## 4-Hydroxybenzenesulfonyl Chloride

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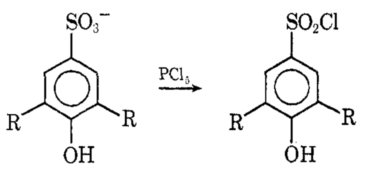
A variety of 3,5-disubstituted 4-hydroxybenzenesulfonyl chlorides have been reported in the literature.[1-4] They were obtained either from the reaction of the corresponding sulfonate salt with a chlorinating agent or by direct chlorosulfonation of the corresponding phenol. The parent compound, 4-hydroxybenzenesulfonyl chloride (I), apparently resisted synthesis because of the reactive, unhindered phenolic group. Anschutz[5] reported in 1908 that treatment of potassium 4-hydroxybenzenesulfonate with phosphorus pentachloride yielded the dichlorophosphate ester of I.



$R = CH_3$, Cl, Br

We have reinvestigated this reaction and found that sodium 4-hydroxybenzenesulfonate (II) treated with phosphorus pentachloride under a variety of conditions gave product mixtures showing no hydroxyl absorption in the infrared. Reactions of chlorosulfonic acid with II or phenol gave complex reaction mixtures which failed to yield the desired sulfonyl chloride. When II was treated with thionyl chloride using dimethylformamide as solvent, small amounts of intractable oils were obtained which showed very little hydroxyl absorption.

We have found, however, that, if II is suspended in a substantial excess of thionyl chloride containing a catalytic amount of dimethylformamide for several hours at 60°, an 80–90% yield of I is obtained, mp 68–70°. A complicating feature of the work-up is the fact that this material absorbs sufficient water to form an oily layer when poured over ice, making filtration impossible. Extraction techniques result in a partitioning of the dimethylformamide between the aqueous and organic phases. The low melting point of I contributes to purification difficulties. Unsuccessful attempts were made to isolate I by sublimation, distillation, and conventional recrystallization. A technique[6] found to be useful for converting the oily reaction product to a more easily handled solid is to dissolve it in benzene, freeze the dry benzene solution, add hexane to the frozen solution, and collect the white precipitate produced as the mixture warms to room temperature. The hydroxysulfonyl chloride is then easily recrystallized from methylene chloride.

This material was found to be quite stable when stored at 0° under a nitrogen atmosphere. If all traces of dimethylformamide are removed, I is stable at room temperature when protected from atmospheric moisture. Conditions have been found[7a,b] for conversion of I into high molecular weight polymer.

A brief examination of other catalysts has shown[8] that some organophosphorus compounds (*e.g.*, triphenylphosphine, triphenylphosphine oxide, and hexamethylphosphoramide) can be used for the production of I. These reagents do not give as high conversions under the same conditions as dimethylformamide.

In 1965 King and Smith[9] published an article dealing with the sulfur–chlorine stretching band in sulfonyl chlorides. They reported the preparation of I from the reaction of phosphorus pentachloride and II. The similarity of their reported melting behavior (mp 90–92°) with that of Anschutz (mp 87–88°) combined with our observation that I has bands at 375 and 338 $cm^{-1}$ compared with King's report of bands at 377, 354, and 343 $cm^{-1}$, has led us to believe that their product was incorrectly identified.[10]

