appears that the transition state for the rearrangement of this substrate is "product-like," *i.e.*, bearing a close structural resemblance to 2^+. The rearranged cations directly succeeding the transition state for these two substrate should markedly differ in stability with 1^+ being much more stable than 2^+. This should result in a shift in transition state structure[16] for 1^+ toward a more nearly "symmetrical" transition state with an attendant decrease in the amount of positive charge at C-4 in the transition state. This is consistent with the relatively small stabilizing effect of the methoxy group of **1** in the transition state.

Experimental Section

4-Methoxy-4-methylcyclohexadienone (1).—This material was prepared as described by Hecker.[7] The product was produced in 31% yield, purified by preparative glpc (130°, diethylene glycol succinate) and had the following properties: mp 61–61.5° (lit.[7] mp 62–63°); ir (CCl_4) 1675 (>C=O), 1640 (C=C), 1200 cm^{-1} ($COCH_3$); nmr δ 6.15 (d, CH=CHC=O), 6.65 (d, CH=CHC=O), 3.14 (s, OCH_3), 1.38 (s, CH_3).

Rearrangement of 1 in Concentrated Hydrochloric Acid.—A 50-mg portion of 1 was treated with 1 ml of concentrated HCl for 3 days with vigorous stirring. The yellowish solution was extracted with several portions of ether. The ether was dried (Na_2SO_4) and removed on a rotary evaporator. The residue was dissolved in 5 ml of methanol and treated with 106 mg of Na_2CO_3 and 114 mg of CH_3I. After refluxing for 3 days the solution was cooled, filtered, and diluted with ether. The ether solution was washed with water and dried over Na_2SO_4, and the ether removed on a rotary evaporator. The crude product was subjected to glpc analysis (10% diethylene glycol succinate, 140°) and one peak was observed. This peak was collected and its ir spectrum was shown to be virtually identical to that obtained from the methylation of 2-methylhydroquinone (Aldrich Chemical Co).

2,4-Dimethoxytoluene.—2,4-Dimethoxybenzyl mesylate was prepared by allowing 2,4-dimethoxybenzyl alcohol, triethylamine, and methanesulfonyl chloride in benzene to react at room temperature.[17] From 431 mg of 2,4-dimethoxybenzyl alcohol there was obtained 213 mg (35%) of mesylate ester, ir, no OH, 1380 cm^{-1} (sulfonate). The crude mesylate was reduced in refluxing ether for two days with an excess of $LiAlH_4$. A small sample of the reduction product was isolated by preparative glpc (10%, diethylene glycol succinate, 140°). An ir spectrum of this material was substantially different from that of the methylated rearrangement product. In fact, a comparison of ir spectra showed that <5% methoxy migration had occurred in the acid-catalyzed rerrangement of 1.

Kinetic Procedures.—All rate constants reported in this paper were obtained by monitoring the dissappearance of dienone of 240 nm[7] using either a Beckman DK-1A or Gilford Model 2400 spectrophotometer. The kinetic data were processed by using a nonlinear least-squares program written for the Wang 700 computer. Most of the results reported in Table I are average values based on three or more runs. A concentrated solution of dienone was prepared in ethanol and 2–5 μl of this solution was deposited in the end of a stirring rod. The reaction was initiated by plunging the stirring rod into a cuvette containing acid of the desired strength (previously equilibrated) and monitoring the absorbance as a function of time. Acid concentrations were determined by titrating weighed amounts of acid with previously standardized base.

Basicity of 1 in Perchloric Acid.—To estimate the degree of protonation of 1 we measured the absorbance of solutions of 1 in perchloric acid at 295 nm as a function of time and extrapolated back to the time of mixing either graphically or by using the nonlinear kinetics program. The cyclohexadienyl cations produced by the protonation of 4-dichloromethyl-4-methylcyclohexadienone[1] and 4,4-dimethylcyclohexadienone[2,4] have λ_{max} 295 nm. Neutral 1 has virtually no absorption at this wavelength. These results are presented in Table II.

Registry No.—1, 23438-17-7.

