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Aromatic Substitution in the Gas Phase. Ambient Behavior of Phenol toward t-C$_4$H$_9^+$ Cations

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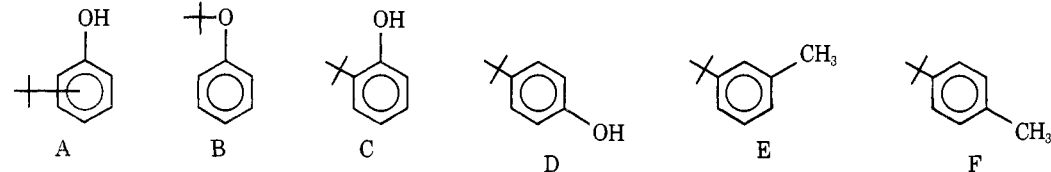*Contribution from the University of Rome, 00100 Rome, Italy. Received August 2, 1976*

Abstract: The reactivity of phenol toward t-C$_4$H$_9^+$ cations, obtained in the dilute gas state from the γ-radiolysis of neopentane, is characterized by a typical ambident behavior. The competition between the n-type and the π-type nucleophilic centers of the substrate is kinetically biased in favor of O-alkylation, leading to the predominant (ca. 8:1) formation of *tert*-butyl phenyl ether with respect to *tert*-butylphenols under conditions, i.e., high neopentane pressure and the presence of a gaseous base (NH$_3$), which favor kinetic control of products. Ring-alkylated arenium ions appear, however, to be more stable than the isomeric oxonium ion, as indicated by the higher yields of *tert*-butylphenols under conditions of increasing thermodynamic control of products, reaching a 4:1 excess over the ether at the lowest pressure investigated (20 Torr). The results of competition experiments show that phenol reacts faster than toluene with gaseous t-C$_4$H$_9^+$, the apparent k_{phenol}:$k_{toluene}$ ratio ranging from 2.0 to 4.4. The isomeric composition of ring-alkylated products underlines the electrophilic character and the remarkable *positional* selectivity of the t-C$_4$H$_9^+$ attack, yielding exclusively ortho- and para-substituted isomers, whose ratio depends on the pressure of the system and the presence of NH$_3$. Thus, the ortho:para ratio, that reaches a 0.4 value under conditions of kinetic control of products, decreases as the pressure is lowered, down to the 0.04 value measured at 20 Torr. The mechanism of the gas-phase alkylation, and of the subsequent isomerization processes that appear of intermolecular nature, are discussed and compared with those of related alkylation reactions, both in the gas phase and in solution.

Meaningful comparison of the *intrinsic* reactivity of the oxygen atom (n-type center) and of the ring (π-type center) of phenol and aromatic ethers toward charged electrophiles remains a difficult problem, despite extensive kinetic, spectroscopic, and NMR investigations concerning, in particular, protonation and alkylation.[1-7]

The major difficulty arises from the inherently close reactivity of the substituent group and of the ring, which makes their competition for the electrophile exceedingly sensitive to the reaction environment, especially to solvation and ion-pairing effects, preventing any generalization of the results concerning a specific reaction medium.

The problem of assessing the *intrinsic* reactivity scale of the nucleophilic centers of phenol and related compounds, i.e., of determining a kinetically significant reactivity ratio independent of any particular reaction environment, appears eminently suitable for exploitation of a recently developed technique,[8-10] that allows the study of aromatic substitutions by charged electrophiles in the dilute gas state, in the absence of solvation, counterions, etc., and further permits the direct determination of the *substrate* and *positional* selectivity of the attack.

The present paper deals with the gas-phase alkylation of phenol by the t-C$_4$H$_9^+$ cation, a relatively mild electrophile,

Table I. Alkylation Products from the Gas-Phase Reaction of t-$C_4H_9^+$ with Phenol

System composition, Torr						Rel yields of products, %[b]					
neo-C_5H_{12}	O_2	NH_3	Phenol	Toluene	$k_{phenol}/$ $k_{toluene}$[a]	A	B	C	D	E	F
720	5	5	0.22	0.61	4.4	15	85	33	67	6	94
720	5	5	0.41	0.21	2.0	16	84	25	75	10	90
720	10	c	0.59	0.32	2.1	30	70	35	65	11	89
715	5		0.25	0.52	2.9	20	80	20	80	10	90
720	10		0.26	0.25	3.2	11	89	27	73	12	88
250	5		0.33	0.25	2.0	35	65	13	87	16	84
250	5		0.33	0.33	2.1	37	63	13	87	14	86
100	2	2	0.27	0.26	2.3	60	40	6	94	18	82
100	2	2	0.26	0.22	3.4	60	40	11	89	18	82
100	2	2	0.27	0.22	3.8	61	39	8	92	16	84
100	2		0.41	0.22	3.2	67	33	9	91	21	79
20	2		0.33	0.50	3.9	82	18	3	97	44	56
20	2	d	0.33	0.51	3.7	82	18	4	96	47	53

