and 0.12 mL (1.9 mmol) of liquid N_2O_4 at 0 °C. The mixture was stirred for 1 h at 0 °C and washed quickly with cold NaCl-saturated water (2 × 5 mL), sodium carbonate saturated water (1 × 5 mL), and again with NaCl-saturated water (1 × 5 mL). All of the aqueous layers were combined and rewashed with methylene chloride (2 × 5 mL). All the organic phases were combined, dried with anhydrous sodium sulfate, and taken to dryness under vacuum to yield 70 mg (84%) of *N*-nitrosopentanesultam (**8c**) as a yellow oil, which was stored at -20 °C: NMR ($CDCl_3$) δ 3.85 (t, J = 7.0 Hz, 2 H), 3.48 (t, J = 7.0 Hz, 2 H), 1.90 (m, 4 H), 1.45 (m, 2 H); UV λ 405, 390 (max), 378 (sh) nm.

***N*-Butylmethanesulfonamide.** To 2.55 g (34.9 mmol) of *n*-butylamine in 50 mL of CH_2Cl_2 at 0 °C was added 2.00 g (17.5 mmol) of methanesulfonyl chloride, and the mixture was stirred for 30 min (the entire apparatus was flushed with argon to remove any CO_2, and a KOH trap was used to stop any CO_2 diffusion into the reaction vessel). The mixture was allowed to warm to 25 °C, and then it was washed with dilute HCl. The organic phase was dried with anhydrous sodium sulfate, and the solvent was removed under vacuum to yield 2.40 g (91%) of a colorless oil, which became solid just below room temperature: NMR ($CDCl_3$) δ 4.68 (br s, 1 H), 3.10 (m, J = 6 Hz, 2 H), 2.94 (s, 3 H), 1.48 (m, 4 H), 0.91 (m, 3 H); IR ($CHCl_3$) 1320, 1160, 1083, 859, 980, 760 cm^{-1} (lit.[23] IR 1083, 855, 978, 760 cm^{-1}).

***N*-Nitroso-*N*-butylmethanesulfonamide (9).** The nitrosation of *N*-butylmethanesulfonamide was carried out as described for *N*-nitrosopentanesultam (**8c**). The nitrosation of 500 mg (3.31 mmol) yielded 490 mg (82%) of *N*-nitroso-*N*-*n*-butylmethanesulfonamide (**9**) as a yellow oil, which became solid when stored at -20 °C: NMR ($CDCl_3$) δ 3.70 (t, J = 7 Hz, 2 H), 3.30 (s, 3 H), 1.35 (m, 4 H), 0.80 (m, 3 H); UV ($CHCl_3$) λ 413, 395, 380 (sh) nm.

Decompositions. The nitroso derivatives (~25 mg) in 5 mL of CCl_4 or $CHCl_3$ (5 mL) containing ~200 mg (13-fold molar excess) of finely powdered anhydrous sodium carbonate were heated in sealed tubes totally immersed in a bath at 79 °C. The mixtures were stirred in darkness, and aliquots were removed periodically, filtered to remove sodium carbonate and other salts, and then monitored by UV-vis spectra for the concentration of the nitroso sulfonamide group (at the absorption band at 390-395 nm). At the completion of the reaction, the products were determined via the ^1H NMR spectra (80 MHz).

Decomposition of *N*-Nitrosopropanesultam (8a) in the Presence of Ammonia. A solution of *N*-nitrosopropanesulfonamide (25.0 mg, 0.17 mmol) and ammonia (7.6 mL, 0.34 mmol) in 1 mL of $CDCl_3$ was deaerated by freeze-thaw cycles (liquid N_2, 0.01 Torr) and allowed to stand in a sealed tube at 28 °C; rapid nitrogen evolution was noted. Analysis by NMR indicated a half-life of 3 h. After 21 h, the supernatant was decanted from the solid, which had formed (which was washed with $CDCl_3$). The $CDCl_3$ phase contained propanesultam (7%), propanesultone (3%), and *N*-nitrosopropanesultam (4%). The solid, dissolved in D_2O/DO^- consisted of the anions of 3-hydroxypropanesulfonic acid (18%) and 3-aminopropanesulfonic acid (14%), and what appears to be a polymer (41%) with the probable repeat unit ~~(~~$NHCH_2CH_2CH_2SO_2$~~)~~ (broad ^1H NMR signals observed). A dilute run in 1 mL of $CDCl_3$ containing 2.0 mg (0.013 mmol) of the nitroso sultam and 40 mL (1.8 mmol) of NH_3 gave yields of the above compounds of 7%, 4%, 6%, 9%, 18%, and 58%, respectively.