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(16) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(17) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

Structural Effects on the Acid–Base Properties of Some Closely Related Phosphinic Acids and Phosphine Oxides[1]

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Received March 17, 1972

Several isomeric cyclic and acyclic C_8 phosphinic acids and some isomeric cyclic and acyclic C_8 methylphosphine oxides have been synthesized, and their acidity and basicity, respectively, have been determined. The effect of structural branching is acid weakening with the phosphinic acids and base weakening with the phosphine oxides. The presence of a four-membered ring which includes the phosphorus heteroatom tends to be acid strengthening with the phosphinic acids, and it tends to be base weakening with the phosphine oxides. The reasons for these structural effects are discussed.

The acid–base properties of molecules are due to a combination of internal effects and environmental effects,[3] and the relative ability of these effects to stabilize the acids and their conjugate bases or the bases and their conjugate acids. The relative ability of these effects to stabilize the acid or base forms of a molecule are determined only by the structure of the molecule if one uses a constant solvent environment. The structural effects on acid and base properties of some isomeric aliphatic phosphinic acids and phosphine oxides are reported in this study. Since only aliphatic phosphinic acids and phosphine oxides are involved, the important internal effect is an inductive effect, and the important environmental effect is a solvation effect.

All but one of the phosphinic acids listed in Table I were synthesized by treatment of phosphorus oxychloride or phosphorus trichloride with the appropriate Grignard reagent followed by hydrolysis. The exception was cyclic phosphinic acid (1) which was produced by treating 2,4,4-trimethyl-2-pentene with phosphorus trichloride in the presence of aluminum chlo-

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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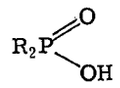
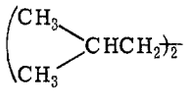
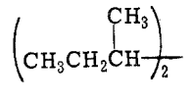
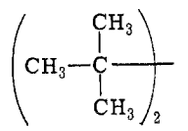
(3) E. J. King, "Acid–Base Equilibria," Pergamon Press, Oxford, 1965.

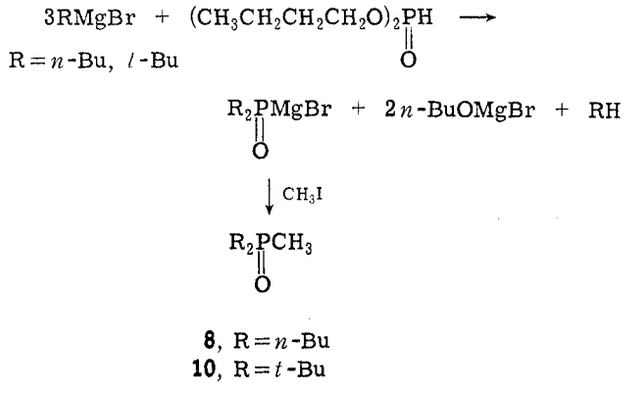
TABLE I
ACIDITIES OF PHOSPHINIC ACIDS IN 75% ETHANOL AND 25% WATER



Compd	R_2	pK_A[a]
1		4.66
2	$(CH_3)_2$	4.72
3	$(CH_3CH_2CH_2CH_2)_2$	5.24
4		5.60
5		5.75
6		6.26

[a] Each value, to be considered followed by ±0.05, was calculated from the average of two or more $pH_{1/2}$ values as read directly from the chart.

ride as described by McBride and coworkers.[4] Cyclic phosphine oxide (**9**) listed in Table II was prepared in a manner similar to phosphinic acid (**1**).[5] Phosphine oxide (**7**) is made by use of the appropriate Grignard reagent with phosphorus oxychloride. Phosphine oxides **8** and **10** were made in 73 and 25% yields, respectively, by use of the appropriate Grignard reagent with di-*n*-butyl phosphite, and the initially formed product is subsequently treated with methyl iodide.