[a] Ratio of total reactivity of phenol (O-alkylated + C-alkylated products) to that of toluene. For the standard deviation of data, see text.
[b] Standard deviation ca. 10%. [c] Containing 5.0 Torr of $N(CH_3)_3$. [d] Containing 2.0 Torr of $N(CH_3)_3$.

whose reactivity toward arenes has been recently investigated in the gas phase.[11,12]

Experimental Section

Materials. Phenol and toluene were research grade chemicals from Merck Co., and their purity, with special regard to the absence of alkylated derivatives, was checked by GLC, using the same columns employed for the analysis of the irradiation products. Neopentane, O_2, CH_4, NH_3, and $N(CH_3)_3$ were obtained from Matheson Co., with a stated purity exceeding 99.99 mol %, and were used without further purification.

The isomeric $tert$-butylphenols, required as standard in the GLC of products, were prepared from the Friedel-Crafts reaction of t-C_4H_9Cl with phenol, in the presence of $AlCl_3$, then resolved and purified by preparative GLC over a 4-m Apiezon "L" grease column at 150 °C, and identified by IR and NMR spectrometry. Further confirmation of the identity of the individual $tert$-butylphenols was achieved by methylation with $(CH_3)_2SO_4$, followed by gas chromatographic and spectrometric comparison of the ethers formed with authentic $tert$-butylanisoles samples.

A specimen of $tert$-butyl phenyl ether was prepared according to Stevens,[13] from the reaction of i-C_4H_8 with phenol in the presence of H_2SO_4, and purified by preparative GLC over a 4-m Apiezon "L" grease column at 110 °C.

Procedure. The gaseous reaction mixtures were prepared, according to standard vacuum techniques, introducing the bulk constituent of the system, neopentane (or methane), and the required gaseous additives (O_2, NH_3, $N(CH_3)_3$) together with fragile, weighed glass ampule(s) containing the aromatic substrate(s), into evacuated and carefully outgassed 1000-mL Pyrex bulbs, that were sealed before irradiation, as described elsewhere.[11,12] However, the relatively low volatility of phenol, and its ready adsorption onto the surface of the Pyrex vessel, must be taken into account. Accordingly, the amount of phenol introduced into the system was kept slightly above the theoretical limit posed by the vapor pressure at the irradiation temperature.

Furthermore, the sealed Pyrex vessels were stored for several hours in a thermostatic oven, regulated at the irradiation temperature, after breaking the fragile ampule containing phenol, in order to allow a steady and reproducible equilibrium between the adsorbed and the gas-phase phenol to be reached.

In any event, the concentration of phenol in the gas phase was deduced from a GLC analysis of a small gaseous sample withdrawn from the vessel just before irradiation, rather than from the weighed amount of phenol introduced into the system. Despite such precautions, the actual gas-phase concentration of phenol during irradiation could be determined only within a comparably wide uncertainty range (±30%), and therefore represents the most significant source of error in the measurement of the k_{phenol}:$k_{toluene}$ ratio.

The irradiations were carried out at a dose of 1.2 Mrad, at a dose rate of 0.55 Mrad h⁻¹, in a 220 Gammacell from Nuclear Canada Ltd., at temperatures from 21 to 27 °C.

The analytical procedure to determine the reaction products must take into account the low volatility and the easy adsorption of $tert$-butylphenols, which prevents direct GLC of an aliquot of the irradiated gas withdrawn from the vessel with a syringe. In order to prevent selective losses of phenols, and to obtain reproducible yields, the analysis was carried out by freezing the irradiated vessel with liquid nitrogen, introducing a known volume of diethyl ether, and allowing the closed system to warm up to room temperature.