***N*-Nitro-*N*-methylmethanesulfonamide (16, R = R′ = CH_3).** *N*-Methylmethanesulfonamide (50 mg, 0.46 mmol) was added to 0.33 mL (5.2 mmol) of 70% nitric acid at 0 °C. Concentrated sulfuric acid (0.18 mL, 3.3 mmol) was added dropwise, and the reaction mixture was stirred for 1 h at 0 °C. Ice was added, and the mixture was extracted with methylene chloride (3 × 5 mL). The organic phase was washed with cold 5% sodium bicarbonate solution (until the pH of the aqueous layer became neutral), dried over anhydrous sodium sulfate, and filtered, and the solvent was removed. Sublimation yielded 60 mg (85%) of white crystals, mp 40-41 °C: IR ($CDCl_3$) 1580, 1370, 1290, 1170 cm^{-1}; NMR ($CDCl_3$) δ 3.50 (s, 3 H)8 3.55 (br s, 3 H).

The decomposition of this compound in $CDCl_3$ solutions (0.01 M) at 95 °C, in a sealed evacuated glass tube with a 13 molar excess of dry sodium carbonate yielded exclusively methyl methanesulfonate (δ 3.02 and 3.92) with a half-life of ~535 h.

The Decomposition of *N*-Isobutyl-*N*′-(4-tolylsulfonoxy)-diimide *N*-Oxide (18). The title compound[5] in $CDCl_3$ (0.1 M solution) in the presence of a 13 molar excess of dry sodium carbonate was heated in a sealed, evacuated glass tube at 60 °C. Samples were removed periodically, and their NMR spectra were run. After 7 days (~2 half-lives), signals for isobutyl 4-toluenesulfonate, 2-methyl propane, and 4-toluenesulfonic acid, the reported products, were seen, but no signals attributable to an *E* isomer.

Thermal Stability of *N*-Nitropropanesultam (10). *N*-Nitropropanesultam (5 mg) in 1 mL of $CDCl_3$ was sealed under vacuum in an NMR tube, which was then heated at 79 °C. After 42 h, the NMR spectrum was identical with that of pure *N*-nitropropanesultam.

Acknowledgment. This work was supported by the D. Mead Johnson Foundation, BRSG Grant SO7 RR07041 awarded by the Biomedical Research Support Grant Program, Division of Research Resources Institutes of Health, and Grant 19488 from the Institute of General Medical Sciences of the U.S. Public Health Service.

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Relative Reactivity of 1-Adamantyl Radicals toward Diphenylphosphide and Benzenethiolate Ions

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Received August 25, 1986

Competition experiments of diphenylphosphide (Ph_2P^-) and benzenethiolate (PhS^-) ions toward *p*-anisyl radicals gave a kP/kS ratio of 52 in liquid ammonia. In competition experiments between the same nucleophiles toward 1-adamantyl radicals, the kP/kS ratio could not be determined in liquid ammonia (>1000). These competition experiments were also performed in Me_2SO, and *p*-anisyl radicals gave then a kP/kS ratio of 8.4 and 1-adamantyl radicals a kP/kS ratio of 830. This difference in selectivity is attributed to the greater stability of 1-adamantyl radicals compared to that of *p*-anisyl radicals. Competition experiments of 1-bromoadamantane and *p*-bromoanisole toward Ph_2P^- ions gave almost the same reactivity (k(1-BrAd)/k(*p*-BrAn) = 0.96), suggesting that the radical anion intermediates in these reactions transfer their odd electrons to both substrates with similar rates.