8, R = *n*-Bu
10, R = *t*-Bu

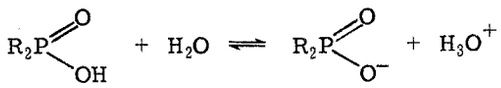
The pK_A values of the series of phosphinic acids given in Table I were determined in 75% ethanol by titration with aqueous sodium hydroxide using a method described previously.[6]

The pK_{BH^+} values of the phosphine oxides listed in Table II were found by nmr chemical shift measurements of methyl protons in sulfuric acid solutions of methyl phosphine oxides.[7-9] Trimethylammonium chloride was used as the internal reference. The H_0 scale was used to determine the effective sulfuric acid concentration.[10,11] The following equation was used in the evaluation of the pK_{BH^+}'s. The slope (m) and

$$\log \frac{\delta_B - \delta_{obsd}}{\delta_{obsd} - \delta_{BH^+}} = \log \frac{[BH^+]}{[B]} = m(pK_{BH^+} - H_0)$$

intercept (mpK_{BH^+}) were determined by least-squares analysis.

One of the important factors in the ordering of the pK_A values of the aliphatic phosphinic acids listed in Table I appears to be a solvation effect in a manner similar to that found in aliphatic carboxylic acids.[12a] The equilibrium involved in the exhibition of acid properties by phosphinic acids is an ionogenic one,[3] *i.e.*, one in which the proton transfer is associated with the creation of ions. With this type of equilibrium,



solvation is much more important in the stabilization of the conjugate base anion produced than in the stabilization of the neutral acid.[12b] Therefore any factor that hinders solvation will be acid weakening. The small methyl groups in compound **2** do not effectively interfere with solvation, and the ring structure of compound **1** "pulls back" the methyl groups from the reaction site allowing it to be readily solvated. A strong inductive effect in the form of an electron-withdrawing effect seems to be operative in compound **1** also. This effect stabilizes the anion relative to the free acid even more and makes **1** an even stronger acid than one would predict. The source of this electron withdrawing effect is the strained four-membered ring.[13] The steric hindrance toward solvation increases somewhat with the *n*-butyl, isobutyl, and *sec*-butyl groups of compounds in compounds **3**, **4**, and **5**. The hindrance reaches a maximum with the *tert*-butyl group of compound **6**. The acidity consequently is weakest for this compound as shown by its pK_A.

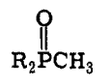
The base properties of phosphine oxides are shown by the equilibrium of the phosphine oxide with its conjugate acid. In this equilibrium solvation is more

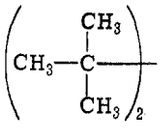
$$R_3P{=}O + H_3O^+ \rightleftharpoons R_2P{=}O^+H + H_2O$$

important in stabilizing the conjugate acid cation produced than in stabilizing the neutral phosphine oxide. Therefore any factor that hinders solvation will be base weakening for the phosphine oxide. A combination of solvation and inductive effects seems to be the determining factor in the relative basicities of the phosphine oxides listed in Table II. Here it is seen that the trimethylphosphine oxide (**7**) is essentially equal in basicity to di-*n*-butylmethylphosphine

(4) J. J. McBride, Jr., E. Jungermann, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, **27**, 1833 (1962).
(5) S. E. Cremer and R. J. Chorvat, *ibid.*, **32**, 4066 (1967).
(6) D. F. Peppard, G. W. Mason, and C. M. Andrejasich, *J. Inorg. Nucl. Chem.*, **27**, 697 (1965).
(7) P. Haake and G. Hurst, *J. Amer. Chem. Soc.*, **88**, 2544 (1966).
(8) P. Haake, R. D. Cook, and G. Hurst, *ibid.*, **89**, 2650 (1967).
(9) G. C. Levy, J. D. Cargioli, and W. Racela, *ibid.*, **92**, 6238 (1970).
(10) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 1 (1957).
(11) M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).
(12) (a) G. S. Hammond and D. H. Hogle, *ibid.*, **77**, 338 (1955); (b) G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 9.
(13) I. J. Miller, *Tetrahedron*, **25**, 1349 (1969).