### Experimental Section

**4-Hydroxybenzenesulfonyl Chloride (I).**—A solution of 300 g (2.5 mol) of thionyl chloride and 3.0 g of dimethylformamide was quickly added to 98.1 g (0.5 mol) of sodium 4-hydroxybenzenesulfonate. The resulting mixture was stirred at 60° for 3.5 hr. At the end of this time, the mobile, nearly homogeneous reaction mixture was poured over 800 g of ice with vigorous stirring. An oily lower layer was produced and was dissolved in 300 ml of methylene chloride. The aqueous layer was extracted with 2 × 200 ml of methylene chloride and the combined organic solutions were washed with 200 ml of ice water. The organic solution was dried over $MgSO_4$ and solvent was removed *in vacuo*. The oil remaining was dissolved in 300 ml of benzene and dried over $MgSO_4$ and the solution was frozen. Hexane was added and the solution was allowed to warm to room temperature. The white precipitate was removed as it formed (3 × 30 ml of hexane used). The product was dried in a vacuum desiccator, yielding 80.7 g (84%) of crude I, mp 63–69°. Recrystallization from methylene chloride at −70° and twice at 0° yielded I: mp 68–70°; ir (Nujol mull) OH at 2.9 $\mu$, $SO_2$ at 7.4 and 8.6 $\mu$; nmr ($CDCl_3$) $\delta$ 6.70 (1 H, s, OH), 7.04 (2 H, d, $J$ = 9 Hz, protons ortho to OH), 7.94 (2 H, d, $J$ = 9 Hz, protons ortho to $SO_2Cl$). *Anal.* Calcd for $C_6H_5ClO_3S$: C, 37.5; H, 2.6; S, 16.7; Cl, 18.4. Found: C, 37.4; H, 2.7; S, 16.7; Cl, 18.4.

**Registry No.**—I, 4025-67-6; sodium 4-hydroxybenzenesulfonate, 825-90-1.

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(1) T. Zincke and W. Glahn, *Ber.*, **40**, 3039 (1907).

(2) S. Oae and R. Kiritani, *Bull. Chem. Soc. Jap.*, **38**, 1543 (1965).

(3) W. L. Hall, *J. Org. Chem.*, **31**, 2672 (1966).

(4) W. L. Hall, U. S. Patent 3,530,177, issued to General Electric Co., 1970.

(5) R. Anschutz, *Justus Liebigs Ann. Chem.*, **358**, 92 (1908).

(6) R. W. Campbell, U. S. Patent 3,658,899, issued to Phillips Petroleum Co., 1972.

(7) (a) R. W. Campbell, U. S. Patent 3,549,595, issued to Phillips Petroleum Co., 1970; (b) R. W. Campbell and H. Wayne Hill, Jr., U. S. Patent 3,565,862, issued to Phillips Petroleum Co., 1971.

(8) H. Wayne Hill, Jr., and R. W. Campbell, U. S. Patent 3,673,247, issued to Phillips Petroleum Co., 1972.

(9) J. F. King and D. J. H. Smith, *Can. J. Chem.*, **43**, 1870 (1965).

(10) After this note was submitted for publication, it was learned by the authors *via* private communication that King had independently arrived at the same conclusion.

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## The Reaction of (Carbethoxymethylene)triphenylphosphorane with ω-Nitrostyrenes and Isatoic Anhydrides

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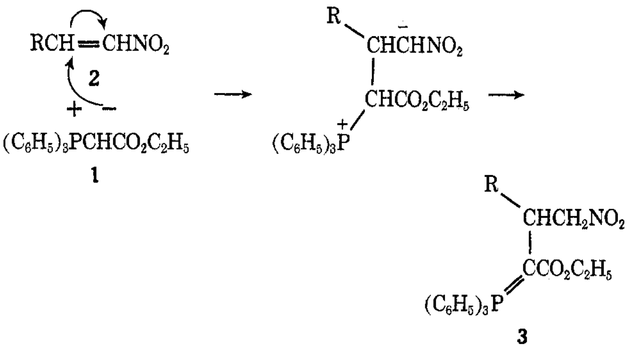
Our continuing interest in the reactions of phosphonium ylides for the production of novel, synthetically useful ylides[1] and new heterocyclic systems[1,2] led us to investigate the reaction of (carbethoxymethylene)triphenylphosphorane (**1**) with ω-nitrostyrenes and isatoic anhydrides.

