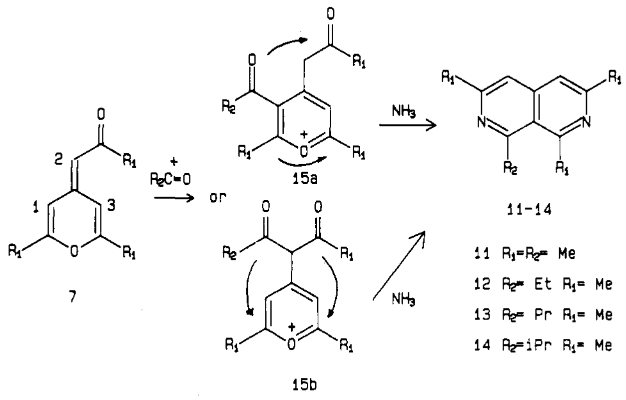
Scheme III



(CDCl$_3$) δ 24.1 (3,6-*C*H$_3$), 29.1 (1,8-*C*H$_3$), 116.2 (4,5-*C*), 120.9 (8a-*C*), 142.5 (4a-*C*), 153.5 (3,6-*C*), 159 (1,8-*C*); MS (70 eV), *m/e* (relative intensity) 187 (16.2), 186 (100), 185 (48), 171 (12), 144 (7), 115 (8), 77 (8), 53 (6), 51 (8), 42 (8), 39 (11).

1-Ethyl-3,6,8-trimethyl-2,7-naphthyridine (12): mp 36–37 °C; yield 39%; R_f 0.47 (diethyl ether). Anal. Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.92; H, 8.01; N; 13.95. ^{1}H NMR (CDCl$_3$) δ 1.4 (t, 3 H), 2.6 (s, 6 H), 3.06 (s, 3 H), 3.4 (q, 2 H), 7.14 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ 14.61 (CH$_2$*C*H$_3$), 24.02 (3-*C*H$_3$), 24.13 (6-*C*H$_3$), 28.56 (8-*C*H$_3$); 32.71 (*C*H$_2$CH$_3$); 116.02 (4-*C*), 116.38 (5-*C*), 119.5 (8a-*C*), 142.66 (4a-*C*), 153.06 (3-*C*), 153.82 (6-*C*), 158.25 (8-*C*), 163.60 (1-*C*); MS (70 eV), *m/e* (relative intensity) 201 (8), 200 (49), 199 (30), 186 (13), 185 (100), 172 (16).

1-Propyl-3,6,8-trimethyl-2,7-naphthyridine (13): mp 50 °C; molecular distillation, 110 °C (1.5 mbar); yield 23%; R_f 0.65 (diethyl ether). Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.51; H, 8.46; N, 13.02. ^{1}H NMR (CDCl$_3$) δ 1.07 (t, 3 H), 1.81 (m, 2 H), 2.6 (s, 6 H), 3.09 (s, 3 H), 3.35 (m, 2 H), 7.14 (s, 2 H); ^{13}CNMR (CDCl$_3$) δ 14.25 (CH$_2$CH$_2$*C*H$_3$); 24.10 (3-*C*H$_3$), 24.23 (6-*C*H$_3$), 28.56 (8-*C*H$_3$), 24.73 (CH$_2$*C*H$_2$CH$_3$), 41.8 (*C*H$_2$CH$_2$CH$_3$), 116.10 (4-*C*), 116.40 (5-*C*), 119.65 (8a-*C*), 142.77 (4a-*C*), 153.12 (3-*C*), 153.82 (6-*C*), 158.4 (8-*C*), 162.78 (1-*C*); MS (70 eV), *m/e* (relative intensity) 214 (5), 200 (14.4), 199 (100), 186 (67), 185 (10).