Nucleophilic substitution by the $S_{RN}1$ mechanism is a well-established process.[1,2] This mechanism has been proposed for aliphatic systems with electron-withdrawing groups,[1] unactivated aromatic systems,[2] vinyl halides,[3]

0022-3263/87/1952-2166$01.50/0

perfluoroalkyl iodides,[4] bridgehead halides,[5-7] neopentyl halides,[8,9] and halocyclopropanes.[10-12] Except for aliphatic systems bearing electron-withdrawing groups, the $S_{RN}1$-reactive substrates share the common characteristic of being unreactive in familiar S_N1 and S_N2 processes. Also, alkylmercury halides of the type RHgX react by the chain mechanism of nucleophilic substitution.[13]

The relative reactivity among different nucleophiles toward aryl radicals,[14-17] together with the absolute rate of coupling of aryl radicals with nucleophiles,[18,19] is known. The relative reactivity found between the most reactive nucleophile diphenylphosphide ion (Ph_2P^-) and the less reactive nucleophile benzenethiolate ion (PhS^-) is less than 100 in competition experiments with phenyl radicals in liquid ammonia.[14] With phenyl radicals and other aromatic radicals the absolute rate constants have been measured by electrochemical methods,[19] and it has been proposed that with several aromatic radicals they react with nucleophiles at a rate constant close to the diffusional value.

Nothing is known about the relative reactivity of nucleophiles toward simple alkyl radicals such as bridgehead, cyclopropyl, and neopentyl radicals and also the relative reactivity between aromatic and aliphatic halides in $S_{RN}1$ reactions. It is our purpose to study the relative reactivity of nucleophiles among these substrates in $S_{RN}1$ reactions.

The propagation steps for $S_{RN}1$ reactions of one substrate with two competing nucleophiles Nu_1^- and Nu_2^- are shown in Scheme I.

Scheme I

$$(RX)^{\bullet -} \rightarrow R^\bullet + X^- \quad (1)$$

$$R^\bullet + Nu_1^- \xrightarrow{k_{Nu_1^-}} (RNu_1)^{\bullet -} \quad (2)$$

$$R^\bullet + Nu_2^- \xrightarrow{k_{Nu_2^-}} (RNu_2)^{\bullet -} \quad (3)$$

$$(RNu_1)^{\bullet -} + RX \rightarrow RNu_1 + (RX)^{\bullet -} \quad (4)$$

$$(RNu_2)^{\bullet -} + RX \rightarrow RNu_2 + (RX)^{\bullet -} \quad (5)$$

As it has been pointed out, the ratio of concentration of the substitution product RNu_1 and RNu_2 derived from nucleophiles Nu_1^- and Nu_2^-, respectively, would be indicative of the relative rate constant kNu_1/kNu_2 of both reactions (eq 2 and 3). This will be so if the propagation steps are more frequent than the termination steps and if the nucleophiles and the intermediate radical anions are not involved in side reactions.[14]

It has been reported that 1-haloadamantanes react with different nucleophiles by the $S_{RN}1$ mechanism in liquid ammonia, such as Ph_2P^-, Ph_2As^-, PhS^-, $PhSe^-$, $PhTe^-$, Se^{2-}, and Te^{2-}, and that they do not react with carbanionic nucleophiles, diethyl phosphite, and amide ions, nucleophiles which are known to react with aryl radicals.[5-7]

From all the nucleophiles that react with 1-adamantyl radicals, those derived from arsenic, selenium, and tellurium react with a reversible reaction such as eq 6,[5,7] so they

$$1\text{-Ad}^\bullet + PhSe^- \rightleftharpoons (1\text{-AdSePh})^{\bullet -} \rightleftharpoons 1\text{-AdSe}^- + Ph^\bullet \quad (6)$$

$$1\text{-Ad}^\bullet + Ph_2P^- \rightarrow (1\text{-AdPPh}_2)^{\bullet -} \xrightarrow{\text{e.t.}} 1\text{-AdPPh}_2 \quad (7)$$

$$1\text{-Ad}^\bullet + PhS^- \rightarrow (1\text{-AdSPh})^{\bullet -} \xrightarrow{\text{e.t.}} 1\text{-AdSPh} \quad (8)$$

are not suitable to determine relative reactivities.[13] The only nucleophiles that fulfill the conditions of irreversible coupling with 1-adamantyl radicals are Ph_2P^- and PhS^- nucleophiles (eq 7 and 8 (1-Ad$^\bullet$ is the 1-adamantyl radical and e.t. is electron transfer)).