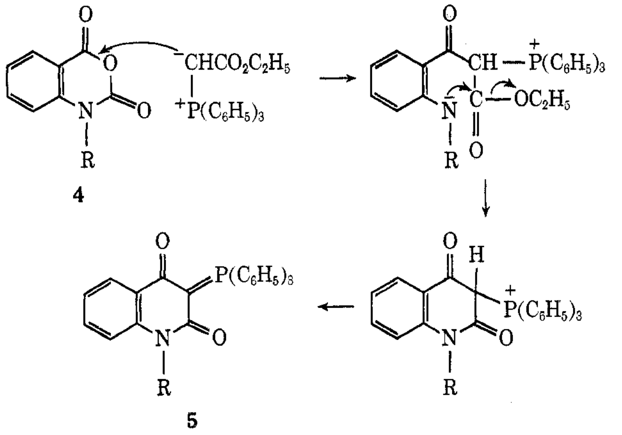
(Carbethoxymethylene)triphenylphosphorane (**1**) added to nitrostyrenes **2** (Scheme I) to give resonance-stabilized ylides **3**.

SCHEME I



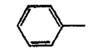
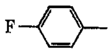
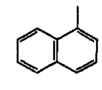
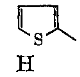
The reaction of **1** with isatoic anhydrides **4** to give resonance-stabilized ylides **5** is outlined in Scheme II.

SCHEME II



The products from the reactions are summarized in Table I. The analytical and spectral data are in agreement with the assigned structures.

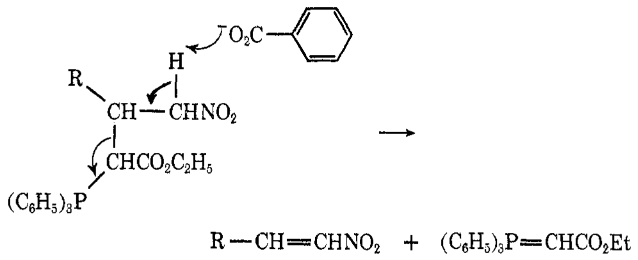
TABLE I[a]

| Compd | R | Mp, °C | Yield, % |
|---|---|---|---|
| **3a** |  | 142–144 | 38 |
| **3b** |  | 156–157 | 30 |
| **3c** |  | 198–199 | 73 |
| **3d** |  | 170–171 | 18 |
| **5a** | H | 320 dec | 50 |
| **5b** | $CH_3$ | 252–253 | 44 |

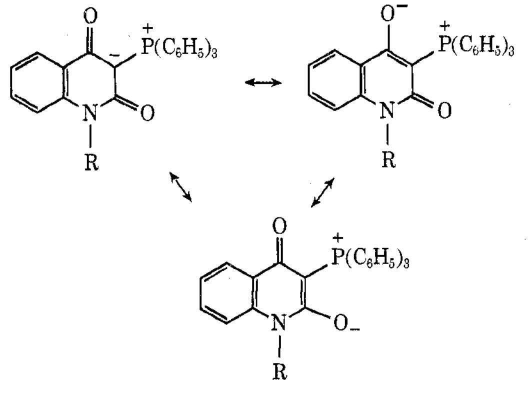
[a] Satisfactory analytical data (±0.3% for C, H, and N) were reported for all new compounds listed in the table.

The products **3** exhibited a carbonyl band at 1620 $cm^{-1}$ (Nujol) compared to 1600 $cm^{-1}$ for the corresponding band in **1**. Their nmr spectra showed characteristic peaks at δ 0.41 (t, 3 H, $CH_3$ of ethyl) and 3.7 (q, 2 H, $CH_2$ of ethyl). The ir spectra of **5a** showed bands at 1625, 1610 (sh), and 1590 $cm^{-1}$. **5b** exhibited carbonyl bands at 1595 and 1580 $cm^{-1}$ (sh) and showed a singlet (3 H) at δ 3.4 ($NCH_3$) in the nmr.

The phosphonium ylides **3** failed to undergo the Wittig reaction with aldehydes (benzaldehyde, *p*-nitrobenzaldehyde, *p*-chlorobenzaldehyde) under a variety of conditions. This contrasts with the behavior of the phosphonium ylides derived from **1** and Mannich bases[1] and can be attributed either to the steric effect of the trisubstituted carbon situated α to the carbanion carbon or to the presence of the nitro group. When benzoic acid, which is known to catalyze the reactions of **1** with ketones,[3] was added to the reaction between **3a** and *p*-chlorobenzaldehyde, the corresponding nitrostyrene was regenerated and no Wittig reaction product was detected by tlc.