TABLE II
BASICITIES OF PHOSPHINE OXIDES[a]



Compd	R_2	pK_{BH^+}	Intercept	m	No. of points
7	$(CH_3)_2$	−1.48 ± 0.44	−0.90 ± 0.24	−0.61 ± 0.08	7
8	$(CH_3CH_2CH_2CH_2)_2$	−1.51 ± 0.29	−0.92 ± 0.18	−0.61 ± 0.04	10
9		−2.88 ± 0.17	−1.41 ± 0.07	−0.49 ± 0.01	11
10		−3.41 ± 0.22	−1.63 ± 0.09	−0.48 ± 0.02	10

[a] The slope (m) and intercept (mpK_{BH^+}) were determined by least-squares analysis.

oxide (**8**), but 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**9**) is a weaker base. The relatively weak basicity of phosphine oxide (**9**) is contrary to what would be expected based on solvation effects. The "tied-back" nature of this cyclic phosphine oxide (**9**) makes it easier to solvate the conjugate acid cation. However, the strained four-membered ring structure in **9** causes a decrease in electron density on the oxygen atom[13] which is the potential protonation site. This decrease in electron density on the oxygen atom of **9** outweighs the improved solvation possibilities for its protonated form resulting in a net decrease in basicity for the phosphine oxide. This decrease in basicity with increasing ring strain has been observed with alicyclic ketones.[14,15] A similar increase in positive charge at phosphorus as ring strain increases has been noted in cyclic phosphates.[16-19] This has been attributed to a lowered occupation of the phosphorus 3d orbitals. The weakest base of the series is di-*tert*-butylmethylphosphine oxide (**10**) whose protonated form is greatly hindered from solvation by the bulky *tert*-butyl groups.

Experimental Section

The instruments used in this work were a modified Precision-Dow Recordomatic titrator and a JEOL C-60HL high resolution nuclear magnetic resonance spectrometer. The elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Some Phosphine Oxides and Phosphinic Acids.—Trimethylphosphine oxide (**7**) was made by the method of Burg and McKee.[20] 1,2,2,3,4,4-Hexamethylphosphetane 1-oxide (**9**) was synthesized using the procedure of Cremer and Chorvat.[5,21] Dimethylphosphinic acid (**2**) was prepared by the method of Nakamoto, Ferraro, and Mason.[22]

1,1,2,3,3-Pentamethyltrimethylenephosphinic Acid (**1**).—The procedure of McBride and coworkers[4] was followed (on a 1-mole of PCl_3 basis) up to the point at which the water-washed organic phase, containing the acid chloride as the principal product, was separated. One liter of an aqueous solution of 2 *M* NaOH was added (over a period of 30 min) to the stirred organic phase. The aqueous phase was separated, heated at 80° for 1 hr, cooled, and acidified with a slight excess of concentrated hydrochloric acid. A colorless crystalline solid separated from the solution which was isolated by filtration and recrystallized from *n*-heptane, mp 74.5–75°, 85% yield.

Di-*tert*-butylphosphinic Acid (**6**).—This compound was first described as being prepared by the addition of an ether solution of phosphorus trichloride to an ether solution of *tert*-butyl magnesium chloride.[23] We have used a modification of this procedure in which the reagents were added in the reverse order to obtain a much higher yield of product (45%). The purity of the product was such that it could be used in radiometric studies, mp 210°.

Details of the preparation and purification of the compound by this modified procedure are given elsewhere.[24]

Di-*n*-butylphosphinic Acid (**3**).—This compound was prepared in the same manner as di-*tert*-butylphosphinic acid (**6**) except that *tert*-butyl chloride and phosphorus trichloride were replaced by *n*-butyl bromide and phosphorus oxychloride. Consequently the oxidation step was not needed. Also the purification procedure differed markedly from that used for di-*tert*-butylphosphinic acid. The purification was carried out in the following manner. Following completion of the Grignard reaction the ether phase was washed twice with water and extracted with 1 *M* aqueous sodium hydroxide. The aqueous sodium hydroxide extract was heated at 80° for 2 hr, cooled, washed three times with benzene, and acidified with a light excess of concentrated HCl. The aqueous solution was extracted with isobutyl alcohol, and the alcoholic extract was washed with four portions of water. Upon evaporation of the alcohol a colorless crystalline solid product was obtained. It was recrystallized from *n*-heptane (60% yield), mp 68.5–69.5° (lit.[23] mp 68.5–69°).