We now report the relative reactivities of Ph_2P^- and PhS^- as nucleophiles with 1-bromoadamantane and for comparison with *p*-bromoanisole. We also have determined the relative reactivities of these two substrates with Ph_2P^- as nucleophile.

Results and Discussion

The relative reactivity of Ph_2P^- ion vs. pinacolone enolate ion is 5.9 in liquid ammonia, and that of PhS^- ion vs. pinacolone enolate ion is 0.08, both toward phenyl radicals. Combination of both reactivities gave a relative reactivity of Ph_2P^- ions vs. PhS^- ions of about 70 in liquid ammonia, but there was not a straightforward competition between these two nucleophiles.

We chose *p*-bromoanisole to find the relative reactivity of Ph_2P^- ion vs. PhS^- ion toward *p*-anisyl radicals in liquid ammonia because Ph_2P^- ion is formed from triphenylphosphine and sodium metal in liquid ammonia (see Experimental Section), and the substitution product of the competition is also triphenylphosphine in reaction with phenyl radicals; some error can be introduced if some of the triphenylphosphine were left. With *p*-bromoanisole the substitution product is *p*-anisyldiphenylphosphine, and *p*-anisyldiphenylphosphine oxide is formed in the workup, which has a GLC retention time different from that of triphenylphosphine oxide.

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Table I. Photostimulated Reaction of 1-Bromoadamantane and *p*-Bromoanisole with Ph_2P^- and PhS^- Ions in Me_2SO[a]

expt	substrate,[b] 10^3M	nucleophile, 10^3M	$h\nu$, min	Br^-	product, yield[c] % substitution product
1	1-BrAd 17.5	PhS^- 19.5	180	76.0	70.3
2[d]	9.54	10.6	120	73.5	69.5
3	9.54	10.6	60	70.0	69.8
4	13.5	14.8	60[e]	3	f
5	9.99	Ph_2P^- 11.1	60	75.0	70.3[k]
6[g]	10.8	12.0	15	71.0	49.5[k]
7[h]	15.4	17.1	10	70.0	48.0[k]
8	9.27	10.3	15[e]	5	*f*
9[i]	*p*-BrAn 18.3	PhS^- 20.3	120	*f*	73.0
10	9.54	10.6	60	*f*	71.4
11	13.9	15.5	60[e]	3	*f*
12	10.1	Ph_2P^- 11.2	15	73.0	65.6
13[j]	11.0	12.2	15	79.0	68.4
14	9.54	10.6	15[e]	4	*f*
15	1-AdSPh 0.10	9.80	20	*f*	5[k]

[a] Reactions carried out in 100 mL of Me_2SO, 25 °C, under nitrogen. [b] 1-BrAd = 1-bromoadamantane, *p*-BrAn = *p*-bromoanisole, 1-AdSPh = 1-adamantanyl phenyl sulfide. [c] Yields based on substrate concentration; the substitution products were determined by GLC using internal standard, and the phosphines as phosphines oxides. [d] Adamantane 4% yield. [e] Dark reaction. [f] Not quantified. [g] Adamantane 11.5% yield. [h] Adamantane 15% yield. [i] Anisole 8.5% yield. [j] Anisole 10% yield. [k] The substitution product was 1-adamantyldiphenylphosphine.

Table II. Competition Experiments of 1-Bromoadamantane and *p*-Bromoanisole with Ph_2P^- and PhS^- Ions[a]

expt	substrate,[b] 10^3M	Ph_2P^-, 10^3M	PhS^-, 10^3M	solvent	yields[c] phosphine, 10^4M	yields[c] sulfide, 10^4M	kP/kS
1	*p*-BrAn (5.1)	10.4	60.1	NH_3	18.5	2.80	42
2	*p*-BrAn (5.5)	10.1	94.9	NH_3	22.4	3.55	67
3	*p*-BrAn (10.1)	20.3	83.0	NH_3	58.7	6.01	47
							52 (av, expt 1–3)
4	1-BrAd (5.0)	9.7	80.1	NH_3	45.5	*d*	
5	1-BrAd (5.3)	10.3	60.3	NH_3	48.8	*d*	
6	1-BrAd (10.1)	19.7	120.6	NH_3	95.3	*d*	
7	*p*-BrAn (11.7)	20.0	81.2	Me_2SO	52.1	31.3	9.5
8	*p*-BrAn (10.1)	20.0	122.4	Me_2SO	32.0	19.6	7.4
							8.4 (av, expt 7 and 8)
9	1-BrAd (5.1)	9.9	79.8	Me_2SO	22.6	0.25	840
10	1-BrAd (4.6)	10.1	41.6	Me_2SO	18.0	0.11	820
							830 (av, expt 9 and 10)