The phosphonium ylides **5** also failed to react with aldehydes and were not affected by refluxing with alcoholic potassium hydroxide solution. This behavior reflects the extra stabilization (as compared to **1**) afforded by the second carbonyl group and the conjugation possible in the resonance forms.



## Experimental Section

Melting points were taken in open capillary tubes and were not corrected. Nmr spectra were recorded on a Varian Model A-60 spectrometer using TMS as an internal standard ($CDCl_3$ solvent).

**Phosphonium Ylides (3a–d).**—A solution of the nitrosytrene (0.01 mol) and (carbethoxymethylene)triphenylphosphorane (0.01 mol) in dioxane (50 ml) was refluxed for 3 hr. The dioxane was evaporated under reduced pressure to give a brown gum, which crystallized from ethyl acetate–petroleum ether (bp 30–60°). One recrystallization from the same solvents gave analytically pure material.

**Phosphonium Ylides (5a,b).**—A solution of the isatoic anhydride (0.01 mol) and (carbethoxymethylene)triphenylphos-

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(1) M. von Strandtmann, M. P. Cohen, C. Puchalski, and J. Shavel, Jr., *J. Org. Chem.*, **33**, 4306 (1968).

(2) M. von Strandtmann, D. Connor, and J. Shavel, Jr., *J. Heterocycl. Chem.*, **9**, 175 (1972).

(3) C. Ruchardt, S. Eichler, and P. Panse, *Angew. Chem.*, **75**, 858 (1963).

phorane (0.01 mol) in dioxane (50 ml) was refluxed for 17 hr The dioxane was evaporated under reduced pressure. The residue was recrystallized from ethyl acetate–methylene chloride to give analytically pure material.

**Attempted Reaction of Phosphonium Ylides (3a, 3c, and 5b) with Aldehydes.**—The reaction of **3a**, **3c**, and **5b** with benzaldehyde, *p*-nitrobenzaldehyde, and *p*-chlorobenzaldehyde was investigated in dioxane and benzene at reflux temperatures and room temperature for periods as long as 24 hr. In all cases the starting material was recovered. Extensive decomposition of the ylide took place when the reaction was run in DMF at 130°.

**Registry No.**—**1,** 1099-45-2; **2a** (R = Ph), 102-96-5; **2b** (R = *p*-F–Ph), 706,08-1; **2c** (R = 1-naphthyl), 4735-49-3; **2d** (R = 2-thienyl), 874-84-0; **3a** (R = Ph), 37709-90-3; **3b** (R = *p*-F–Ph), 37709-91-4; **3c** (R = 1-naphthyl), 37709-92-5; **3d** (R = 2-thienyl), 37709-93-6; **4a** (R = H), 118-48-9; **4b** (R = Me), 10328-92-4; **5a** (R = H), 37709-95-8; **5b** (R = Me), 37709-96-9.

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# Planarity of the Carbon Skeleton in Various Alkylated Olefins

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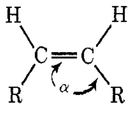
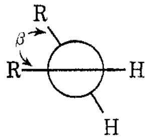
The planarity and extent of bond angle deformation in an alkene is of increasing interest to both the theoretical and the experimental chemist. In principle, a carbon–carbon double bond may experience both in-plane nonbonded repulsions, **1**, and out-of-plane "torsional strain,"[1] **2**, as a result of steric interactions. The strain in an alkene has traditionally been estimated experimentally from thermochemical data.[1,2] More recently, the force field method of calculation has been found to give reliable estimates of the strain energy and the structure of a variety of alkenes.[3]