1-Isopropyl-3,6,8-trimethyl-2,7-naphthyridine (14): colorless oil; molecular distillation 90 °C (1 mbar); yield 27%; R_f 0.90 (diethyl ether). Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.36; H, 8.47; N, 13.00. ^{1}H NMR (CDCl$_3$) δ 1.37 (d, 6 H), 2.58 (s, 3 H), 3.12 (s, 3 H), 4.09 (q, 2 H), 7.05 (s, 1 H), 7.09 (s, 1 H). ^{13}C NMR (CDCl$_3$) δ 23.13 (CH*C*H$_3$), 24.0 (3-*C*H$_3$), 24.25 (6-*C*H$_3$), 29.06 (8-*C*H$_3$), 33.64 (1-*C*HCH$_3$), 115.54 (4-*C*), 116.40 (5-*C*), 119.14 (8a-*C*), 142.71 (4a-*C*), 152.59 (3-*C*), 153.62 (6-*C*), 157.81 (8-*C*), 167.13 (1-*C*); MS (70 eV), *m/e* (relative intensity) 214 (19), 200 (13.8), 199 (100), 186 (15.3), 183 (9.5), 172 (10.9).

Registry No. **7**, 39588-76-6; **11**, 88300-52-1; **12**, 88300-64-5; **13**, 108418-80-0; **14**, 98929-07-8; CH_3COCl, 75-36-5; CH_3CH_2COCl, 79-03-8; $CH_3CH_2CH_2COCl$, 141-75-3; $(CH_3)_2CHCOCl$, 79-30-1.

Molecular Mechanics Parameters for Organophosphines

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The molecular mechanics technique has been successfully applied to model numerous classes of organic compounds.[1] Most common functional groups can currently be handled by the MM2 force field,[2] which has replaced its MM1 predecessor.[3] However, some functional groups that were parameterized for MM1 were not updated and transferred to MM2 until recently. Since the two force fields are substantially different, it is not a very good approximation to use the older MM1 parameters with the MM2 force field. We wish to report here the MM2 parameter set for organophosphines. The latest version of the MM2 program has these values already incorporated.[2] The new parameters, listed in Table I, can be read directly into older program versions. It should be pointed out that using MM1 parameters[4] instead may lead to errors. For example, recent work by Rithner and Bushweller[5] found some significant discrepancies between experimental and calculated energy barriers by using the MM1 values in the MM2 force field.

Table I. Parameters

atom type				$V1$	$V2$	$V3$
				Torsional		
3	1	1	25	0.000	0.000	0.400
1	25	2	2	0.000	0.000	0.400
1	1	25	2	–0.050	–0.100	0.300
2	25	1	5	0.050	0.000	0.200
1	1	1	25	0.000	0.000	0.400
5	1	1	25	0.000	0.000	0.330
1	1	25	5	–0.530	–0.400	0.600
5	1	25	5	0.000	0.000	0.428
5	1	25	1	0.050	0.000	0.420
2	2	25	2	0.000	0.000	0.330
2	2	2	25	0.000	16.250	0.000
5	2	2	25	0.000	16.250	0.000
1	1	25	1	–0.150	0.000	0.500

Bond Stretching and Dipole Bond Moment

bond type	K_s	l_o	μ
5–25	3.33	1.4370	0.50
1–25	2.91	1.8560	0.83
2–25	2.91	1.8280	1.04

Bending

atom types			K_b	θ_o
	2	25	0.500	
2	25	2	0.480	93.200
1	25	2	0.480	92.500
5	25	5	0.438	93.400
5	1	25	0.360	111.000
1	25	5	0.480	95.000
1	1	25	0.480	111.500
1	25	1	0.576	96.000
2	2	25	0.380	120.000

In general, we have found good agreement between the available experimental data and our calculations. Table II displays the more important compounds which were used to derive our parameters.[6-12] Where experimental

