Acknowledgment. We thank the Centre National de la Recherche Scientifique and the Société Nationale Elf-Aquitaine for continuous support, the Compagnie Française des Pétroles for financial support, and help in the collection, by Dr. M. Dastillung, of the Mahakam samples.

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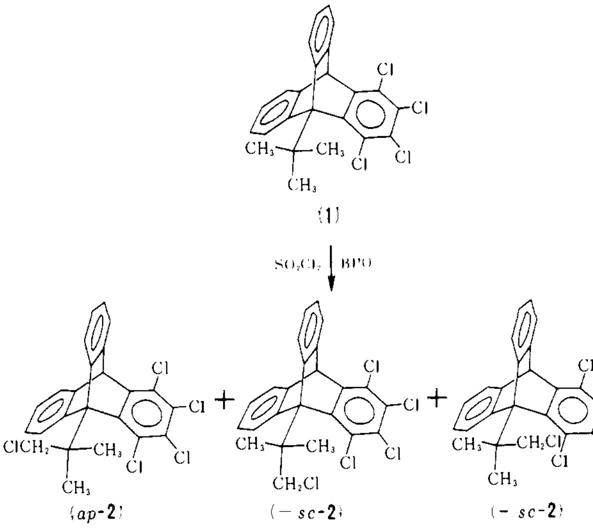
Received July 18, 1979

Differential Reactivity of the Methyls in a *tert*-Butyl Group[1]

Sir:

Chemically identical ligands in a group of local C_{3v} symmetry, such as the hydrogen atoms in a methyl group or the methyl substituents in a *tert*-butyl group, are usually treated as nondistinguishable in organic chemistry, because in most circumstances they are interchanged rapidly on the laboratory time scale by rotation. In principle, however, the methyls in the *tert*-butyl group of a molecule $(CH_3)_3CCXY_2$ can exhibit different reactivities to give diastereoisomers, since their environments are not equivalent. Although rapid internal rotation will prevent realization of this difference, it should become recognizable if the rotation is frozen: the compound will then produce two kinds of diastereoisomers on substitution at the *tert*-butyl group with two different reaction rates. We report in this communication that this situation is realized in 9-*tert*-butyl-1,2,3,4-tetrachlorotriptycene (**1**).



(1)

When **1** in chlorobenzene was treated with sulfuryl chloride under reflux for 1 h with a small amount of benzoyl peroxide, the chromatographic fraction of the monochlorinated products (**2**) showed an ±*sc*/*ap* ratio of 3.2:1 according to the ^{1}H NMR spectrum. Although the separation of the *ap* and ±*sc* isomers was tedious, it was found that the ±*sc* forms were destroyed by chromatography on alumina. The pure *ap*-**2** eluted by hexane–benzene (6:4) had the following properties: mp 251.2–252.5 °C; ^{1}H NMR (CCl_4) δ 2.38 (6 H, s), 4.51 (2 H, s), 6.02 (1 H, s), 6.8–8.0 (8 H, m).[2]

The formation ratio (3.2:1) of the ±*sc* to the *ap* forms was reproducible; yet the negligibility of isomerization during the reaction must be established. The rates of isomerization represented by eq 2 were measured at two temperatures: $k_1 = 1.21 \times 10^{-4}$ and $k_{-1} = 1.28 \times 10^{-4}\ s^{-1}$ at 208 °C, $k_1 = 2.49 \times 10^{-5}$ and $k_{-1} = 2.60 \times 10^{-5}\ s^{-1}$ at 185 °C. Thus a rough estimate of the rates of isomerization at the boiling point of chlorobenzene (132 °C) is possible: it takes 14 days for effecting the conversion of 5% of the materials which is considered to be no more than the error limit of the integration in NMR spectroscopy.

$$ap\text{-}\mathbf{2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \pm sc\text{-}\mathbf{2} \qquad (2)$$

The preferential attack on the ±*sc* methyls over the *ap* by the factor of 1.6 is caused by the presence of the chloro group in 1 position. This conclusion is drawn because 9-*tert*-butyl-1-chlorotriptycene afforded chlorination products in a 2.6:1 ±*sc*:*ap* ratio, whereas 9-*t*ert-butyl-2,3-dichlorotriptycene gave a mixture of monochlorinated products with a 2:1 ratio of the ±*sc* and the *ap* forms, which is the statistical value.

Two explanations are possible for the observed preference of the ±*sc* methyls in the reaction. One is to ascribe the phenomenon to a steric effect. Since X-ray analysis of **1** has revealed that the *tert*-butyl group is tilted against the *peri*-chloro group,[3] the *ap* methyl is pushed into the triptycyl moiety. This might make the ±*sc* methyls more exposed to the attack of chlorine atoms. The other is to consider the participation of the chloro group in the 1 position: a chloro group is known to facilitate radical formation, although not to a very extensive degree.[4]

Photobromination of hydrocarbons is known to give better

0002-7863/80/1502-1173$01.00/0

selectivity than chlorination and thus should enhance the formation ratio of the ±*sc* to the *ap* form[5] if the chloro group participates in stabilizing the transition state. Contrariwise, the ratio should be almost invariant if the steric factor dominates. In the event, bromination of **1** with bromine by irradiation gave an ±*sc*:*ap* ratio of 5.6. ±*sc*-9-(2-Bromo-1,1-dimethylethyl)-1,2,3,4-tetrachlorotriptycene was obtained 90% pure: ^{1}H NMR ($CDCl_3$) δ 2.14 (3 H, s), 2.36 (3 H, s), 4.39 (2 H, apparent s), 6.10 (1 H, s), 6.95–8.15 (8 H, m). Chlorination with chlorine by irradiation may also be used for the diagnosis, since chlorination with sulfuryl chloride is known to be slightly more selective than chlorination with chlorine.[6] Again, if the steric effect is a dominating factor, chlorination with chlorine should give an almost invariant ±*sc*:*ap* ratio, whereas, if the participation of the chloro group is important in eq 1, the ±*sc*:*ap* ratio should be diminished. We found that the actual reaction gave an ±*sc*:*ap* ratio of 2.0 which is the statistical value; i.e., the participation hypothesis is verified.

