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Carbon Acidity. 63. Equilibrium Ion Pair Acidities of Some Phosphorus-Substituted Carbon Acids

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Ion-pair C–H acidities are reported as $\mathrm{p}K_{\mathrm{CsCHA}}$ for bis(diphenylphosphino)methane (**1**, 31.1), (*p*-phenylbenzyl)diphenylphosphine (**3**, 31.0), *p*-tolyldiphenylphosphine (**4**, 37.9), and several of the corresponding phosphine oxides. The diphenylphosphine group is about as anion stabilizing as *p*-biphenyl. The $\mathrm{Ph_2P(O)}$ group is additionally stabilizing because of enhanced ion-pair interaction. The $\mathrm{p}K_{\mathrm{CsCHA}}$ of benzyldiphenylphosphine (**2**) can be estimated to be about 32.

Carbanions derived from phosphine oxides can provide useful alternatives to the Wittig reaction.[1] A number of equilibrium pK values for the CH acidity of various phosphine oxides has been reported.[2-5] Tertiary phosphine substituents also stabilize carbanions; thus alkylphosphines can be metalated to provide synthetically useful intermediates.[6] Unfortunately, data on quantitative carbon acidities of phosphines are limited. Several kinetic acidity studies have been reported,[7] but the equilibrium acidity of bis(diphenylphosphino)methane (**1**) reported for dimethyl sulfoxide ($\mathrm{Me_2SO}$) solution by the Bordwell group[8] indicates that the diphenylphosphine group is more carbanion-stabilizing than indicated by relative kinetic acidities. In this paper we present quantitative ion-pair carbon acidity values for several phosphines in the cesium cyclohexylamide (CsCHA)–cyclohexylamine (CHA) system ($\mathrm{p}K_{\mathrm{CsCHA}}$). Some results are also presented for phosphine oxides for comparison with the Russian work.

Results and Discussion

The phosphines studied were **1**, benzyldiphenylphosphine (**2**), (*p*-phenylbenzyl)diphenylphosphine (**3**), and *p*-tolyldiphenylphosphine (**4**). The visible or long-wavelength UV bands of the cesium salts in CHA are summarized in Table I. Acidities expressed as $\mathrm{p}K_{\mathrm{CsCHA}}$ were determined from equilibria with suitable indicator systems (eq 1) and corrected to a per hydrogen basis as detailed earlier.[9]

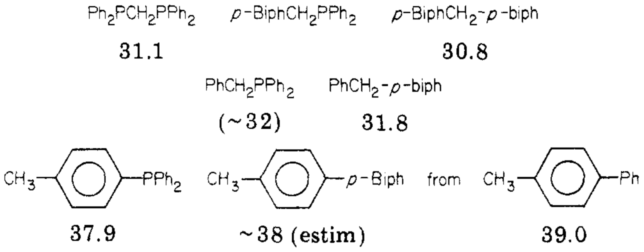
$$\mathrm{RH} + \mathrm{R'^-Cs^+} \xrightleftharpoons{\mathrm{CHA}} \mathrm{R^-Cs^+} + \mathrm{R'H} \qquad (1)$$

Table I. Spectral Data for Cesium Salts of Phosphines and Phosphine Oxides in Cyclohexylamine and Derived $\mathrm{p}K_{\mathrm{CsCHA}}$ Values

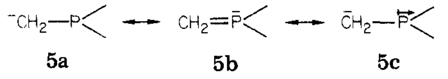
no.	carbon acid	λ_{max}, nm	$10^{-3}\,\epsilon$	$\mathrm{p}K_{\mathrm{CsCHA}}$
1	bis(diphenylphosphino)methane			31.1
2	benzyldiphenylphosphine	342[a]		~32
3	(*p*-phenylbenzyl)diphenylphosphine	473	12.0 ± 0.8	31.0
4	*p*-tolyldiphenylphosphine	365	16.3 ± 1.3	37.9
6	benzyldiphenylphosphine oxide	325	15.3 ± 1.0	24.9
7	(*p*-phenylbenzyl)diphenylphosphine oxide	420	30.0 ± 0.8	24.2
8	*p*-tolyldiphenylphosphine oxide	325	20.1 ± 0.6	32.6

[a] Reference 13.

