihydro-5H-benzo[4,5]cyclohepta[1,2-*b*]naphthalen-5-one.)

(16) In addition to the "ortho substituent" formally inherent in any  $\alpha$ -substituted naphthalene.

(17) H. A. Hammond, J. C. Doty, T. M. Laakso, and J. L. R. Williams, *Macromolecules*, **3**, 711 (1970).

(18) The product distribution could be monitored by the following methods: (a) vpc (2 m  $\times$  0.25 in. column, 15% SE-30 on 60-80 acid washed Chromosorb W, helium carrier gas, 230°; flow rate 50 ml/sec; retention times 9.5 (1) and 11.2 min (2)); (b) tlc (alumina, petroleum ether (bp 40-60°)-benzene (3:1),  $R_f$ (1) 0.35,  $R_f$ (2) 0.26); (c) nmr (100 MHz, 8.04 (multiplet, 8-H of 1) and 8.14 ppm (singlet, 1-H of 2) downfield from Me<sub>4</sub>Si).

(19) Practically, a disappearance of 1 was realized.

(1) G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I-IV, Wiley-Interscience, New York and London, 1963-1964.

(2) C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses," Wiley-Interscience, New York, N. Y., 1970, p 653.

(3) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam, 1965, p 174.

(4) N. L. Allinger, M. P. Cava, D. C. De Jongh, C. R. Johnson, N. A. Lebel, and C. L. Stevens, "Organic Chemistry," Worth, New York, N. Y., 1971, p 358.

(5) D. E. Pearson and C. A. Buehler, *Synthesis*, 455 (1971).

(6) G. Baddeley, *J. Chem. Soc.*, 232 (1944); *Quart. Rev., Chem. Soc.*, **8**, 355 (1954).

(7) M. S. Newman and K. G. Ihman, *J. Amer. Chem. Soc.*, **80**, 3652 (1958).

(8) P. H. Gore in ref 1, Vol. III, p 1.

(9) F. R. Jensen and G. Goldman in ref 1, Vol. III, p 1003.

(10) G. A. Olah in ref 1, Vol. I, p 25.

(11) G. Baddeley, *J. Chem. Soc.*, s99 (1949).

(12) P. H. Gore, *Chem. Rev.*, **55**, 229 (1955).

ation of naphthalene with benzoyl chloride and traces of catalysts at reflux temperatures reportedly favors the formation of **1** predominantly.<sup>20-22</sup>

The mechanistic and synthetic implications of the results reported in this communication, which represent the most significant evidence to date of the incursion of reversibility in Friedel-Crafts acylations, is under active investigation.

(20) D. E. Pearson and C. A. Buehler, *Synthesis*, 533 (1972).

(21) S. Chodroff and H. C. Klein, *J. Amer. Chem. Soc.*, **70**, 1647 (1948).

(22) L. L. Leont'eva and I. P. Tsukervanik, *Uzb. Khim. Zh.*, **11**, 44 (1967); *Chem. Abstr.*, **68**, 86960 (1968).

Israel Agranat,\* Yu-Shan Shih, Yael Bentor

Department of Organic Chemistry

The Hebrew University of Jerusalem

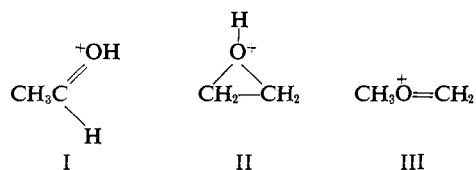
Jerusalem, Israel

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### Nucleophilic Attack on Protonated Oxiranes in the Gas Phase. Identification of the $C_2H_5O^+$ Isomeric Ion Corresponding to Protonated Ethylene Oxide

Sir:

In recent years the  $C_2H_5O^+$  structural isomers corresponding to protonated acetaldehyde (I), protonated ethylene oxide (II), and the methoxymethyl cation (III)



have been the subject of extensive investigations directed primarily at developing methods for identifying isomeric ions.<sup>1-9</sup> These investigations have utilized labeling experiments in conjunction with studies of metastable ion characteristics,<sup>1,2,6-8</sup> collision induced decompositions at high energies,<sup>2,6</sup> thermochemical studies,<sup>3,5,9</sup> and a number of studies in which ion-molecule reactions involving  $C_2H_5O^+$  isomers as reactants, intermediates, or products have been reported.<sup>3-5</sup> While the possibility of distinguishing I and II from III on the basis of metastable ion characteristics and specific ion-molecule reactions has been clearly demonstrated, it has not proven possible to provide definitive evidence for the existence of a unique ion corresponding to structure II. The only possible exception are some subtle differences in proton transfer reactions involving I and II as reported by Blair and Harrison.<sup>3</sup> Failure to identify II has been attributed to the possible rearrangement of this isomer to the sig-

(1) B. G. Keyes and A. G. Harrison, *Org. Mass. Spectrom.*, submitted for publication.