[a] Reactions carried out in 300 mL of refluxing liquid ammonia under nitrogen, irradiation time 60 min (expt 1–6); reactions carried out in 100 mL of Me_2SO, 25 °C under nitrogen, irradiation time 15 minutes (expt 7–10). [b] *p*-BrAn = *p*-bromoanisole, 1-BrAd = 1-bromoadamantane. [c] Expt 1–3 7, 8, phosphine is *p*-anisyldiphenylphosphine, quantified as its oxide, and sulfide is *p*-anisyl phenyl sulfide; expt 4–6, 9, 10, phosphine is 1-adamantyldiphenylphosphine, quantified as its oxide, and sulfide is 1-adamantyl phenyl sulfide. [d] 1-Adamantyl phenyl sulfide was not possible to quantify accurately.

It is known that diphenyl sulfide reacts under photostimulation with acetone enolate ions to give phenyl radicals and benzenethiolate ions.[20] Phenyl radicals then react with acetone enolate ion to give phenylacetone. In our experimental conditions *p*-anisyl phenyl sulfide does not react with Ph_2P^- ion substantially (<5%), thus this competing reaction did not disturb our competition experiments.

In the photostimulated reaction of *p*-bromoanisole with Ph_2P^- and PhS^- ion as nucleophiles, we found a relative reactivity of kP/kS of 52 (expt 1–3, Table II), similar to the relative reactivity found with phenyl radicals in liquid ammonia.

In order to determine the kP/kS ratio toward 1-adamantyl radicals, we performed the photostimulated reaction of 1-bromoadamantane with Ph_2P^- and PhS^- ions in liquid ammonia. Although a large excess of PhS^- ions was used, it was not possible to measure the relative reactivity of both nucleophiles toward 1-adamantyl radicals because very small amounts of 1-adamantyl phenyl sulfide were formed. We estimated that the kP/kS ratio is larger than 1000 in liquid ammonia (expt 4–6, Table II).

It is known that Me_2SO is a good solvent for $S_{RN}1$ reactions,[21] but only liquid ammonia has been used with 1-haloadamantanes as substrate. We studied the photostimulated reaction of *p*-bromoanisole and 1-bromoadamantane with Ph_2P^- and PhS^- ions in Me_2SO.

In the photostimulated reaction of 1-bromoadamantane with PhS^- ions there was a 70% yield of reaction in 60 min and 76% yield in 180 min of irradiation, and there was no dark reaction in the same experimental conditions (expt 1–4, Table I). With Ph_2P^- ions there was a 70% yield of reaction, but in only 10 min of irradiation. The reduction product adamantane was formed in about 10% yield, but the dimeric product of 1-adamantyl radicals, 1,1-biadamantyl, was not formed, though it was found in liquid ammonia.[5] There was not a reaction in the dark (expt 5–8, Table I). Almost the same results were found with *p*-bromoanisole as substrate (expt 9–14, Table I). From our results it is concluded that Me_2SO is a suitable solvent for our studies.

In the photostimulated reaction of *p*-bromoanisole with Ph_2P^- and PhS^- ions in Me_2SO, it was found that the relative reactivity kP/kS ratio is only of 8.4 (expt 7–8, Table II). This decrease in the selectivity of *p*-anisyl radicals toward these nucleophiles could be ascribed to an increase in the rate of coupling of PhS^- ions toward *p*-

