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Aromatic Substitution at Ortho-Positions

BY R. D. BROWN

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The interpretation of aromatic substitution in benzene derivatives in terms of the simple LCAO molecular-orbital approximation has now attracted the attention of a number of authors.[1-8] Early attempts[1,2] were concerned only with a demonstration that the theory points to *o*-, *p*-substitution for some kinds of derivatives, and *m*-substitution for others, in general agreement with observation. Dewar[4] considered the more sophisticated problem of *o*:*p* ratios. His results indicated that only in cases where the benzene substituent is very electronegative would the *p*-position be *electronically* more activated than *o*-, with the inference that the observed preponderance of *p*-substitution is occasioned in part at least by steric factors.[9] Additional weight is lent to Dewar's results because he was able to account qualitatively for trends in the *o*:*p* ratio as the nature of the substituent is varied.

If however the benzene substituent is a conjugated hydrocarbon system, as in biphenyl and styrene, the uncertainty about the electronegativity parameter disappears and the molecular-orbital approximation provides an unequivocal prediction of the electronic activities. For biphenyl the *o*-positions are predicted[5] to be appreciably more reactive than the *p*-positions. In this case, then, the observed low *o*:*p* ratio must be ascribed to steric factors. This result is not peculiar to biphenyl; similar relative electronic reactivities of *o*- and *p*-positions are predicted for vinyl- and 1-butadienyl substituents, as shown in Table I, and indeed there seems little doubt that for any conjugated hydrocarbon system as substituent the MO approximation will ascribe a greater electronic reactivity to the *o*-position as has been suggested by Roberts and Streitwieser. The results of Table I strictly apply only for the completely planar molecules. It is known[10] that biphenyl is on the average non-planar in the vapor phase, and presumably also in solution, and this would effectively reduce the disparity in the *o*:*p* reactivities, but it will not affect the qualitative relationship.

TABLE I

ATOM LOCALIZATION ENERGIES[3] ($-\beta$)

	Biphenyl	Styrene	1-Phenylbutadiene
Ortho	2.400	2.370	2.313
Para	2.447	2.424	2.377

The attribution of the observed superior reactivity of the *p*-position in biphenyl to steric effects rather than to a failure in the MO theory is supported by some further theoretical work of Dewar.[6] He has computed approximate atom localization energies for a considerable number of polycyclic aromatic hydrocarbons. In all cases where the position of substitution is known experimentally it coincides with the position which theory predicts to be electronically most reactive, with the single exception of triphenylene. But in this molecule the 1-position, which has a steric environment analogous to an *o*-position in biphenyl, is predicted to be the most active, while substitution is observed[11] to occur in the 2-position. In all other cases considered by Dewar the most reactive positions predicted by theory have steric environments much more favorable for chemical attack.

Since the only two molecules for which substitution occurs predominantly at positions other than those predicted by the MO localization theory are those for which the steric environments of the electronically most reactive positions are unfavorable for substitution, it seems justifiable to attribute the predominant *p*-substitution in biphenyl to steric hindrance of the *o*-positions.

Remick[12] has suggested, in terms of the qualitative electronic theory, that the superior reactivity of the *p*-position in biphenyl is to be anticipated solely on electronic grounds, using the principle that "the electromeric effect will operate more readily the more extended the conjugation becomes." However if this principle is applied to biphenyl in the same way in which Remick applies it[13] to explain the α-activation of pyrrole, furan and derivatives, it would point to *o*-activation; indeed Remick has noticed just this kind of difficulty[14] in applying the principle to other benzene derivatives.

Finally it should be observed that the data for styrene in Table I differ considerably from the figures recently published by Roberts and Streitwieser.[15] Both the absolute values of the localization energies and their relative values (their data indicate a greater *p*- than *o*-reactivity) are in error. The correct values, together with values of the free valences ($N_{\max} = \sqrt{3}$) for comparison,[8] are listed in Table II. It will be observed that the free valences confirm the superior electronic reactivity of the *o*- as compared with the *p*-position.

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[1] G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935).

[2] G. W. Wheland, *ibid.*, **64**, 900 (1942).

[3] C. Sandorfy, *Bull. soc. chim.*, **16**, 615 (1949).

[4] M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949).

[5] R. D. Brown, *Experientia*, **6**, 376 (1950).

[6] M. J. S. Dewar, THIS JOURNAL, **74**, 3357 (1952).

[7] J. D. Roberts and A. Streitwieser, *ibid.*, **74**, 4723 (1952).

[8] For an account of the correlation of localization energies and free valences with chemical reactivities see R. D. Brown, *Quart. Rev.*, **6**, 63 (1952).

[9] More than this cannot be said because the appropriate electronegativity parameters for the various substituents are very uncertain.

[10] O. Bastiansen, *Acta Chem. Scand.*, **4**, 926 (1950).

[11] E. Clar, "Aromatische Kohlenwasserstoffe," Springer Verlag, Berlin, 1941, p. 104.

[12] A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 103.

[13] Reference 12, pp. 104-105.

[14] Reference 12, p. 104.

[15] Dr. Roberts has kindly informed the author of his agreement with the present figures for styrene, and that the incorrect data in ref. 7 were due to errors in transcription.

TABLE II

MOLECULAR-ORBITAL DATA FOR STYRENE

Position	$A(-\beta)$	F	Position	$A(-\beta)$	F
β	1.704	0.821	*m*	2.546	0.395
α	2.424	.415	*p*	2.424	.415
o	2.370	.443			

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Metathetical Reactions of Silver Salts in Solution. III. The Synthesis of Nitrate Esters[1]

BY ARTHUR F. FERRIS, KATHARINE W. MCLEAN, IRMA G. MARKS AND WILLIAM D. EMMONS

RECEIVED APRIL 27, 1953

It has been found in this Laboratory that the use of silver nitrate in acetonitrile is a very convenient method for preparing laboratory quantities of extremely pure nitrate esters. The method has an additional advantage in that the reaction may be conveniently followed by periodic weighing of the silver halide precipitated.