Chart I. Comparison of $\mathrm{p}K_{\mathrm{CsCHA}}$



The comparison summarized in Chart I shows that the $\mathrm{Ph_2P}$ group is about as carbanion-stabilizing as a *p*-biphenylyl group. Accordingly, the $\mathrm{p}K_{\mathrm{CsCHA}}$ of benzyldiphenylphosphine (**2**), which was not determined accurately at this time, can be estimated to be about 32. The data confirm the effect of the $\mathrm{Ph_2P}$ group shown previously for **1** in $\mathrm{Me_2SO}$[8] but by themselves do not suffice to indicate the mechanism of carbanion stabilization by neutral P(III). The usual explanation involves charge delocalization to phosphorus by way of d–p π bonding as symbolized by **5b** (eq 2); however, in a detailed ab initio study of methylenephosphorane, Lischka[10] has shown that even in this more favorable case of a phosphonium ylide, the involvement of phosphorus d orbitals is minimal.[10] An alternative involves the stabilizing effect of an induced dipole on phosphorus, the effect of polarization as symbolized by **5c**.



(2)

5a **5b** **5c**

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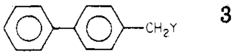
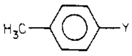
Table II. Comparison of Ph_2P and $Ph_2P(O)$ Substituents on pK_{CsCHA}

compd	pK_{CsCHA} for Y = H	PPh$_2$	P(O)Ph$_2$	ΔpK- (P-PO)
$PhCH_2Y$	41.2	~32	24.9	~7
	39.0	31.0	24.2	6.8
	41.2	37.9	32.6	5.3

One operational distinction between **5b** and **5c** would be provided by measures of the charge population at the carbanion carbon; **5c** implies a full localized charge. One such measure in other systems is the comparison of pK_{Me_2SO} with pK_{CsCHA}. For carbon acids with delocalized carbanions both sets of pK's are comparable and correlate excellently with each other.[9] Localized carbanions have an additional coulombic driving force for forming ion pairs and generally show ion pair pK's lower than ionic pK's. For **1**, however, the pK_{CsCHA} (31.1) is actually higher than the pK_{Me_2SO} (29.9).[8] In this case the two bulky Ph_2P groups may prevent sufficiently close approach of the Cs^+ and thereby invalidate this criterion. Although the present data do not establish the interaction mechanism, they will undoubtedly provide a useful alliance with other subsequent approaches.

The importance of ion pairing has been demonstrated previously for phosphine oxides.[7] These functions are generally several pK units less acidic in Me_2SO than in ethers in which ion pairing is important. The pK_{CsCHA} values summarized in Table I confirm the relatively high carbanion-stabilizing effect of the phosphine oxide substituent in ion-pair acidities. But they also confirm the Russian conclusion that increased interaction with the gegenion is principally responsible. Note that the conversion of a Ph_2P group to $Ph_2P(O)$ produces almost as much acid strengthening in the p position of toluene as in a benzylic position (Table II). The results are more consistent with an almost constant increment associated with stronger ion pairing involving the added P–O dipole rather than with the proportionality effects of normal substituent behavior.

Experimental Section

Melting points were determined on a Buchi Apparatus and are not corrected. Visible and UV spectra were measured on a Cary 118 spectrometer. Analyses were by the Analytical Services Laboratory, University of California.

Benzyldiphenylphosphine (2) and Oxide 6. The phosphine **2** was prepared by the general Grignard method of Grim, McFarlane, and Davidoff[11] from benzyl chloride and chlorodiphenylphosphine in 53% yield and recrystallized twice from absolute ethanol followed by Kugelrohr distillation; mp 74 °C (lit.[12] mp 74 °C). This compound is air sensitive and may also be light sensitive. Accurate acidity measurements are not available at this time but preliminary studies do show that the pK_{CsCHA} is about 32 with a probable error of less than ±1 unit.[13]

The oxide was prepared by oxidation with H_2O_2 in THF or even by recrystallization from O_2-containing ethanol; mp 192 °C (lit.[14] mp193–194 °C).

Bis(diphenylphosphino)methane (1). This compound was purchased from Pressure Chemical Co. and recrystallized from 95% ethanol: colorless needles; mp 120–121 °C (lit.[15] mp120.5–1.5 °C).

Table III. Summary of Equilibrium Ion Pair Acidity Measurements

carbon acid	indicator[a]	log K	n[b]	pK (per H)
1	TPM	−0.60 ± 0.07	4	31.15 ± 0.07
	TpTM	−2.19 ± 0.12	3	31.15 ± 0.12
	BDPM	0.42 ± 0.08	4	30.92 ± 0.08
3	p-BBP	−0.79 ± 0.05	8	31.03 ± 0.12
	BDPM	0.51 ± 0.18	8	30.98 ± 0.18
4	p-MB	−0.90 ± 0.15	4	38.05 ± 0.15
	DXM	1.42 ± 0.10	9	37.7 ± 0.1
6	7	0.71 ± 0.01	8	24.89 ± 0.13
7	4,5-MP	1.25 ± 0.13	8	24.18 ± 0.13

[a] Abbreviations and pK_{CsCHA} values for indicators[4] are as follows: TPM, triphenylmethane, 31.45; p-MB, p-methylbiphenyl, 38.95; DXM, dixylylmethane, 36.3; TpTM, tri-p-tolylmethane, 33.04; BDPM, p-biphenyldiphenylmethane, 30.17; 4,5-MP, 4,5-methylenephenanthrene, 22.94; p-BBP, p-benzylbiphenyl, 31.82.
[b] Number of determinations.

