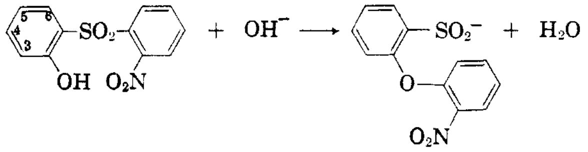
Communications TO THE EDITOR

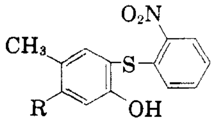
Steric Acceleration through Regulation of Rotational Conformation[1]

Sir:

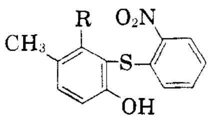
McClement and Smiles[2] discovered that the base-promoted (Smiles) rearrangement of 2-hydroxy-2′-nitrodiphenyl sulfones to 2-sulfino-2′-nitrodiphenyl ethers is strongly accelerated by 6-methyl groups. They offered an electronic interpretation of the effect, but Bunnett and Zahler[3] considered the electronic interpretation unconvincing and showed that the acceleration could be easily understood from steric considerations. We now present proof of the steric origin of the effect, and show that the magnitude of the acceleration is much greater than indicated by McClement and Smiles.



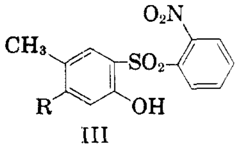
Mixtures of 4-substituted- and 6-substituted-2-hydroxy-5-methyl-2′-nitrodiphenyl sulfides (I and II, respectively) were formed by condensation of *o*-nitrobenzenesulfenyl chloride with 3,4-dimethylphenol, 3-chloro-*p*-cresol, and 3-bromo-*p*-cresol.



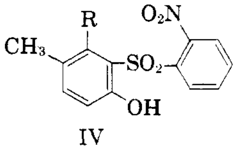
I



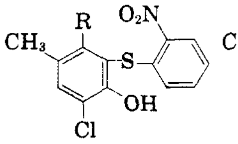
II



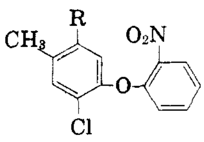
III



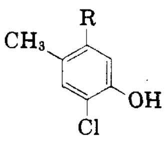
IV



V



VI



VII

The mixtures were separated by chromatography on alumina, and the minor component was assigned structure II. In each case, this assignment was confirmed by chlorination of the minor component to a sulfide of structure V, oxidation to the corresponding sulfone, rearrangement, and desulfination to form an ether of structure VI, identical to the ether formed by condensation of the appropriate 3-substituted-6-chloro-*p*-cresol (VII) with *o*-chloronitrobenzene. Sulfones of types III and IV were produced by oxidation of the corresponding sulfides. The following properties were observed for compounds of types I, II, III and IV:

		Calc'd		Found	
Compound	m.p., °C.	C	H	C	H
I, R = CH_3	163–165	61.06	4.75	60.93	4.81
I, R = Cl	191–193	52.79	3.41	53.10	3.58
I, R = Br	198–200	45.89	2.96	45.88	2.96
II, R = CH_3	175–177	61.06	4.75	61.17	4.75
II, R = Cl	175–177	52.79	3.41	52.77	3.58
II, R = Br	173–176	45.89	2.96	46.15	3.26
III, R = CH_3	178–181	54.71	4.26	54.40	4.23
III, R = Cl	128–130	47.64	3.08	47.34	3.24
III, R = Br	152–154	41.95	2.71	41.61	2.90
IV, R = CH_3	140–142	54.71	4.26	54.51	4.32
IV, R = Cl	169–171	47.64	3.08	47.71	3.26
IV, R = Br	154–156	41.95	2.71	42.32	2.85

The Smiles rearrangement of the sulfones of types III and IV was kinetically first order in 50% aqueous dioxane. About a 25% excess of sodium hydroxide was used to promote the reaction, and the rate was followed by potentiometric acid-base titration, an analytical procedure which was quite satisfactory with III and IV (R = H or CH_3) but furnished only approximate rates with III and IV (R = Cl or Br). Rate coefficients were as follows:

Sulfone	Rate coefficient (min.$^{-1}$)	
	at 46.0°	at 0.0°
III, R = H	1.9×10^{-2}	
III, R = CH_3	1.6×10^{-2a}	$3.6 \times 10^{-5a,b}$
III, R = Cl	*ca.* 1.2×10^{-3}	
III, R = Br	*ca.* 1.2×10^{-3}	
IV, R = CH_3		>3.0
IV, R = Cl		*ca.* 0.8
IV, R = Br		>3.0

[a] Determination by Mr. Kenneth Pruitt. [b] Estimated from rate coefficients at 46.0° and 25.0°.

All the sulfones (III) with an unsubstituted 6-position rearranged rather slowly at 46°, and all those (IV) with 6-substituents rearranged very rapidly at 0° (IV, R = CH_3 and IV, R = Br

---

[1] Work supported by the Office of Ordnance Research U. S. Army.

[2] C. S. McClement and S. Smiles, J. Chem. Soc., 1016 (1937).

[3] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 369 (1951).

rearranged completely within one minute at 0°). Since the reaction is strongly accelerated by both electron-attracting and electron-releasing 6-substituents, the cause of the acceleration is proved to be steric and not electronic. The magnitude of the acceleration can be judged from the rates of rearrangement of the isomers III and IV, R = CH_3; moving the methyl group from the 4- to the 6-position causes an increase in rate of 100,000-fold or more.

