temperature. The mixture was poured onto ice and dichloromethane (500 mL) was added. The organic layer was separated, washed with water, dried over sodium sulfate, and evaporated to furnish a brown residue which was dissolved in 10% NaOH solution. The solution was extracted with ether, and the aqueous layer was acidified with 2 N HCl. The brown solid was collected and the process repeated to afford 18.0 g (61%) of a mixture of keto acids **2** and **3**. The mixture of **2** and **3** (18 g) was dissolved in NH_4OH solution (30%, 600 mL). Zinc dust (60 g) and a few crystals of $CuSO_4$ were added and the mixture vigorously stirred at reflux for 12 h. The mixture was filtered and the solid washed with 10% NaOH and H_2O. The combined filtrates were acidified with HCl, and the grey solid was collected and dried under reduced pressure affording 13 g (78%): ^1H NMR ($CDCl_3$) δ 4.60, 4.88 (s in 1:2 ratio), 6.6 to 8.4 (c), 11.8 (bs, CO_2H). The grey solid was fractionated into pure acids **4** and **5** by multiple crystallization from nitromethane, choroform, benzene, and a mixture of benzene–hexane. The progress of the separation of the two isomers **4** and **5** was monitored by ^1H NMR [**4**, 4.88 (s, 2 H); **5**, 4.60 (s, 2 H)]. Compound **4** crystallized first. The following fractions were obtained: **4** (6.5 g), **5** (2.2 g), and a mixture of **4** and **5** (4 g).

2-(2-Fluoro-8-napthylmethyl)benzoic acid (4): mp 160–162 °C (benzene, sublimes); IR (KBr) 1700 cm^{-1} (C=O); UV λ_{max} (MeOH) 320 (ϵ 1.47 × 10^3), 313 (0.73 × 10^3), 306 (0.76 × 10^3), 288 (5.88 × 10^3), 283 (6.60 × 10^3), 278 (7.35 × 10^3), 273 (4.56 × 10^3), 268 (3.80 × 10^3), 263 (4.41 × 10^3); ^1H NMR ($CDCl_3$) δ 4.84 (s, 2 H, $-CH_2-$), 7.0–7.8 (c, 9 H, aromatic), 8.1 (c, 1 H, C-7 H), 11.7 (bs, 1 H, CO_2H). Anal. Calcd for $C_{18}H_{13}FO_2$: C, 77.13; H, 4.67; F, 6.78. Found: C, 77.04, 76.92; H, 4.64, 4.65; F, 6.73, 6.74.

2-(2-Fluoro-6-napthylmethyl)benzoic acid (5): mp 153–154 °C (benzene); IR (KBr) 1700 cm^{-1} (C=O); UV λ_{max} (MeOH) 323 (ϵ 1.73 × 10^3), 315 (1.0 × 10^3), 308 (1.26 × 10^3), 302 (8.0 × 10^2), 294 (1.0 × 10^3), 280 (5.60 × 10^3), 271 (6.66 × 10^3), 263 (5.86 × 10^3); ^1H NMR ($CDCl_3$) δ 4.60 (s, 2 H, $-CH_2-$), 7.0–7.8 (c, 9 H, aromatic), 8.13 (d, 1 H, J = 8 Hz, C-7 H), 10.0–11.0 (b, 1 H). Anal. Calcd for $C_{18}H_{13}FO_2$: C, 77.13; H, 4.67; F, 6.78. Found: C, 76.91, 76.96; H, 4.83, 4.75; F, 6.77, 6.69.

2-Fluorobenz[*a*]anthraquinone (8) and 3-Fluorbenz[*a*]anthraquinone (9). A suspension of **4** (1.0 g; 3.7 mmol) in concentrated sulfuric acid (70 mL) was stirred at room temperature for 90 min. The mixture was then poured onto crushed ice. The yellow suspension was filtered through celite, washed with water, and eluted with tetrahydrofuran (500 mL). Evaporation of the THF solution, after drying over sodium sulfate, furnished a yellow solid which was oxidized in glacial acetic acid (50 mL) with potassium dichromate (7 g) at reflux for 40 min. The mixture was poured onto ice and filtered through Celite. Elution of celite with THF (300 mL) and subsequent evaporation furnished quinone **8**, 600 mg (62% from **4**). A sample for analysis was prepared by two crystallizations from acetone. A similar reaction sequence with **5** (920 mg) furnished **9** (600 mg; 66% from **5**).