After many such freezing-thawing cycles, and careful washing of the vessel walls with the ethereal solution, known aliquots of the latter were analyzed by GLC, using a Hewlett-Packard Model 5700A or a C. Erba Model 2400 T gas chromatograph, equipped with FID units. The analysis was carried out with a 4-m Apiezon "L" column, operated at 110 °C up to elution of phenol, then programmed at the rate of 32 °C min⁻¹ to the final temperature of 150 °C.

The yields of the products were determined from the area of the correspondent elution peaks, using appropriate calibration factors, which are particularly necessary in this case, owing to the appreciable difference of the FID response to arenes, ethers, and phenols. The *absolute* yield of a given product is defined as the ratio between the moles of product formed and the moles of the $tert$-butyl ions produced in the system by the γ-radiolysis. The moles of product can be determined with reasonable accuracy by GLC, while the moles of t-$C_4H_9^+$ formed can be calculated with a considerably larger uncertainty from the dose absorbed by the gas, measured in turn with a standard Fricke dosimeter, and the known G_{t-$C_4H_9^+}$ value (vide infra).

Results

Table I gives the yields of the products from the gas-phase alkylation of phenol, carried out in competition with toluene in the pressure range 20-720 Torr, in the presence of O_2 and of different concentrations of NH_3 or $(CH_3)_3N$. This table gives, in particular, the ratio of O-alkylation to C-alkylation of phenol, and the isomeric composition of ring-alkylated products from both substrates, together with the apparent k_{phenol}:$k_{toluene}$ ratios, whose unusually large scatter is primarily traced to the errors in the measurement of the actual concentration of phenol in the gas phase during the irradiation. As in other cases, the absolute yields of alkylated aromatics are of

limited significance, and strongly dependent on the irradiation conditions. In fact, the aromatic substrate is only one of the nucleophiles, either initially present in the gas or formed from its radiolysis, which compete for the gaseous $t\text{-}C_4H_9^+$ ion. Furthermore, there is a considerable uncertainty concerning the dose received by the gas, the precise G value for the $t\text{-}C_4H_9^+$ formation, and its pressure dependence in the range of interest. Finally, alkylation does not necessarily represent the only reaction channel available to $t\text{-}C_4H_9^+$ in its attack to a strongly basic substrate, such as phenol (vide infra). For the purposes of the present discussion, it is therefore sufficient to point out that alkylation of arenes is a major reaction pathway of the *tert*-butyl cation in the systems studied, with overall *absolute* yields whose *order of magnitude* can be evaluated around 20–30% in neat neopentane at 720 Torr. The absolute yields further increase at lower pressures, as the substrate concentration becomes predominant over those of other nucleophiles.

The ionic character of the alkylation is confirmed by the observation that the absolute yields are strongly depressed by small concentrations of NH_3, an effective interceptor of the *tert*-butyl cation. Thus, the overall absolute yields of alkylated products are typically reduced to ca. 6% in neopentane (720 Torr) containing only 5 Torr of NH_3.

The major features of the gas-phase alkylation can be summarized as follows. Phenol is more reactive than toluene toward $t\text{-}C_4H_9^+$, as indicated by the apparent k_{phenol}:$k_{toluene}$ ratio of 3.1 ± 0.8. O-Alkylation, that predominates at 720 Torr, exceeding ring alkylation by a ratio of ca. 8:1, undergoes a regular decrease as the pressure is lowered, down to the ratio of 1:4 measured at 20 Torr. As previously reported,[11] the composition of alkylated products from toluene is characterized by the lack of ortho substitution, and by a para: $\frac{1}{2}$ meta ratio decreasing with the pressure, from the value of ca. 25 measured at 720 Torr to the value of ca. 2.3 observed at 20 Torr. For a correct interpretation of the effects of pressure on the alkylation of phenol it is perhaps worth emphasizing that $[C_6H_5OH]$ was kept constant at all pressures, i.e., that the mole fraction of phenol in the gas was *higher* in the low-pressure systems. Concerning ring alkylation of phenol, no meta substitution is observed at any pressure, and the $\frac{1}{2}$ ortho:para ratio of ca. 0.2 measured at 720 Torr decreases with the pressure, down to the value of ca. 0.02 at 20 Torr. On the other hand, the relative reactivity of phenol and toluene, measured by the apparent k_{phenol}:$k_{toluene}$ ratio, appears essentially independent of the pressure and of the concentration of gaseous bases, at least within its rather large experimental uncertainty.