(p-Phenylbenzyl)diphenylphosphine (3) and Oxide 7. In a glovebag filled with argon, 0.72 mL (4 mmol) of chlorodiphenylphosphine was added dropwise to 0.2 g of lithium metal in 20 mL of dry THF. Formation of lithium diphenylphosphide was accompanied by development of a red color. After 2 h the mixture was stoppered, removed from the glovebag, and added dropwise via cannula to a THF solution of 0.494 g (2 mmol) of p-phenylbenzyl bromide, until a red color persisted. The mixture was then stirred for an additional hour. Evaporation and fractional sublimation of the crude product [130 °C (0.003 mm)] afforded 440 mg (62.5% yield) of the desired phosphine **3**: mp 162–164 °C; high-resolution mass spectrum parent peak at m/e 352.1385 (calcd for $C_{25}H_{21}P$, 352.1381), m/e (relative intensity) 43 (48.7), 57 (22.9), 77 (8.5), 152 (13.9), 165 (20.2), 167 (100.0), 168 (17.4), 183 (17.7), 185 (9.4), 201 (14.0), 352 (26.4), 353 (7.3). This material oxidizes readily to the corresponding phosphine oxide; it should be used with degassed solvents.

Recrystallization of the crude product of another preparation from oxygen-saturated ethanol afforded 587 mg (83% yield after two steps) of white material (mp 251.5–253 °C) identified as the desired phosphine oxide **7**: high-resolution mass spectrum, parent peak at m/e 368.1319 (calcd for $C_{25}H_{21}OP$, 368.1325), m/e (relative intensity) 44 (20.9), 57 (13.8), 77 (14.9), 152 (11.1), 165 (16.3), 167 (36.3), 201 (100.0), 202 (12.8), 243 (9.1), 367 (23.6), 368 (51.3), 369 (10.2), 370 (1.1).

Anal. Calcd for $C_{25}H_{21}OP$: C, 81.50; H, 5.75; P, 8.41. Found: C, 81.59; H, 5.89; P, 8.50.

p-Tolyldiphenylphosphine (4) and Oxide 8. Commercial **4** (Fluka AG) was recrystallized three times from 95% ethanol and sublimed at 58–60 °C (0.02 torr): colorless crystals; mp 68.5–9.5 °C (lit.[16] mp 67–68.5 °C).

A solution of peracetic acid in acetic acid was prepared by slightly warming 1.77 g of 30% H_2O_2 (ca. 1.6 mL) with 8.63 g (ca. 8 mL) of acetic anhydride until the two phases became homogeneous; this solution now contained ca. 0.015 mol of peracetic acid. The peracetic acid solution was added dropwise to 2.76 g (0.01 mol) of **4** in 12 mL of CH_2Cl_2 and 8 mL of acetic acid. After the initial heat liberation, the system was allowed to cool to room temperature and was stirred overnight. The reaction mixture was diluted with water and extracted with benzene. The benzene extracts were combined, washed with aqueous 10% KOH, evaporated, and crystallized from cyclohexane–acetone (19:1) to afford 2.48 g (85% yield) of white crystals, mp 132.5–133.5 °C (lit.[17] mp 129–130 °C).

Acidity Measurements. Acidity determinations were accomplished by the general method described previously.[18] The experimental results are summarized in Table III, and the resulting

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$\mathrm{p}K_{\mathrm{CsCHA}}$ values are summarized in Table I.

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Registry No. **1**, 2071-20-7; **1·Cs**, 80359-57-5; **2**, 7650-91-1; **2·Cs**, 80359-58-6; **3**, 80359-59-7; **3·Cs**, 80359-60-0; **4**, 1031-93-2; **4·Cs**, 80359-61-1; **6**, 2959-74-2; **6·Cs**, 80359-62-2; **7**, 80359-63-3; **7·Cs**, 80359-64-4; **8**, 6840-28-4; **8·Cs**, 80359-65-5; benzyl chloride, 100-44-7; chlorodiphenylphosphine, 1079-66-9; lithium diphenylphosphide, 4541-02-0; *p*-phenylbenzyl bromide, 2567-29-5; 4-(phenylmethyl)-1,1-biphenyl, 613-42-3; 1-methyl-1,1′:4,1″-terphenyl, 28952-41-2; 4,4″-methylenebis[1,1′-biphenyl], 3901-32-4; 4-methyl-1,1′-biphenyl, 644-08-6.