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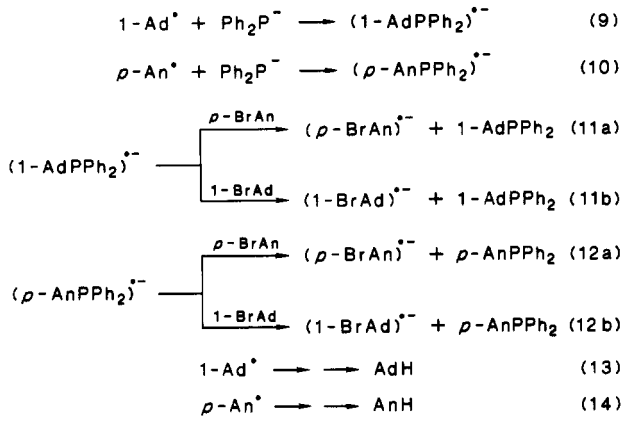
Scheme II



anisyl radicals. It was suggested that the rate of coupling of phenyl radicals with Ph_2P^- ion is diffusional in liquid ammonia at −33 °C.[14] In Me_2SO at 25 °C, the rise of the reaction temperature will affect only the rate of coupling of *p*-anisyl radicals with PhS^- ions. Also we have to consider the change from a polar protic solvent such as liquid ammonia to a polar aprotic solvent such as Me_2SO, which also could change the relative reactivities of these nucleophiles.

In the photostimulated reaction of 1-bromoadamantane with Ph_2P^- and PhS^- ions, we found a relative reactivity of kP/kS ratio of 830 (expt 9 and 10, Table II). As in the case of *p*-anisyl radicals, there is a decrease on the relative reactivity compared with the competition experiments in liquid ammonia.

In order to know if Ph_2P^- ion could react under irradiation with the substitution product 1-adamantyl phenyl sulfide, thus increasing the kP/kS ratio, we studied the photostimulated reaction of 1-adamantyl phenyl sulfide with a large excess of Ph_2P^- ions, and after 20 min of irradiation, less than 5% yield of reaction occurred (expt 15, Table I).

The fact that 1-adamantyl radicals are about 100 times more selective than *p*-anisyl radicals toward these two nucleophiles could be ascribed to the greater stability of 1-adamantyl radicals compared to that of *p*-anisyl radicals. We estimate that 1-adamantyl radicals are about 17 kcal/mol more stable than phenyl radicals.[22]

When two substrates react separately, the overall reactivity is determined not only by the propagation cycle but also by the relative rates of initiation and termination; when they react together, as in the competition experiments, they suffer the same initiation and termination steps, and the relative rates of electron transfer from the radical anion intermediate of the propagation cycle to the substrates are measured.

In competition experiments between *p*-bromoanisole and 1-bromoadamantane with Ph_2P^- ion in Me_2SO, the most important reaction steps are those sketched in Scheme II.

In the photostimulated competitive reaction of 1-bromoadamantane and *p*-bromoanisole with Ph_2P^- ions in 100 mL of Me_2SO we found that both substrates have a close relative reactivity (k(1-BrAd)/k(*p*-BrAn) = 0.96).

This result is indicative that the radical anions formed in eq 9 and 10 transfer their odd electrons to both substrates at almost the same rate (eq 11 and 12). Although the reduction potentials of these compounds are not known in Me_2SO, the electron-transfer reactions to *p*-bromoanisole and 1-bromoadamantane, which are expected to have similar reduction potential, are also expected to be energetically favorable and thus very fast.[23]

The fact that in this system the electron-transfer rates are the same regardless of the nature of the substrates shows that a change from *p*-anisyl to 1-adamantyl is less important than a change in the leaving groups. Comparing, for instance, the reaction of iodobenzene and bromobenzene with pinacolone enolate ion shows the former to react 7.3 times faster than the latter.[24]

Experimental Section

General Methods. The general method was the same as described before.[5,15,16] Gas chromatographic analyses were performed in a Varian Aerograph Series 1400 with a flame-ionization detector equipped with a data processor Chromatopack C-R1A (Shimadzu). Analyses were performed by using a 1.5% O.V-101 on 80–100-mesh Chromosorb G, 1.5-m × 3.5-mm stainless still columns. Potentiometric titrations were carried out in a Digital pH meter Seybold equipped with an electrode Ag/Ag^+ with internal reference and standard solution of $AgNO_3$.