The protonation of *tert*-butyl phenyl ether by CH_5^+ and $C_2H_5^+$ ions, carried out by irradiating a gaseous system containing CH_4 (760 Torr), O_2 (5 Torr), and the ether (0.5 Torr), gave phenol as the major product, together with considerably smaller (ca. 20%) yields of higher boiling compounds, tentatively identified as the *tert*-butyl ethers of isomeric *tert*-butylphenols. The most significant result of these experiments was, however, the conspicuous absence of *tert*-butylphenols among the reaction products.

Discussion

The electrophile used in the present study is the gaseous $t\text{-}C_4H_9^+$ cation, formed in high yields from the γ-radiolysis of neopentane and thermalyzed by a large number of unreactive collisions with the neopentane molecules, as discussed in details in the previous papers of this series.[11,12]

The relatively stable alkyl cation, $\Delta H_f^\circ = 169$ kcal/mol, can react exclusively as a Lewis acid with toluene, whose proton affinity (PA), 189.9 kcal/mol,[14] is lower than the PA of isobutene, 193 kcal/mol.[14,15] On the other hand, proton transfer from $t\text{-}C_4H_9^+$ to phenol, whose PA reaches 195–196 kcal/mol,[16] cannot be ruled out on energetic grounds, and therefore the *tert*-butyl cation can conceivably behave both as a Lewis acid and as a Brønsted acid toward C_6H_5OH. From these considerations, it appears that the phenol/toluene reactivity ratio given in Table I, which refers exclusively to the alkylation channel, sets only the *lower limit* of the overall nucleophilic reactivity of phenol toward the gaseous $t\text{-}C_4H_9^+$ ion.

The experimental features of gas-phase *tert*-butylation of C_6H_5OH are consistent with a mechanism involving as the first and rate-determining step the competitive attack of the alkyl cation to the n-type and π-type nucleophilic centers of the ambident substrate, yielding respectively the oxonium ion I,

$$C_6H_5OH + R^+ \longrightarrow$$

(1a)

(1b)
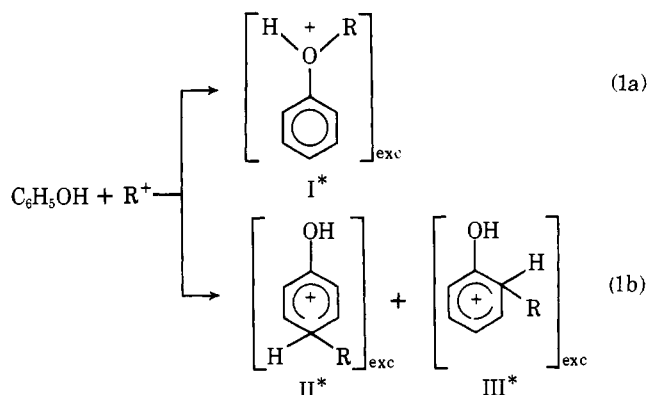
or the arenium ions II and III, excited by the exothermicity of the reaction, roughly extimated to exceed 27 kcal/mol.[17]

Unless collisionally stabilized, the excited oxonium ions I can undergo isomerization to the arenium ion II, which on the


(2)

(3)
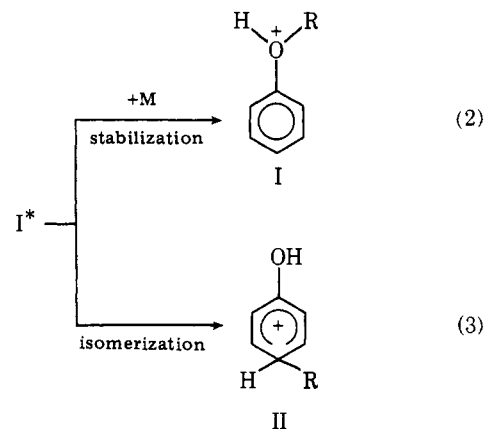
grounds of the low-pressure results appears thermodynamically more stable.

Eventually, the stabilized oxonium and arenium ions lose a proton to a gaseous base (e.g., NH_3, or another molecule of substrate) contained in the system, yielding the observed products, namely, *tert*-butyl phenyl ether from I, and respectively o- and p-*tert*-butylphenol from III and II. Concerning the isomerization process, only *tert*-butyl group shifts affect the yields and the nature of the alkylated products, while the intramolecular proton shifts, that are likely to occur at a relatively high rate within the excited arenium ions, will not be considered in the following discussion. Inconclusive evidence on the nature of the isomerization process is provided by the data summarized in Table I, whose only firm indication, related to the considerable increase of para substitution observed at low pressures without any detectable accumulation of m-*tert*-butylphenol, spells against the occurrence of an intramolecular mechanism involving 1,2 alkyl shifts, analogous to that operative in the gas-phase *tert*-butylation of arenes.[11,12] This point is clearly demonstrated by the sharp contrast existing with the pressure dependence of the isomeric composition

of *tert*-butyltoluenes, illustrated in Table I.