Diisobutylphosphinic Acid (**4**).—The same procedure as was given above for making di-*n*-butylphosphinic acid (**3**) was fol-

(14) E. M. Arnett, R. P. Quirk, and J. W. Larsen, *J. Amer. Chem. Soc.*, **92**, 3977 (1970).
(15) H. J. Campbell and J. T. Edward, *Can. J. Chem.*, **38**, 2109 (1960).
(16) R. L. Collin, *J. Amer. Chem. Soc.*, **88**, 3281 (1966).
(17) D. B. Boyd, *ibid.*, **91**, 1200 (1969).
(18) G. M. Blackburn, J. S. Cohen, and I. Weatherall, *Tetrahedron*, **27**, 2903 (1971).
(19) A. L. Mixen and W. R. Gilkerson, *J. Phys. Chem.*, **75**, 3309 (1971).
(20) A. B. Burg and W. E. McKee, *J. Amer. Chem. Soc.*, **73**, 4590 (1951).
(21) The methylphosphonous dichloride used in this procedure was kindly provided by the Ethyl Corporation.
(22) K. Nakamoto, J. R. Ferraro, and G. W. Mason, *Appl. Spectrosc.*, **23**, 521 (1969).
(23) P. C. Crofts and G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **75**, 3379 (1953).
(24) G. W. Mason, S. Lewey, and D. F. Peppard, *J. Inorg. Nucl. Chem.*, in press.

lowed here using isobutyl bromide to give a colorless crystalline product in a 60% yield, mp 46–47° (lit.[25] mp 38–40°).

Di-*sec*-butylphosphinic Acid (5).—The same procedure as was reported above for making di-*n*-butylphosphinic acid (**3**) was followed here for making **5** by using *sec*-butyl chloride to give product in a 60% yield. The final recrystallization step was omitted since the product is a liquid at room temperature. This is the first time a pure sample of this compound has been reported, the only other report being that of a crude sample.[26]

Anal. Calcd for $C_8H_{19}O_2P$: C, 53.92; H, 10.75; P, 17.38. Found: C, 54.10; H, 10.84; P, 17.51.

Di-*n*-butylmethylphosphine Oxide (8).—To a stirred Grignard solution prepared from 411 g (3.0 mol) of *n*-butyl bromide and 73 g (3.0 mol) of magnesium in 1 l. of diethyl ether was added dropwise (over a period of 1 hr) 194 g (1.0 mol) of di-*n*-butyl phosphite. A total of 142 g (1.0 mol) of methyl iodide was added and the mixture heated under reflux for 1.5 hr. The cooled solution was stirred with 500 ml of concentrated HCl and the organic phase (upper layer) was separated. The organic phase was washed successively with two 250-ml portions of water, one 250-ml portion of 1 *M* NaOH, and one 250-ml portion of water. The ether, *n*-butyl alcohol, and water were removed from the organic phase (the latter two under high vacuum since they were quite difficult to remove) to give 128.7 g (73%) of colorless solid product, mp 34–35° (lit.[27] mp 35°).

Di-*tert*-butylmethylphosphine Oxide (10).—The same procedure as was reported above for making di-*n*-butylmethylphosphine oxide (**8**) was used here for making **10** by using *tert*-butyl chloride in place of *n*-butyl bromide. The final product was purified by fractional distillation, and the purified product was obtained in a 25% yield. This is a vastly improved yield over the 2% yield of product reported from the reaction of *tert*-butylmagnesium chloride with methylphosphonic dichloride.[28]

Registry No.—**1**, 35210-25-4; **2**, 3283-12-3; **3**, 866-32-0; **4**, 15924-57-9; **5**, 35210-27-6; **6**, 677-76-9; **7**, 676-96-0; **8**, 14062-37-4; **9**, 16083-94-6; **10**, 18351-81-0.