Materials. *p*-Bromoanisole, 1-bromoadamantane, triphenylphosphine, and diphenyl disulfide were analytical grade, commercially available products used as received. The nucleophiles Ph_2P^- and PhS^- were prepared in situ following the same procedure as reported.[15,16] Me_2SO (Mallinckrodt, AR) was dried over molecular sieves (4 Å) for 2 days, distilled under dry nitrogen and reduced pressure and then stored with nitrogen and molecular sieves (4 Å, 10% w/v) as reported.[25]

Photostimulated Reactions. These reactions were carried out in a photochemical reactor equipped with four 250-W lamps with maximum emission at 350 nm (Philips, Model HPT, water refrigerated).

Photostimulated Reaction of 1-Bromoadamantane with Ph_2P^- Ions in Me_2SO. Approximately 300 mL of ammonia previously dried over Na were distilled into a 500-mL three-necked, round-bottom flask equipped with a cold finger, nitrogen inlet, and magnetic stirrer. To the ammonia was added triphenylphosphine (1.11 mmol) followed by the addition of small pieces of Na metal (2.3 mmol). To the orange solution formed *t*-BuOH was added (1.1 mmol) to neutralize the amide ions formed by protonation of the phenyl anions formed. The ammonia was allowed to evaporate under positive pressure of dry nitrogen, and 100 mL of dry degassed Me_2SO was added. All the residue was dissolved and again degassed, and 1-bromoadamantane (1.0 mmol) was added and the flask was either maintained in the dark or subjected to irradiation for 60 min. The reaction was quenched with NH_4NO_3. To this solution was added 200 mL of cold distilled water, and the solution was then extracted with three portions of 30 mL each of methylene chloride. The organic extract was oxidated following the procedure reported.[26] To quantify the substitution product by GLC n-$C_{32}H_{66}$ was added as internal standard. The reduction product adamantane was quantified by using naphthalene as internal standard.

Photostimulated Reactions of 1-Bromoadamantane with PhS^- Ions in Me_2SO. The nucleophile was prepared in the same form as Ph_2P^- ions. Diphenyl disulfide (0.53 mmol) was added to 200 mL of dry liquid ammonia, and then Na metal (1.06 mmol) was added in small pieces and the ammonia allowed to evaporate under dry nitrogen. To the white residue was added 100 mL of dry degassed Me_2SO, and 0.95 mmol of 1-bromoadamantane was added. The colorless solution obtained was irradiated for 120 min.

(22) Calculated by Benson's additivity rules, see: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; Chapter 2, pp 73, 272, and 289.

(23) The related compound Ph_3P has a reduction potential of −2.75 V, a more negative value than that of 1-bromoadamantane (−2.38 V) or *p*-bromoanisole (estimated −2.30 to −2.34 V) (DMF vs. sce) (see: Santhanam, K. S. V.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 1118. Lambert, F. L.; Albert, A. H.; Hardy, J. P. *J. Am. Chem. Soc.* **1964**, *86*, 3155. Sease, J. W.; Burton, F. G.; Nickol, S. C. *J. Am. Chem. Soc.* **1968**, *90*, 2595). We thank a reviewer for helpful suggestions on this subject.

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The reaction was quenched by adding NH_4NO_3 and extracted as described previously. The substitution product was quantified by GLC using 4-bromobiphenyl as internal standard.

Photostimulated Reaction of *p*-Bromoanisole with Ph_2P^- and PhS^- Ions in Me_2SO. These reactions were carried out by following the same procedure as before, with the same internal standards.

General Procedure for Competition Experiments. The nucleophile Ph_2P^- and PhS^- ions were simultaneously prepared in liquid ammonia as in the preceding reactions. Then the ammonia was allowed to evaporate and dry degassed Me_2SO was added. The substrate, 1-bromoadamantane or *p*-bromoanisole, was quickly added, and the flask was irradiated as stated in Table II. The reactions were worked-up as before and quantified by GLC. Molar response factors were determined and used in the calculations of GLC results in all cases.