The reaction of alkyl halides with silver nitrate under heterogeneous conditions has been used for many years as a preparative method for alkyl nitrates. Experiments wherein ethanol was used as a solvent for the reaction[2] have led largely to nitric acid and the mixed ethyl alkyl ether derived from the alkyl halide. The enormous solubility of silver nitrate in acetonitrile is well known,[3] and the use of silver nitrate in acetonitrile to prepare 2,4,6-trinitrobenzyl nitrate from the corresponding bromide has been described.[4] It would appear, however, that the virtues of silver nitrate in acetonitrile for synthesis of nitrates have not been generally recognized, since in even very recent work[5] nitrates have been prepared by the heterogeneous reaction.

Most primary and secondary alkyl iodides, many bromides and active chlorides react rapidly enough at room temperature or slightly above to be useful in preparative work. The following nitrates were prepared in the yields indicated: *n*-hexyl nitrate from *n*-hexyl bromide (77%) and from *n*-hexyl iodide (67%), *n*-octyl nitrate from *n*-octyl iodide (61%), benzyl nitrate from benzyl chloride (64%), methallyl nitrate from methallyl chloride (45%), 2-octyl nitrate from 2-octyl iodide (46%), 2-nitratoethanol from 2-bromoethanol (70%), nitratoacetonitrile from iodoacetonitrile (32%), ethyl lactate nitrate from ethyl α-bromopropionate (59%), and ethyl hydracrylate nitrate from ethyl β-bromopropionate (58%). These yields undoubtedly do not represent the optimum obtainable, since most of the experiments were carried out on a small scale with consequent large mechanical losses.

Experimental[6]

The procedures described herein for ethyl hydracrylate nitrate and methallyl nitrate are typical of thóse used for the preparation of the other esters. All boiling points are uncorrected.

Ethyl Hydracrylate Nitrate.—To a solution of 20.0 g. (0.118 mole) of silver nitrate in 100 ml. of dry, distilled acetonitrile was added a solution of 9.1 g. (0.05 mole) of ethyl β-bromopropionate in 25 ml. of acetonitrile. After three days at room temperature 9.0 g. (96%) of silver bromide was recovered by filtration. The filtrate was poured into a liter of ice-water, and the oil which separated extracted into two 50-ml. portions of methylene chloride. After drying, the solvent was removed by distillation at atmospheric pressure, and the residue was distilled at reduced pressure to yield 4.7 g. (58%) of ethyl hydracrylate nitrate, b.p. 60–64° (1.5 mm.), $n^{25}{}_D$ 1.4258, $d^{20}{}_4$ 1.262.

Anal. Calcd. for $C_5H_9O_5N$: C, 36.81; H, 5.56; N, 8.59. Found: C, 37.11; H, 5.72; N, 8.46.

Methallyl Nitrate.—To a solution of 18.7 g. (0.11 mole) of silver nitrate in 30 ml. of dry acetonitrile was added 9.1 g. (0.10 mole) of methallyl chloride. After five days at room temperature a total of 13.1 g. (92%) of silver chloride was collected on a filter. The filtrate was worked up as described above, and the residue was fractionated through a short packed column to give 5.3 g. (45%) of methallyl nitrate, b.p. 83–88° (215 mm.), $n^{25}{}_D$ 1.4221, $d^{20}{}_4$ 1.064.

Anal. Calcd. for $C_4H_7O_3N$: C, 41.02; H, 6.03; N, 11.96. Found: C, 41.51; H, 6.40; N, 12.19.

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[1] This work was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] K. A. Burke and F. G. Donnan, *J. Chem. Soc.*, **85**, 555 (1904); J. W. Baker, *ibid.*, 987 (1934).

[3] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Third Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 68.

[4] L. F. Fieser and W. von E. Doering, THIS JOURNAL, **68**, 2252 (1946).

[5] J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952).

[6] We are indebted to Mr. Al Kennedy and Miss Annie Smelley for analytical data.

Silicon-containing Aromatic Phosphorus Derivatives

BY KURT C. FRISCH[1] AND HAROLD LYONS

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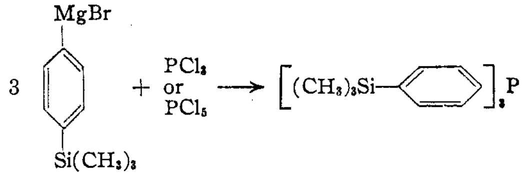
The purpose of this investigation was the preparation of aromatic silanes containing nuclear substituted phosphorus groups. The presence of phosphorus groups in aromatic silanes should impart certain physical properties useful in applications such as plasticizers, lubricants and oil additives. This paper deals with the preparation of some model compounds of this type.

p-Trimethylsilylphenylmagnesium bromide (I) was treated with phosphorus tri- and pentachloride, using equimolecular amounts of the reactants. In both cases, the main product consisted of tris-(*p*-trimethylsilylphenyl)-phosphine (II)



I II

In the reaction with phosphorus pentachloride, in addition to the above described crystalline phosphine (II), another liquid product was obtained which is presumably bis-(*p*-trimethylsilyl)-chlorophosphine (III).

Tris-(*p*-trimethylsilyl)-phosphine (II) is very resistant to oxidation. Refluxing the phosphine

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[1] E. F. Houghton & Co., Philadelphia, Penna.