(25) K. A. Petrov, N. K. Bliznyuk, and V. P. Korotkova, *J. Gen. Chem. USSR*, **30**, 2967 (1960).

(26) P. J. Christen and L. M. van der Linde, *Rec. Trav. Chim. Pays-Bas*, **78**, 543 (1959).

(27) G. M. Kosolapoff and R. F. Struck, *Proc. Chem. Soc., London*, 351 (1960).

(28) A. D. Brown, Jr., and G. M. Kosolapoff, *J. Chem. Soc. C*, 839 (1968).

Notes

Birch Reduction of Biphenylene. Formation of 4,5-Benzobicyclo[4.2.0]octa-2,4-diene

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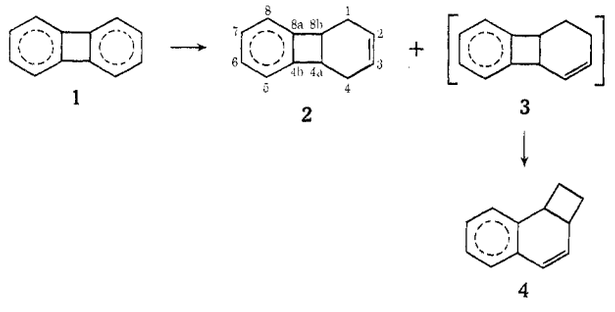
Received March 3, 1972

Braun's report[1] of the characterization of the products from the reaction of benzyne and 1,3-cyclohexadiene prompts us to report our findings in the Birch reduction of biphenylene (**1**).



Baker reported[2] that reduction of **1** by sodium in liquid ammonia yielded 30% biphenyl plus unsaturated oil. Atkinson[3] found that the mixture of products obtained by alkali metal reduction in liquid ammonia underwent disproportionation during distillation, reforming a small amount of biphenylene (**1**). Barton[4] found reduction with lithium in ethylamine–diethylamine (1:4 ratio) at 0° to give 85% biphenyl plus small amounts of 1-phenylcyclohexene and a tetrahydrobiphenylene.

Our results differ from those cited. Reduction of **1** using sodium or lithium in liquid ammonia plus anhydrous ether plus ethanol yielded a mixture which glc indicated was composed of unreacted **1**, 1,4,4a,8b-tetrahydrobiphenylene (**2**), and 4,5-benzobicyclo[4.2.0]-octa-2,4-diene (**4**), with the latter two in a ratio of about 4:1. Biphenyl was specifically sought by nmr and glc, but none was found.

Braun[1] isolated **4** from the reaction of benzyne and 1,3-cyclohexadiene and proposed its formation by the rearrangement of 1,2,4a,8b-tetrahydrobiphenylene (**3**), which was the expected minor 1,2 addition product. Thus, our obtaining **4** instead of **3** by a different route supports Braun's proposed rearrangement of **3**. However, neither we nor Braun have isolated **3** or established whether the rearrangement occurs spontaneously or is caused by the glc work-up. It may be significant that two tetrabromo compounds with the same skeletal structure as **3** have been reported[5] and seem stable.

Braun[1] characterized **4**, which exhibits a uv absorption spectrum typical of styrene derivatives rather than benzocyclobutene derivatives.[6] Previously unreported **2** exhibits the uv spectrum (ETOH) typical of a benzocyclobutene derivative and a molecular

(1) A. M. Braun, *J. Org. Chem.*, **35**, 1208 (1970).

(2) W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954).

(3) E. R. Atkinson and F. E. Granchelli, private communication cited in M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, pp 267 and 283.

(4) J. W. Barton and D. J. Walsh, unpublished work mentioned by Barton in "Nonbenzenoid Aromatics," Vol. I, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, pp 56–57.

(5) J. W. Barton and K. E. Whitaker, *J. Chem. Soc. C*, 28 (1968).

(6) M. P. Cava, R. J. Pohl, and M. J. Mitchell, *J. Amer. Chem. Soc.*, **85**, 2080 (1963).