Further evidence on the isomerization mechanism was sought via an independent approach to the gaseous *tert*-butylphenyloxonium ion (I), involving the protonation of *tert*-butyl phenyl ether with the strong Brønsted acids CH_5^+ and $C_2H_5^+$, obtained in the dilute gas state from the radiolysis of methane,[18] e.g.

$$t\text{-}C_4H_9OC_6H_5 + CH_5^+ \rightarrow I^* + CH_4 \qquad (4)$$
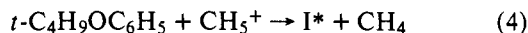
It should be noted that the excitation energy of I from reaction 4 is significantly higher than from reaction 1a,[19] and that the reaction environment is also somewhat different, since replacement of neopentane with methane as the bulk constituent of the gas is likely to affect the efficiency of collisional stabilization.

Nevertheless, without discounting these differences, the results of the protonation experiments, yielding phenol as the major product *without detectable formation of tert-butylphenols*, provide strong evidence against the intramolecular nature of the isomerization process.

Isomerization pathways which appear plausible, or at least not conflicting with the available evidence, are of intermolecular nature and could involve either migration of a free *tert*-butyl cation from the excited oxonium ion (I), which implies *reversible O-alkylation*, or the electrophilic attack of I on a phenol molecule. The latter pathway, based on the alkylating ability of the *excited* oxonium ion, is consistent with the results from the gas-phase *tert*-butylation of anisole,[20] and with the behavior of aromatic oxonium ions in superacid media.[6]

Irrespective of the specific isomerization pathway, the high yields of ether obtained under conditions of *kinetic control* of products, i.e., at high neopentane pressures, which ensure effective collisional deactivation, and in the presence of gaseous bases, which cause fast deprotonation of the ionic intermediates, indicate that O-alkylation is kinetically predominant in the gas phase.[21] On the other hand, the extensive isomerization observed at low pressures suggests that thermodynamic factors (of energetic and possibly entropic nature) favor formation of the ring-alkylated ion II.

Both these results find independent support in recent mass spectrometric investigations. Preferential attack of a gaseous electrophile, the CH_3CO^+ cation, to the oxygen atom of phenols was in fact indirectly inferred in the ICR study of Benezra and Bursey,[22] who found the acetylation rate, appreciable for 3,5-di-*tert*-butylphenol, to fall below detection limits for the isomeric 2,6-di-*tert*-butylphenol, a result rationalized with the steric hindrance to O-acetylation caused by the bulky ortho substituents.

The higher stability of the ring-substituted arenium ion (II) with respect to the isomeric oxonium ion (I), suggested by the present study, in particular by the pressure dependence of the composition of products, finds independent, if indirect, support in the available thermochemical and mass spectrometric data.[23]

Finally, it is worth mentioning the high positional selectivity displayed by the gaseous *tert*-butyl cation in its electrophilic attack on phenol, which causes exclusive ortho/para substitution without the formation of detectable traces of the meta isomer, and the gradual increase of the para-substituted isomer at the lower pressures, which again underlines the higher stability of the para arenium ion (II), not only with respect to the oxonium ion (I), but also in comparison with the ortho arenium ion (III).

Conclusions

The results outlined in the previous sections provide a definite answer to the question concerning the competition between the n-type and π-type nucleophilic centers of phenol for a typical charged electrophile, such as the free $t\text{-}C_4H_9^+$ ion, in the dilute gas phase, a nearly ideal reaction environment where the intrinsic reactivity scale is not affected by extraneous and variable phenomena, namely, solvation, ion pairing, etc. The present study shows, in fact, that attack on the oxygen atom is *kinetically predominant*.

However, the para-substituted arenium ion is *more stable* than the oxonium ion, which consequently undergoes extensive isomerization, presumably of intermolecular nature, when the reaction is carried out at low pressures.

