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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[13] Allinger, N. L.; Hickey, M. J. *Tetrahedron* **1972**, 28, 2157 and subsequent papers.

[14] Allinger, N. L.; Imam, M. R.; Frierson, M. R.; Yuh, Y. H.; Schafer, L. *Mathematics and Computational Concepts in Chemistry*, Trinajstic, N., Ed.; E. Horwood, Ltd.: Chichester, England, 1986; p 8.

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

Kofi Ofosu-Asante and Leon M. Stock*

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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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

Table I. Reductive Deuteriation of Aryl Aldehydes and Ketones[a]

compound	principal product	conditions			isolated yield, %
		pressure, psi	temp, °C	time, h	
acetophenone	ethylbenzene-*1,1*-d_2	20	25	4	69
2-acetonaphthone	2-ethylnaphthalene-*1,1*-d_2	12	55	4	73[a]
benzophenone	diphenylmethane-*1,1*-d_2	25	55	4–5	82
9-fluorenone	fluorene-*9,9*-d_2	25	55	12	80
α-tetralone	1,2,3,4-tetrahydronaphthalene-*1,1,4,4*-d_4	25	55	3–4	76
1-naphthaldehyde	1-methylnaphthalene-*1,1*-d_2	12	25	5	72[a]

[a] Approximately 90% of the starting material was converted.

there were several methods for the conversion of carbonyl groups into methylene-d_2 fragments.[1] However, most of these methods required several steps or suffered from other drawbacks. For example, the reduction of a carbonyl group to an alcohol by lithium aluminum deuteride followed by formation of the tosylate and further reaction with lithium aluminum deuteride leads to alkenes as well as alkanes and the Clemmenson reduction suffers from the disadvantage that the hydrogen atoms on adjacent aliphatic and aromatic carbon atoms are exchanged simultaneously.[1-3]

We recently reported a selective method for the exchange of benzylic hydrogen atoms using a palladium catalyst in acetic acid-*d* under a dideuterium atmosphere.[4] Inasmuch as palladium catalyzes the conversion of carbonyl groups adjacent to aromatic rings into methylene or methyl groups,[5] we became interested in the prospect of using this method to provide compounds with benzylic methylene-d_2 groups selectively. The results for several aromatic carbonyl compounds are given in Table I.

When the aromatic carbonyl compounds were reacted with dideuterium in the presence of a 10% palladium on carbon catalyst in acetic acid-*d* at 25–55 °C, the carbonyl groups were readily reduced. The products were separated and purified by distillation. Generally, high yields of the hydrocarbons were obtained in the first attempts to carry out the reaction. Reduction of the aromatic ring appears to be the principal side reaction. The ^{1}H NMR spectra of the products were compared with the ^{1}H NMR spectra of unlabeled authentic samples and the extent of ^{2}H incorporation was determined by examination of the ^{2}H NMR spectra. In all cases, the products were very selectively deuteriated in the benzylic position.

The results for the reduction of α-tetralone and the other aryl alkyl ketones underscore the high selectivity of the reaction. The catalytic method gave products with less than 5%, if any, deuterium on the adjacent carbon atom and none in the aromatic ring. In contrast, the Clemmenson reduction gave products that were labeled not only at the former carbonyl carbon atom but also at the ring positions and at the adjacent aliphatic carbon atoms.[2] The spectroscopic evidence also revealed that the carbonyl group in α-tetralone was reduced and that the benzylic hydrogen atoms at the 4 position were selectively exchanged. This observation is consonant with earlier observations.[4]

Catalytic reductions of this kind have been postulated to proceed in two steps in which the starting material is first converted to the benzyl alcohol and then hydrogenolysis (deuteriolysis) occurs to yield the hydrocarbon.[5] The high degree of selectivity observed in the palladium-catalyzed reactions precludes dehydration of the benzylic alcohol to an alkene as an intermediate step. Specifically, we did not obtain 1,2,3,4-tetrahydronaphthalene-*1,1,2,4,4*-d_5. Moreover, when the reactions of fluorenone and α-tetralone were stopped after the consumption of 1 mol of dideuterium, the intermediate secondary alcohols were isolated. These observations support the formulation of the reaction as a two-step process.[5,6]

Experimental Section

All the compounds examined in this study were obtained commercially. The physical and spectroscopic properties recorded for these materials were consistent with information in the literature and they were not purified. The catalyst (10% Pd/C) was obtained from Ventron, Alfa Division, and the dideuterium (99.7% isotopic purity) was provided by Cambridge Isotope Laboratories.

The apparatus and the procedure have been described previously.[4] Typically, acetophenone (3.0 g) in acetic acid-*d* (30 mL) was sealed in a reaction bottle with 10% palladium on carbon catalyst (150 mg, 5% w/w of substrate) and connected to a dideuterium reservoir at an initial pressure of 20 psi. The bottle was vigorously shaken at room temperature for 4 h after which the reaction mixture was diluted with water and the product extracted into pentane. The extract was washed with water and then dried over anhydrous magnesium sulfate. The pentane was removed and the product was purified by distillation. The results are summarized in Table I.

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[1] (a) Cook, D. *J. Org. Chem.* **1976**, *41*, 2173. (b) Green, M. M.; Cook, J.; Schwab, J. M.; Ray, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 3076. (c) Enzell, C. R. *Arkiv Kemi* **1966**, *26*, 87.

[2] Enzell, C. R. *Tetrahedron* Lett. **1966**, 1285.

[3] Djerassi; C.; Shapiro, R. H.; Vandewalle, M. *J. Am. Chem. Soc.* **1965**, *87*, 4892.

[4] Ofosu-Asante, K.; Stock, L. M. *J. Org. Chem.* **1986**, *51*, 5452.

[5] (a) Hudlicky, M. *Reductions in Organic Chemistry*; Wiley: New York, 1984; pp 99–163. (b) Rylander, P. *Catalytic Hydrogenation in Organic Syntheses*; Academic Press: New York, 1979; pp 77 and 100–102. (c) Breitner, E.; Roginski, E.; Rylander, P. N. *J. Org. Chem.* **1959**, *24*, 1855. (d) Mulholland, T. P. C.; Ward, G. *J. Chem. Soc.* **1954**, 4676.

[6] Meschke, R. W.; Hartung, W. H. *J. Org. Chem.* **1960**, *25*, 137.

Decomplexation Studies of Mo(CO)$_5$L Coordination Compounds Containing Organophosphorus Ligands. Determination of the Absolute Configuration of the [(–)-Me(EtO)(HO)P]Mo(CO)$_5$ Complex[1]

Herbert S. Aaron* and David I. Rossman

Research Directorate, Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, Maryland 21010-5423

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The resolution and some reactions of a Mo(CO)$_5$L coordination complex (**1a**) having a chiral P$^{\text{III}}$ ligand were recently reported.[2] Ligand decomplexation of **1a** and of

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[2] Reiff, L. P.; Rossman, D. I.; Szafraniec, L. J.; Aaron, H. S. *Inorg. Chem.* **1986**, *25*, 1451.