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Table II. Calculated and Experimental Molecular Geometries

	obsd (Å or deg)	method, ref	MM1 (calcd)	MM2 (calcd)
methyl phosphine				
P-H	1.423 ± 0.007	ED, 6	1.438	1.4376
P-C	1.858 ± 0.003		1.857	1.8597
H-P-H	93.4		94.5	94.585
H-P-C	96.5 (assumed) (93.4)	MW, 7	95.9	95.957
P-C-H	109.6 ± 1.0		110.5	110.350/111.522
dimethylphosphine				
P-H	1.445 ± 0.02	ED, 6	1.439	1.4381
P-C	1.853 ± 0.003		1.853	1.8578
H-P-C	96.5 (assumed) (96.95)		97.0	96.983
P-C-H	109.8 ± 0.7	MW, 8	110.4	110.235
C-P-C	99.2 ± 0.6		98.0	98.174
trimethylphosphine				
P-C	1.846 ± 0.003	ED, 10	1.847	1.8545
P-C-H	110.7 ± 0.5		110.4	110.268
C-P-C	98.6 ± 0.3		99.3	99.007
ethylphosphine (gauche)				
P-C	1.880 ± 0.002	MW, 11	1.864	1.8667
C-C-P	110.1 ± 0.2		112.5	112.782
ethylphosphine (trans)				
P-C	1.876 ± 0.002	MW, 11	1.861	1.8665
C-C-P	115.2 ± 0.1		115.2	114.374
triphenylphosphine				
P-C	1.828 ± 0.048	X-ray, 12	1.828	1.8282
C-P-C	103.0 ± 0.2		103.1	101.453
P-C-C	124.0 ± 0.38		123.5	124.035
	116.08 ± 0.37		117.5	117.275

Table III. Rotational Barriers (kcal/mol) and Dipole Moments (D)

	barrier			dipole moment		
	obsd	MM1	MM2	obsd	MM1	MM2
methylphosphine	1.96	1.84	1.94	1.10	0.98	0.99
dimethylphosphine	2.22	2.20	2.11	1.23	1.18	1.11
trimethylphosphine	2.6	2.53	2.38	1.19	1.28	1.19
ethylphosphine						
energy difference between gauche terms	0.57 ± 0.28		0.57			
tert-butylphosphine	3.19	2.79	3.01		0.37	0.98
tri-*tert*-butylphosphine	8.6	8.3	8.80		0.70	0.78
isopropylphosphine						
gauche to trans		3.31	3.30			
gauche to gauche		2.85	2.85			
triphenylphosphine				1.40	1.40	1.40
di-*tert*-butylphosphine	<5		5.0			

data were either sketchy or nonexistent, we used ab initio methods to augment our "experimental" data set, as usual.[13] Our calculated P-C bond lengths appear slightly longer than the experimentally determined ones, and this can be attributed to the "electronegativity effect".[14]

The calculated energy barriers and dipole moments, together with the experimental values, are shown in Table III. All of the calculated barriers are within experimental error. Rithner and Bushweller[5] found the rotational barrier with NMR for di-*tert*-butylphosphine to be less than 5 kcal/mol and, by using MM1 parameters with the MM2 force field, calculated a 5.6 kcal/mol barrier. We calculate a barrier of 5.0 kcal/mol with the parameters listed in Table I (see Table III).

Although MM1 parameters may be used in MM2 and are expected to give semiquantitatively correct results the phosphine parameters listed in Table I were derived specifically for the MM2 force field, and their use is recommended for future calculations concerning these compounds.

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Registry No. Methylphosphine, 593-54-4; dimethylphosphine, 676-59-5; trimethylphosphine, 594-09-2; ethylphosphine, 593-68-0; *tert*-butylphosphine, 2501-94-2; triphenylphosphine, 603-35-0; tri-*tert*-butylphosphine, 13716-12-6; isopropylphosphine, 4538-29-8; di-*tert*-butylphosphine, 819-19-2.

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A Convenient and Selective Method for Reductive Deuteriation of Aryl Carbonyl Compounds

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In connection with our studies of the mechanism of the cleavage of carbon-carbon bonds in coal, we needed to label hydroaromatic compounds selectively in their benzylic positions. A survey of the literature revealed that