1



2

Though the quantitative interpretation of photoelectron spectra almost always follows from a previous knowledge of the molecular geometry, in specific cases this can be reversed,[4] and we here offer several examples of this approach to the determination of certain gross geometric features of various alkylated olefins. Very briefly, the basic idea behind our work is that the $\pi$ ionization potential of an olefin (or polyene) will depend strongly on the coplanarity of the 2p$\pi$ AO's, and that twists in the $\pi$ system of a particular molecule can be revealed by comparing its $\pi$-electron ionization potentials with that of a related standard molecule known to be planar. A semiquantitative estimate of the twist angle can be obtained if we then apply the theoretically determined curve of ionization potential *vs.* twist angle derived for ethylene.[5] According to this theoretical curve, the ionization potential of planar ethylene decreases by 3.24 eV on going to the form twisted by 90°.[6]

Recently, Harvey and Nelson[7] showed that the Raman spectrum of perfluoropropene was characteristic of a molecule having a plane of symmetry, in contrast to the report of Bauer and Chang,[8] who studied this molecule by electron diffraction and concluded that it is twisted by 40° about the C=C bond. Several other molecules of this sort were also reported to be twisted according to the diffraction study; the largest twist was reported for *cis*-perfluorobutene-2, 60 ± 2°. We can test this claim by comparing the ionization potentials of a series of cis and trans alkenes, which then leads indirectly to the degree of out-of-plane deformation of the double bond in the crowded isomer.

The photoelectron spectra of *cis*- and *trans*-butene-2 (Figure 1) understandably look very much alike since both molecules are planar[3,9] and differ only in the relative orientation of the ends, which are noninteracting. Note especially that the $\pi$ ionization potentials at 9.29 and 9.32 eV (vertical) are very nearly equal. Extrapolating to the perfluorobutenes, the spectra will again resemble one another closely for the two planar isomers, but, at intermediate angles of twist about the central bond, the $\pi$-bond order is reduced, and the $\pi$ ionization potential will decrease. According to the curves of Merer and Mulliken,[5] a twist of 60° will reduce the $\pi$ ionization potential by 1.5 eV. In the same twisted olefin, the $\pi \rightarrow \pi^*$ interval in the optical spectrum will also decrease greatly over that in the planar configurations.

In Figure 1, we also show the photoelectron spectra of *cis*- and *trans*-perfluorobutene-2 and notice immediately that the two vertical $\pi$ ionization potentials are again virtually identical at 11.46 and 11.55 eV, respectively. We take this result to show that both molecules are planar, or very nearly so ($\pm 10°$). The optical spectra of the two isomers show $\pi \rightarrow \pi^*$ absorption maxima at 1640 (trans) and 1650 Å (cis) again indicating that the $\pi$-bonding strength is very nearly equal in the two systems. The $\pi$ ionization potentials in the perfluoromethyl series seem to vary in a regular way, without any suggestion of nonplanarity in the carbon skeleton. Thus, the vertical $\pi$ ionization potentials of perfluorotetramethylethylene, *cis*- and *trans*-perfluorobutene-2,

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[1] For a general review of strained alkenes, see N. S. Zefirov and V. I. Sokolov, *Russ. Chem. Rev.*, **36**, 87 (1967).

[2] C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, Elmsford, N. Y., 1962.

[3] N. A. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972).

[4] See, for example, C. R. Brundle and M. B. Robin, *ibid.*, **92**, 5550 (1970).

[5] A. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

[6] Actually, the Mulliken–Roothaan diagram relates the total energy to the angle of twist, always at the ground state C–C distance. The molecule, of course, will increase this distance in the excited ionic state, but, by the usual line of reasoning, the energy which most closely represents the transition in the fixed geometry of the ground state will have the maximum Franck–Condon factor, *i.e.*, the vertical ionization potential.

[7] A. B. Harvey and L. Y. Nelson, *J. Chem. Phys.*, **55**, 4145 (1971).

[8] S. H. Bauer and C. H. Chang, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Paper Phys. 14.

[9] A. Almenningen, I. M. Anfinsen, and A. Haaland, *Acta Chem. Scand.*, **24**, 43 (1970).