Long-Range Corner Participation by Cyclopropane. 2. Synthesis and Study of 1-Substituted Tricyclo[3.2.2.$0^{2,4}$]nonanes[1]

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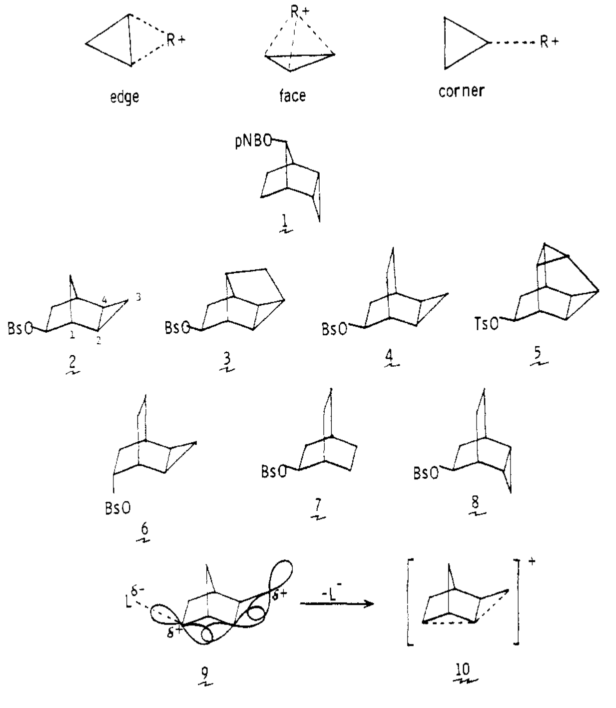
Acidity studies on tricyclo[3.2.2.$0^{2,4}$]nonane-1-carboxylic acid (**16-COOH**) vs. bicyclo[2.2.2]octane-1-carboxylic acid (**17-COOH**) show a slight inductive withdrawal by the cyclopropane ring. In spite of this, acetolysis of (tricyclo[3.2.2.$0^{2,4}$]non-1-yl)methyl tosylate (**16-CH_2OTs**) vs. (bicyclo[2.2.2]oct-1-yl)methyl tosylate (**17-CH_2OTs**) yields evidence of an anchimeric effect of 18.3 at 25 °C for cyclopropane assistance in this solvolysis. Product studies of the acetolysis of **16-CH_2OTs** demonstrate that *cyclopropano* ring expansion is preferred, and 83% of the product is acetate **21**, whereas *ethano* bridge migration is unimportant. These results, as well as studies undertaken in a previous paper, are discussed in terms of corner participation by the cyclopropane ring at the 1-carbinyl group via the back lobe at C-2 of the 2,4-bond.

Long-range effects of cyclopropane rings on carbonium ion processes have been of interest for some time. A review[2] extensively summarizes the work to 1973 and discusses in detail the anchimeric assistance associated with some homocyclopropylmethyl systems which include certain geometric requirements. When these constraints are absent, then no cyclopropyl participation occurs. Most examples of long-range participation by cyclopropane involve the "edge" of the cyclopropane ring interacting with the carbonium ion center, shown schematically in Chart I. When the geometry is ideal for edge participation, extremely large anchimeric effects can be observed, most notably in *endo,anti*-tricyclo[3.2.1.$0^{2,4}$]oct-8-yl *p*-nitrobenzoate (**1**), which solvolyzes 10^{12} times faster than the 7-norbornyl system.[3-7] Since most of the electron density of the bent bonds of cyclopropane is located outside the linear carbon–carbon line, it is not surprising that such participation is preferred.

Chart I



In contrast, participation by the face of the cyclopropane ring has, in the systems studied, been shown not to exist.[8-14] In between these two extremes is "corner" or "end-on" participation, which has been observed in only a few cases but which shows nowhere near the anchimeric effects of edge participation.[2] The best examples of corner participation may be the series of compounds **2**–**5**. The

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(1) (a) Paper 1: Chenier, P. J.; Kiland, P. J.; Schmitt, G. D.; VanderWegen, P. G. *J. Org. Chem.* **1980**, *45*, 5413. (b) A portion of the present paper was presented at the Joint Central-Great Lakes Regional Meeting of the American Chemical Society, Dayton, OH, May 1981, Abstract No. ORGN-264, and at the 1981 Kilpatrick Symposium on Carbenes, Carbenoids, and Cyclopropanes in Organic Synthesis, Illinois Institute of Technology, Chicago, IL, June 1981.

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