Our interpretation of this novel and tremendous steric accelerating effect is essentially that of Bunnett and Zahler. In order for the anion from a 2-hydroxy-2′-nitrodiphenyl sulfone to rearrange, it must first assume a rotational conformation in which the ionized 2-hydroxy group is brought against the broad side of the other ring in the vicinity of the 1′-position. Such conformations have a high free energy owing to steric compressions between the solvated ionized 2-hydroxy group and the carbon atoms of the other ring. In the case of sulfones lacking 6-substituents, other conformations, especially some in which the 6-H is close to the 1′-position, are energetically favored and therefore most heavily populated. For a molecule in a "non-rearranging" conformation to rearrange, it must first rotate against an energy differential to a "rearranging" conformation. Placing a large substituent in the 6-position increases the free energy of "non-rearranging" conformations, especially those in which the 6-position is close to the 1′-position, owing to crowding between a large 6-substituent and the carbon atoms of the other ring. The result is a decrease in the energy differential between "rearranging" and "non-rearranging" conformations, an increase in population in "rearranging" conformations, and a higher rate of rearrangement.

We expect the steric acceleration involves favorable changes in both the energy and entropy of activation, and are continuing our investigation of the kinetics of these reactions.

VENABLE CHEMICAL LABORATORY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA

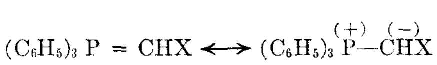
T. OKAMOTO
J. F. BUNNETT

Received February 13, 1956

Triphenylphosphoniumcyclopentadienylide

Sir:

The recent interest in the chemistry of phosphinemethylenes[1] (Ia ⟷ Ib) has culminated in the development by Wittig and his co-workers[2] of a new and valuable olefin synthesis.



$$(C_6H_5)_3\,P = CHX \longleftrightarrow (C_6H_5)_3\,\overset{(+)}{P}-\overset{(-)}{C}HX$$

Ia Ib

$$R_2CO + I \longrightarrow R_2C{=}CHX + (C_6H_5)_3PO$$

From this[2] and from previous work[3] it has emerged that the stability of the phosphinemethylenes (I), their color and their ability to react with carbonyl groups are intimately connected with the distribution of the negative charge in the molecule. Thus, the red phosphinemethylene (I) in which X = phenyl is much less reactive toward carbonyl groups than the yellow analog in which X = H. These substances are poorly stable either in the solid state or in solution, and even the compound I in which X = *p*-nitrophenyl (vermilion color), is said to be unstable in chloroform solution, although "stable for some time" in the crystalline state.[3]

It appeared timely, in view of these reports, to describe our results with triphenylphosphoniumcyclopentadienylide (II), a phosphinemethylene which owes its remarkable stability to the distribution of the negative charge over the cyclopentadienide ring, as part of the aromatic system of (4n + 2) electrons.[4] II was obtained as *pale yellow* crystals, m.p. 229–231° (from toluene); Calc'd for $C_{23}H_{19}P$: C, 84.6; H, 5.9; P, 9.5; M.W. 326. Found: C, 84.7; H, 6.1; P, 9.5; M.W. (Rast), 338. Bands at 6.78(m), 7.03(s), 7.42(m), 7.67(m), 8.25(s), 8.35(m), 8.50(m), 9.05(s) μ (in KBr). The U.V. absorption spectrum of II had $\lambda_{max.}$ at 222 mμ (ϵ 38,200) and 250 mμ (ϵ 21,600) in acetonitrile and exhibited a tailing into longer wave lengths, the ϵ value at 295 mμ being 5,900 and that at 375 mμ, less than 100. No absorption was observed in the visible. II formed a *picrate* of m.p. 142–144° (from benzene); Calc'd for $C_{29}H_{22}N_3O_7P$: C, 62.7; H, 4.0. Found: C, 63.0; H, 4.2.

The phosphinemethylene II is not affected by hot, dilute aqueous or alcoholic potassium hydroxide, does not react with cyclohexanone even at elevated temperatures, does not absorb hydrogen in benzene solution (PtO_2 catalyst) and in general, displays great stability in the solid state or in solution. II is readily soluble in dilute mineral acid, and from this solution it can be reprecipitated by alkali. A solution of II in dilute hydrobromic acid absorbed two molequivalents of hydrogen (Pt-catalyst) at atmospheric pressure and yielded triphenylcyclopentylphosphonium bromide (III), identical with a sample prepared from cyclopentyl bromide and triphenylphosphine. III had m.p. 261–263° (from water), $\lambda_{max.}$ 226 mμ (ϵ 25,200), 262 mμ (ϵ 4,000), 268 mμ (ϵ 4,700) and 271 mμ (ϵ 3,900); Calc'd for $C_{23}H_{24}BrP$: C, 67.2; H, 5.9. Found: C, 67.0, H, 5.8.

The preparation of the phosphinemethylene II

---

[1] *Cf.* G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 28, 355.

[2] G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955); previous references given here.

[3] F. Kröhnke, *Chem. Ber.*, **83**, 291 (1950).

[4] See W. Baker and J. McOmie in J. W. Cook, *Progress in Organic Chemistry*, Academic Press Inc., New York, N. Y., vol. III, 1955, p. 58.