2-Fluorobenz[*a*]anthraquinone (8): mp 184–185 °C (acetone); IR (KBr) 1690 cm^{-1} (C=O); UV λ_{max} (MeOH) 395 (ϵ 2.65 × 10^3), 336 (2.65 × 10^3), 278 (2.65 × 10^4), 252 (1.43 × 10^4), 246 (1.44 × 10^4), 234 (1.44 × 10^4); ^1H NMR ($CDCl_3$) δ 7.0–8.6 (c, 8 H, aromatic), 9.4 (dd, 1 H, J_{H1-F2} = 13 Hz, J_{H1-H3} = 2.5 Hz). Anal. Calcd for $C_{18}H_9FO_2$: C, 78.25; H, 3.28; F, 6.88. Found: C, 77.29, 77.47; H, 3.26, 3.24; F, 6.92.

3-Fluorobenz[*a*]anthraquinone (9): mp 203–205 °C (acetone); IR (KBr) 1690 cm^{-1} (C=O); UV λ_{max} (MeOH) 362 (ϵ 3.7 × 10^3), 330 (3.7 × 10^3), 281 (3.24 × 10^4), 252 (1.99 × 10^4), 246 (1.99 × 10^4), 232 (1.99 × 10^4); ^1H NMR ($CDCl_3$) 7.35–8.5 (c, 8 H), 9.80 (dd, 1 H, J_{H1-H2} = 9.6 Hz, J_{H1-F3} = 6.0 Hz). Anal. Calcd for $C_{18}H_9FO_2$: C, 78.25; H, 3.28; F, 6.88. Found: C, 77.99, 77.97; H, 3.55, 3.49; F, 6.66, 6.64.

2-Fluoro-7,12-dimethylbenz[*a*]anthracene (14). A solution of quinone **8** (700 mg; 2.54 mmol) in dry benzene (200 mL) was added dropwise to a Grignard prepared from magnesium turnings (1.20 g; 0.05 mol) and CH_3I (15.0 g; 0.105 mol) in ether (100 mL). The mixture was refluxed for 10 h. Saturated ammonium chloride (50 mL) and ethyl acetate (100 mL) were added. The organic layer, after drying over sodium sulfate, was evaporated to furnish a yellow gum. The gum was dissolved in dry ethyl acetate (100 mL) and dry HCl was bubbled through the solution at 0 °C for 40 min. After an additional 2 h, the solution was evaporated to dryness. The residue was dissolved in THF (20 mL) and poured into a vigorously stirred suspension of $LiAlH_4$ (200 mg) in ether (150 mL) at room temperature under N_2. After 1 h, excess $LiAlH_4$ was destroyed by addition of saturated NH_4Cl, and the ether layer was dried over sodium sulfate and evaporated to furnish a yellow gum which on column chromatography over silica gel (hexane–benzene; 1:1) furnished pure 2F-DMBA (**14**): 210 mg (30% from **8**); mp 93–94 °C (hexane); UV λ_{max} (MeOH) 293 (ϵ 6.69 × 10^4), 283 (5.95 × 10^4), 273 (3.84 × 10^4), 260 (3.80 × 10^4), 221 (4.00 × 10^4); ^1H NMR ($CDCl_3$) δ 3.00 (s, 3 H, 7-CH_3), 3.30 (s, 3 H, 12-CH_3), 7.0–7.8 (c, aromatic), 8.0 (d, 1 H, J = 9.0 Hz, C-6 H), 8.1–8.5 (c). Anal. Calcd for $C_{20}H_{15}F$: C, 87.56; H, 5.51. Found: C, 87.41; H, 5.51.

A similar reaction sequence with quinone **9** (700 mg) furnished 3F-DMBA (**15**): 170 mg (24% from **9**); mp 113–114 °C (hexane); UV λ_{max} (MeOH) 362.5 (ϵ 0.75 × 10^3), 345 (0.75 × 10^3), 305 (1.50 × 10^3), 294 (6.90 × 10^4), 284 (6.90 × 10^4), 274 (4.68 × 10^4), 262 (4.68 × 10^4), 227 (1.90 × 10^3); ^1H NMR ($CDCl_3$) δ 3.00 (s, 3 H, 7-CH_3), 3.25 (s, 3H, 12-CH_3), 7.12–7.90 (c), 8.02 (d, C-6 H), 8.2–8.45 (c). Anal. Calcd for $C_{20}H_{15}F$; C, 87.56; H, 5.51; F, 6.93. Found: C, 87.64, 87.53; H, 5.51, 5.60; F, 7.02, 6.98.