The *tert*-butyl cation displays a low substrate selectivity, a feature common to many *exothermic* gas-phase substitutions, and a remarkable positional selectivity, giving exclusively ortho/para substitution.

The specific features of the *tert*-butylation process, where the oxonium ion represents a major intermediate, allow direct evaluation of the frequently postulated mechanism involving preliminary bond formation between the electrophile and the n electrons of a substituent ("linear coordination"), followed by the collapse of the n complex to the ortho arenium ion. This reaction sequence has long been suggested for aromatic substitutions giving high yields of the ortho isomer,[24-31] and has been also postulated in the acid-catalyzed rearrangement of aryl ethers to alkylphenols.[32]

Our data fail to support the intervention of this mechanism in the gas-phase *tert*-butylation of phenol, since the oxonium ion (I) is found to isomerize exclusively to the para-substituted arenium ion (II), and the gas-phase protonation of *tert*-butyl phenyl ether promotes dealkylation, rather than formation of o-*tert*-butylphenol.

Whether such behavior is a general one in the gas-phase alkylations, or it depends on the specific properties, in particular the steric requirements,[33] of the *tert*-butyl cation, it cannot be deduced from the presently available data and elucidation of this point will require further investigation.

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(17) Value arrived at by estimating the ΔH_f° value of p-tert-butylphenol from data taken from D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1968, and with the further assumption that the PA of the ring position bearing the *tert*-butyl group is equivalent to that of phenol, 195 kcal/mol. These assumptions lead to an approximate ΔH° value of 119 kcal/mol for II.
(18) Cf. P. Ausloos, S. G. Lias, and A. A. Scala, *Adv. Chem. Ser.*, 58, 264 (1966).
(19) The upper limit for the exothermicity of (4) can be calculated from the PA values of CH_4 and C_6H_5OH to be ca. −70 kcal/mol.
(20) M. Attina, F. Cacace, G. Ciranni, and P. Giacomello, *J. Am. Chem. Soc.*, to be published.

(21) It should be noted, in this connection, that the highest $k_{O-alkylation} \cdot k_{\Sigma C-alkylation}$ ratio measured at atmospheric pressure can only be regarded as a *lower limit*, since occurrence of isomerization processes cannot be ruled out, even at 720 Torr.

(22) S. A. Benezra and M. M. Bursey, *J. Am. Chem. Soc.*, **97**, 3600 (1972). More recent evidence for gas-phase O-acetylation, and the possible isomerization of the intermediate oxonium ions to more stable forms, is provided by D. A. Chatfield and M. M. Bursey, *J. Am Chem. Soc.*, **98**, 6492 (1976).

(23) The relative stability of I and II can be evaluated from (1) the ΔH_f° values of *tert*-butyl phenyl ether (IV) and respectively of *p-tert*-butylphenol (V) and (2) the PA of the oxygen atom of IV vs. that of the alkyl-substituted ring position of V. While experimental ΔH_f° values of IV and V are not available, the data concerning other isomeric alkyl phenyl ethers/*p*-alkylphenols pairs show that the latter are invariably *more stable* by some 10 kcal/mol; cf. (a) M. Badoche, *Bull. Soc. Chim. Fr.*, **8**, 212 (1941). As to the PA values, the following data are relevant. First, para-protonated phenol is *more stable* in the gas phase with respect to the isomeric oxonium ion; cf. (b) D. J. De Frees, R. T. McIver, and W. J. Hehre, private communication to be published, and (c) B. S. Freise, R. L. Woodin, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 6893 (1975), the stability difference obtained with theoretical and ICR methods ranging from 13 to 20 kcal/mol. The preferred ring protonation of phenol is consistent with the small (<5 kcal/mol) difference measured between the gas-phase PA of phenol and anisole; cf. ref 23b and (d) Y. Lau and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 7452 (1976). Furthermore, the ICR isotope exchange experiments of Freiser, Woodin, and Beauchamps show that ring protonation of anisole is energetically preferred with respect to O-protonation. The PA of the oxygen atom is expected to be higher in *tert*-butyl phenyl ether than in anisole, owing to the larger effect of the *tert*-butyl with respect to the methyl group, on the basicity of the n center; cf. (e) J. Long and B. Munson, *J. Am. Chem. Soc.*, **95**, 2427 (1973).