Calculations of Relative Reactivities of Nucleophiles. Equation 15 was employed. $[Nu_1^-]_0$ and $[Nu_2^-]_0$ are initial concentrations, and $[RNu_1]_t$ and $[RNu_2]_t$ are concentrations of products at time t. This equation is based on the assumption that both Nu_1^- and Nu_2^- reactions with the radicals are first order in nucleophile.[27]

$$\frac{kNu_1^-}{kNu_2^-} = \frac{\ln ([Nu_1^-]_0/([Nu_1^-]_0 - [RNu_1]_t))}{\ln ([Nu_2^-]_0/([Nu_2^-]_0 - [RNu_2]_t))} \quad (15)$$

Calculations of Relative Reactivities of Substrates. To calculate the relative reactivity we used eq 16:[27]

$$\frac{k(1\text{-BrAd})}{k(p\text{-BrAn})} = \frac{[p\text{-BrAn}]_0([1\text{-AdPPh}_2] + [\text{AdH}])}{[1\text{-BrAd}]_0([p\text{-AnPPh}_2] + [\text{AnH}])} \quad (16)$$

In this equation we used both products formed from 1-adamantyl radicals (1-adamantyldiphenylphosphine and adamantane) and from *p*-anisyl radicals (*p*-anisyldiphenylphosphine and anisole) because they are products derived from the radicals.

Acknowledgment. E.R.N.B. gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina. INFIQC is jointly sponsored by the CONICET and the Universidad Nacional de Córdoba. This work is partially supported by the Consejo de Investigaciones Científicas y Tecnológicas de Córdoba.

Registry No. Ph_2P^-, 6396-02-7; PhS^-, 13133-62-5; 1-AdSPh, 88459-01-2; 1-bromoadamantane, 768-90-1; *p*-bromoanisole, 104-92-7; 1-adamantyl, 2819-03-6; *p*-anisyl, 2396-03-4.

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Synthesis of Polydentate Ligands with Homochiral Phosphine Centers

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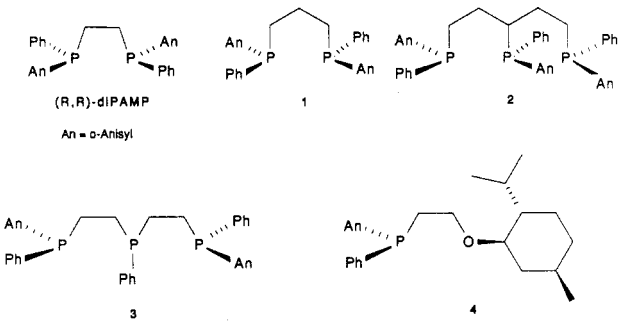
Received October 27, 1986

Optically pure (*S*)-(*o*-methoxyphenyl)phenylvinylphosphine oxide was prepared from (*S*)-(*o*-methoxyphenyl)methylphenylphosphine oxide and *N*,*S*-dimethyl-*S*-phenylsulfoximine and utilized in the preparation of (*S*,*S*)-1,3-propanediylbis[(*o*-methoxyphenyl)phenylphosphine], (*S*,*S*,*S*)-1,3,5-pentanetriyltris[(*o*-methoxyphenyl)phenylphosphine], (*S*,*S*)-bis[2-[(*o*-methoxyphenyl)phenylphosphinyl]ethyl]phenylphosphine, and (*SP*,1′*R*,2′*S*,5′*R*)-[2-[(2′-isopropyl-5′-methylcyclohexyl)oxy]ethyl](*o*-methoxyphenyl)phenylphosphine. These phosphines as complexes with rhodium(I) salts were used in hydrogenation of α-(acetylamino)acrylic acids to provide *N*-acetyl amino acids in optical purities ranging from 22 to 96%.

Among the large number of optically active phosphine ligands that have been used in catalytic asymmetric reactions,[1] only several possess chiral centers at phosphorus.[2] Knowles and co-workers made the initial breakthrough in this chemistry with their synthesis of a C_2-symmetric chiral bisphosphine, (*R*,*R*)-1,2-ethanediylbis[(*o*-methoxyphenyl)phenylphosphine] (diPAMP), and demonstration that the ligand is exceptionally effective in catalytic asymmetric hydrogenation of α-(acylamino)acrylic acids.[2a,b] Although the synthesis of such ligands is laborious, they are usually effective at very low concentrations. Herein we describe new methods for the production of polydentate phosphine ligands and their application to the synthesis of the novel, optically pure phosphine ligands **1**–**4** that are chiral at phosphorus. Ligand **1**, the next higher homologue of the celebrated diPAMP was of particular interest. The results of our investigation of the use of these ligands in the production of optically active α-amino acids by asymmetric hydrogenation are also summarized.



Our methods for the synthesis of ligands **1**–**4** utilize

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