Acknowledgment. Financial assistance from Public Health Service Grant No. CA-21371 from the National Cancer Institute and Environmental Protection Agency Grant No. R 805337 is gratefully acknowledged.

Registry No. 1, 323-09-1; 2, 71276-91-0; 3, 3799-80-2; 4, 71277-74-2; 5, 71250-14-1; 8, 71250-15-2; 9, 71250-16-3; 14, 68141-56-0; 15, 71250-17-4.

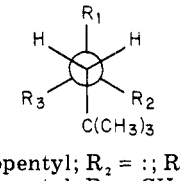
Comments on "Synthesis and Nuclear Magnetic Resonance Study of Neopentyl and (Trimethylsilyl)methyl Derivatives of Phosphorus"

John Jacobus

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Received April 23, 1979

In a recent article, Singh and Reddy[1] deduced the preferred conformations of compounds **2**, **4**, **5**, **12**, **10**, **1**, and **11** (their numbering) by analysis of the nonequivalence of proton resonance signals of the methylene groups of neopentyl ($(CH_3)_3CCH_2$) or (trimethylsilyl)methyl ($(CH_3)_3SiCH_2$) substituents attached to phosphorus. Compounds **2**, **4**, **10**, and **12** exhibit methylene non-



2, R_1 = neopentyl; R_2 = :; R_3 = phenyl
4, R_1 = neopentyl; R_2 = CH_3; R_3 = phenyl
12, R_1 = neopentyl; R_2 = =O; R_3 = phenyl
10, R_1 = phenyl; R_2 = =O; R_3 = methyl
5, R_1 = neopentyl; R_2 = phenyl; R_3 = phenyl
1, R_1 = phenyl; R_2 = :; R_3 = phenyl
11, R_1 = phenyl; R_2 = =O; R_3 = phenyl

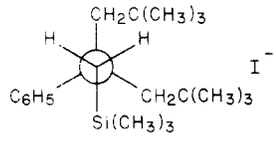
equivalence while compounds **1**, **5**, and **11** do not. (In the Newman projection given here, the rear atom is phosphorus; for **4** and **5** the anion is iodide.) Singh and Reddy concluded that because **2**, **4**, and **12** do not exhibit collapse of the methylene AB quartet (phosphorus coupling ig-

(1) G. Singh and G. S. Reddy, *J. Org. Chem.*, **44**, 1057 (1979).

0022-3263/79/1944-3717$01.00/0

nored) at 160°, these compounds are "locked in structures with the neopentyl groups in trans positions". They further conclude that since for **10** "collapse" of the two methylene doublets (actually two methylene quartets when phosphorus coupling is considered) occurs at 60°, the rotational barrier about the phosphorus–carbon bond in **10** is ca. 16 kcal/mol.

Simple symmetry arguments[2] demand the observed nonequivalence for **2**, **4**, **12**, and **10** without recourse to conformational arguments, and similarly these same arguments demand that **5**, **1**, and **11** not exhibit nonequivalence. Compounds **2**, **4**, **12**, and **10** lack the plane of symmetry in any conformation that **5**, **1**, and **11** possess in a single (noneclipsing) conformation. The methylene protons of **2**, **4**, **12**, and **10** are diastereotopic and observably anisochronous, while those of **5**, **1**, and **11** are enantiotopic and, expectedly under achiral conditions, isochronous. Further, it can be categorically stated that the observed "collapse" of the methylene signals of **10** is accidental, i.e., an artifact of temperature-dependent chemical shifts, and is in no manner an indicator of the phosphorus–carbon rotational barrier. Lastly, for **9**, the



9

observation that the CH_2Si signal is a singlet while that of the $CH_2C(CH_3)_3$ groups is an AB quartet is a priori predictable; the CH_2Si groups are enantiotopic while the $CH_2C(CH_3)_3$ groups are diastereotopic.

In conclusion, no information relative to the conformations of compounds **1**, **2**, **4**, **5**, **9**, **10**, **11**, or **12** can be deduced from this study other than that the phosphorus–carbon rotational barriers of **1**, **5**, and **11** are, as expected, low.

(2) (a) K. Mislow and M. Raban, *Top. Stereochem.*, 1, 1 (1967); (b) J. Jacobus and M. Raban, *J. Chem. Educ.*, **46**, 351 (1969).