A competitive reaction of **1** and 9-*tert*-butyltriptycene (**3**) allows comparison of the reactivities of the methyl groups concerned. If the reactivity of a methyl group in **1** is suppressed relative to that of a methyl in **3**, it may mean that disfavorable steric and/or electronic effects are present in **1**. Relative reactivities of the ±*sc* and the *ap* methyls in **1** were 1.0 and 0.7, respectively, in chlorination with sulfuryl chloride, taking one of the three methyl groups in **3** as a standard. The retardation may not be taken as evidence of the steric effect, if one considers the fact that chlorine atoms are electron-demanding radicals.[7,8] We feel it is informative that the competitive bromination between **1** and **3** gives the relative reactivities of 2.6 and 0.9 for the ±*sc* and the *ap* methyls, respectively.

It has now become clear that identical substituents may react at different rates to produce different rotamers. We conclude from the data shown above that, among three methyls in a *tert*-butyl group of **1**, the ±*sc* methyls are more reactive toward halogen radicals because of chloro-group participation. Other substituents which delocalize the odd electron should enhance the reactivities of the ±*sc* methyls as well.

Finally, the rotational isomers of **2** were found to react quite differently toward Lewis acids, as were the behaviors in chromatography on alumina: ±*sc*-**2** was destroyed by addition of $TiCl_4$ to its solution, whereas $SbCl_5$ was required to destroy *ap*-**2**. The details will be reported elsewhere.

Acknowledgment. We acknowledge the receipt of a grant from Toray Science Foundation which supported this work.

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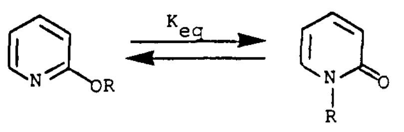
Received July 23, 1979

Photoelectron-Determined Core Binding Energies and Predicted Gas-Phase Basicities for the 2-Hydroxypyridine ⇌ 2-Pyridone System

Sir:

Much attention has been devoted to the gas-phase tautomerism established between 2-hydroxypyridine (**1a**) and 2-pyridone (**2a**, eq 1).[1] In solution the equilibrium position of **1a** ⇌ **2a** lies far to the right,[2] while in the gas phase **1a** is slightly favored.[1,3] As part of our continuing interest in the application of X-ray photoelectron spectroscopy (X-ray PES) to tautomeric equilibria,[4] we have investigated the N_{1s} and O_{1s} binding energies for **1** and **2** as well as that of the analogous 2-hydroxypyridine *N*-oxide (**3a**) and *N*-ethoxy-2-pyridone (**4b**) (eq 2) with the intent of observing core ionizations from those species present in the gas phase. These data allow one to unambiguously confirm the position of the **1a** ⇌ **2a** equilibrium found recently by Beak[1b] and show that the equilibrium for **3a** ⇌ **4a** lies (within the limits of detection of this technique) completely on the side of **4a**. Moreover from a correlation of N_{1s} binding energies for a series of 2-X-pyridines with existing gas-phase basicities, one can estimate the gas-phase basicity of **1a**.



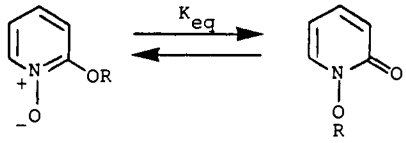
(1)

1a R = H
b R = CH_3

2a R = H
b R = CH_3

$$K_{eq}\ (\text{soln.}) = 910^{2}$$

$$K_{eq}\ (\text{gas}) = 0.4 \pm 0.25^{1b}$$



(2)

3a R = H
b R = CH_2CH_3

4a R = H
b R = CH_2CH_3

For ease of visualization, the N_{1s} and O_{1s} ionization regions of **1a** ⇌ **2a** obtained at 130 °C[5] are presented in Figure 1, while the binding energies for those and related derivatives are compiled in Table I. Relative to pyridine (BE = 404.94 eV)

Table I. O_{1s} and N_{1s} Binding Energies (BE) for Compounds **1–4**[a]

compd	binding energy, eV[b]	
	N_{1s}	O_{1s}
pyridine	404.94 (404.82)[c]	
2-hydroxypyridine (**1a**)	404.96	539.45
2-methoxypyridine (**1b**)	404.68	538.91
2-pyridone (**2a**)	406.61	536.66
N-methyl-2-pyridone (**2b**)	406.33	536.36
N-hydroxy-2-pyridone (**4a**)	408.07[d]	540.08 (O—H) 537.01 (C=O)
N-ethoxy-2-pyridone (**4b**)	407.41	539.58 (OEt) 536.49 (C=O)
pyridine *N*-oxide	408.65[d]	536.00[d]

[a] Each BE is the average of at least three determinations and has a precision of ±0.03 eV unless otherwise noted. [b] Calibrated against a Ne auger line with 804.56-eV kinetic energy (T. D. Thomas and R. W. Shaw, *J. Elect. Spectrosc.*, **5**, 1081 (1974)). [c] Reference 7e. [d] Precision ±0.10 eV.

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