(2) F. W. McLafferty, R. Kornfeld, W. F. Haddon, K. Levsen, I. Sakai, P. F. Bente III, S. Tsai, and H. D. R. Schuddenmage, *J. Amer. Chem. Soc.*, **95**, 3886 (1973).

(3) A. S. Blair and A. G. Harrison, *Can. J. Chem.*, **51**, 703 (1973).

(4) M. T. Bowers and P. R. Kemper, *J. Amer. Chem. Soc.*, **93**, 5352 (1971).

(5) J. L. Beauchamp and R. C. Dunbar, *J. Amer. Chem. Soc.*, **92**, 1477 (1970).

(6) F. W. McLafferty and H. D. R. Schuddenmage, *J. Amer. Chem. Soc.*, **91**, 1866 (1969).

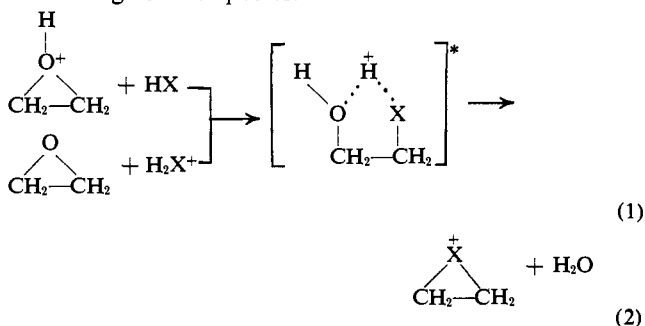
(7) A. G. Harrison and B. G. Keyes, *J. Amer. Chem. Soc.*, **90**, 5046 (1968).

(8) T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5021 (1966).

(9) A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966).

nificantly more stable protonated acetaldehyde isomer I.<sup>10-14</sup> We wish to report a straightforward method, based on the identification of specific ion-molecule reactions using the techniques of ion cyclotron resonance (icr) spectroscopy,<sup>15</sup> for distinguishing the  $C_2H_5O^+$  structural isomer II from I and III. The reactions observed have implications for further studies of the gas-phase reactions of various nucleophiles with protonated oxiranes and related strained ring compounds and bear an interesting relationship to recently reported studies of neighboring group effects in the ionization of  $\beta$ -substituted alcohols.<sup>16</sup>

The gas-phase ion chemistry of ethylene oxide has been reported by several investigators.<sup>3-5</sup> The parent ion reacts to form the protonated parent and, in a higher order process, an ion corresponding to *m/e* 57 ( $C_2H_5O^+$ ).<sup>3</sup> The gas-phase ion chemistry of phosphine has been extensively investigated using icr techniques<sup>17</sup> and high-pressure mass spectrometry.<sup>18</sup> At thermal energies the parent ion reacts to generate only the protonated parent ion.<sup>17,18</sup> The variation of ion abundance with time observed in a trapped ion icr<sup>11</sup> study of a mixture of phosphine and ethylene oxide is shown in Figure 1. In addition to the ions expected, at long times a prominent condensation product is observed at *m/e* 61, corresponding to  $C_2H_6P^+$ .<sup>19</sup> Double resonance experiments identify reactions 1 and 2 with  $HX = PH_3$  as leading to this species.<sup>20</sup>



(10) Recent trapped ion experiments<sup>11</sup> in our laboratory give the proton affinity of ethylene oxide as being 1.0 kcal/mol greater than acetaldehyde.<sup>12</sup> Using  $\Delta H_f(\text{CH}_3\text{CHOH}^+) = 143$  kcal/mol<sup>13</sup> gives 169 kcal/mol as the heat of formation of protonated ethylene oxide. The methoxy methyl cation is of intermediate stability,  $\Delta H_f(\text{CH}_3\text{OCH}_2^+) = 158$  kcal/mol.<sup>14</sup>

(11) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).

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(16) J. K. Kim, M. C. Findlay, W. G. Henderson, and M. C. Caserio, *J. Amer. Chem. Soc.*, **95**, 2184 (1973).

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(18) J. W. Long and J. L. Franklin, *J. Amer. Chem. Soc.*, submitted for publication.

(19) The ion at *m/e* 48 is formed in the reaction  $C_2H_4O^+ + \text{PH}_3 \rightarrow \text{CH}_2\text{PH}_3^+ + \text{CH}_2\text{O}$ . Since this ion is formed at the expense of *m/e* 57 ( $C_2H_5O^+$ ) normally observed in ethylene oxide alone, it is probable that the reactant is the energetically modified  $C_2H_4O^+$  ion discussed by Blair and Harrison, who report observations of a similar reaction in a mixture of acetone and ethylene oxide.

(20) With continuous ejection of *m/e* 35 ( $\text{PH}_4^+$ ) during the reaction sequence, *m/e* 61 still forms to a substantial extent. Reaction 1 is thus an important source of *m/e* 61.