On the other hand, the presence of a *tert*-butyl substituent is also expected to increase the PA of the para position of phenol, in accord with the stabilizing effect of an ipso alkyl substituent at the protonated site of a gaseous arenium ion; cf. (f) J. L. Devlin, III, J. F. Wolf, R. W. Raft, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 1990 (1976). As these two effects tend to cancel each other, the available evidence strongly suggests, albeit certainly does not prove, that the PA values of the oxygen atom of IV, and of the alkyl-substituted ring position of V are comparable, perhaps with a small preference for the latter, and that their difference, if any, can hardly offset the large stability excess of V over IV. Consequently, our experimental evidence pointing to the higher stability of II with respect to I appears quite reasonable on the grounds of independent thermochemical and mass spectrometric data.

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(25) M. J. S. Dewar, "Molecular Rearrangements", P. de Mayo, Ed., Wiley, New York, N.Y., 1963, p 306.

(26) D. E. Pearson and C. A. Buchler, *Synthesis*, 460 (1971).

(27) P. Kovacic and J. J. Hiller, *J. Org. Chem.*, **30**, 1581 (1965).

(28) J. H. Ridd and E. F. V. Scriven, *J. Chem. Soc., Chem. Commun.*, 641 (1972).

(29) R. A. Kretchmer and M. B. McCloskey, *J. Org. Chem.*, **37**, 1989 (1972).

(30) E. C. Taylor and A. McKillop, *Acc. Chem. Res.*, **3**, 345 (1970).

(31) P. Heberfield and P. Paul, *J. Am. Chem. Soc.*, **87**, 5502 (1965).

(32) P. A. Spanninger and J. L. von Rosemberg, *J. Am. Chem. Soc.*, **94**, 1070 (1972), and references cited therein.

(33) However, it has been shown (ref 12) that a *gaseous tert*-butyl ion can efficiently attack the ring positions ortho to a methyl group, provided that they are sufficiently activated, and furthermore the steric hindrance of the OH group is smaller than that of the methyl group.

13C Nuclear Magnetic Resonance Spectroscopic Study of Alkyl Cations. The Constancy of 13C Nuclear Magnetic Resonance Methyl Substituent Effects and Their Application in the Study of Equilibrating Carbocations and the Mechanism of Some Rearrangements[1a]

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Abstract: All C_3 to C_8 alkyl cations were prepared in SbF_5/SO_2ClF solution at low temperature (-78 to -130 °C) and their proton decoupled and coupled 13C NMR spectra were studied. The effect of methyl substituents was determined by comparing the 13C NMR shifts of related carbocations and was found to be constant. These substituent effects were applied in estimating the 13C shifts of the degenerate and nondegenerate equilibrating cations. This method gave good agreement for estimating the 13C NMR shifts in tertiary–tertiary equilibrating ions, as compared with the experimental values. Some thermodynamic properties were also measured for the nondegenerate equilibrating cations. Application of the additive substituent effect method to secondary–secondary equilibrating carbocations showed significant deviations from the experimental 13C NMR shifts. Methyl substituent effects in static and equilibrating carbocations are discussed. Additionally, some carbocationic rearrangements were observed during the course of this work and their mechanisms are discussed.

Since our first report in 1962 of the successful preparation of alkyl cations,[2] the structural elucidation of a continuously increasing number of diverse types of stable carbocations has been accomplished by 1H NMR and 13C NMR spectroscopic studies in low nucleophilic media.[3-5a-c] The NMR methods give particular information about the structure, the trend of charge distribution,[6] bonding,[7] dynamic exchange processes,[4,8] and other properties of carbocations. The NMR chemical shifts and coupling constants have been correlated with the above properties by the molecular comparison of related ions and/or frequently by quantum mechanical molecular orbital calculations.[9-12] The success of these methods has brought about their widespread use in studying carbocations. 13C NMR studies of a significant number of alkyl cations were carried out and reported, as were rearrangements of carbocations.

However, no comprehensive, systematic study was made to establish general trends, if any, of substituent effects.

In the course of our continued studies we undertook a systematic investigation of structurally related alkyl cations by 13C NMR spectroscopy, since small changes in structure produce a relatively large change in the chemical shift for the position substituted. A pertinent point in question is that of the 13C shifts of alkanes, where two systematic studies have resulted in excellent empirical methods for predicting the 13C shifts of any carbon atom of the alkanes.[13,14] The methods are based on comparison of the 13C shift of methane and the observed differences as methyl groups are successively substituted. These differences were defined as the methyl substituent effects.

In the present study all the static C_3 to C_8 alkyl cations were