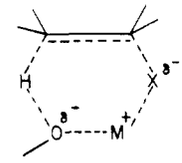
Reactivity of Free and Associated Phenoxides in Syn and Anti Elimination Reactions in Dimethyl Sulfoxide

Enrico Baciocchi,* Renzo Ruzziconi, and Giovanni V. Sebastiani

Dipartimento di Chimica, Università di Perugia, Perugia, Italy

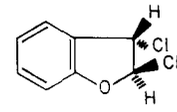
Received March 8, 1979

It is now well recognized that in an E2 elimination the competition between anti and syn pathways can be strongly influenced by the base association.[1] Namely, the relative proportion of the syn process generally increases when the reaction is carried out under experimental conditions favoring the formation of contact pairs or larger aggregates. It has been suggested that syn eliminations promoted by an associated base take place via the transition state **1**, where a presumably advantageous interaction between the leaving group and the positive counterion is possible.

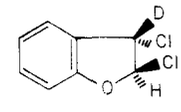


1

In order to get more quantitative information on this problem it seemed of interest to look for systems where the contributions of free ions and contact pairs to the overall rate can be separately evaluated with reasonable precision. This separation appeared possible for reactions promoted by phenoxides in dimethyl sulfoxide (Me_2SO). Thus, we have kinetically investigated the eliminations from *trans*-2,3-dihydro-2,3-dichlorobenzofuran (**2**), its 3-deuterated counterpart (**3**) (syn processes), and 2-phenylethyl chloride (**4**) (anti process), in this base–solvent system. For comparison purpose also the substitution reactions of *n*-butyl bromide (**5**) have been studied. Even though the extent of base association is not very high in Me_2SO, recent studies have shown that it is sufficient to significantly change the relative proportion of syn and anti elimination from 3-hexyl tosylate.[2]



2



3

Results and Discussion

The reactions of **2**–**5** have been carried out in 99% Me_2SO[3] using tetraethylammonium phenoxide as the base in the absence and in the presence of LiBr (0.015–0.15 M). From **2** and **3**, 3-chlorobenzofuran is the exclusive reaction product (see Experimental Section). The quantitative formation of styrene from **4** and *n*-butyl phenyl ether from **5** has been shown by previous work.[4,5]

Kinetics have been followed spectrophotometrically measuring the rate of disappearance of the base at 310–330 nm. The phenoxide concentration has been kept at ca 4 $\times 10^{-4}$ M, that of the substrate being 15–100 fold higher. Excellent first-order plots have been obtained in each case and the second-order rate constants (k_{obsd}) calculated as usual. All kinetic data are collected in Table I.

In consideration of the nature of the salt and its low concentration, it is reasonable to assume that k_{obsd} values obtained in the reactions promoted by tetraethylammonium phenoxide represent the rate constants (k_i) of nonassociated phenoxide ions. The absence of association of tetraethylammonium phenoxide is also clearly shown by the fact that in the presence of tetraethylammonium bromide (up to 0.1 M) there is practically no change in k_{obsd} for the reactions of **2**, **4**, and **5**.

In contrast, k_{obsd} decreases drastically when the reactions are carried out in the presence of LiBr. This is certainly

(1) Sicher, J. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 200; Pánková, M.; Svoboda, M.; Závada, J. *Tetrahedron Lett.* **1972**, 2465 and references cited therein. Bartsch, R. A.; Wiegers, K. E. *Ibid.* **1972**, 3819.

(2) Borchardt, J. L.; Swanson, J. C.; Saunders, W. H., Jr., *J. Am. Chem. Soc.* **1974**, *96*, 3918.

(3) The solution of tetraethylammonium hydroxide in Me_2SO used to convert phenol into phenoxide ions was slightly aqueous (see Experimental Section). Since different amounts of this solution were necessary in the various experiments the use of 99% Me_2SO was considered opportune in order to avoid changes in the water content of the solvent that could significantly influence the reaction rate.

(4) Alunni, S.; Baciocchi, E.; Perucci, P.; Ruzziconi, R. *J. Org. Chem.* **1978**, *43*, 2414.

(5) Berge, A.; Ugelstad, J. *Acta Chem. Scand.* **1965**, *19*, 742. Ugelstad, J.; Ellingsen, T.; Berge, A. *Acta Chem. Scand.* **1966**, *20*, 1593.

0022-3263/79/1944-3718$01.00/0