with a JEOL ES-DVT1 controller. Estimated accuracy for the hyperfine splitting constants, ±0.1 G.

Measurements of Equilibrium Constants. A dimer solution (0.40 mL, 83.8 mM) was put into an ESR cell, and the solution was degassed by three freeze–pump–thaw cycles by using a high-vacuum system and the cell was sealed off. ESR spectra were recorded on a JEOL JES-FE-2XG spectrometer and double integration of the spectra was performed on a JEOL ES-9835B computer data system. Calibration curves were drawn with 1,3,5-triphenylverdazyl solutions[26] (6.92×10^{-7} to 2.05×10^{-6} M) using the same ESR cell and the same instrument settings as above. Equilibrium constants (K) were measured at three different temperatures between 61 and 83 °C, and the measurements were three times repeated. After measurement, all the samples were checked by TLC and it was confirmed that the amounts of the dimers decomposed during the time (ca. 15 min) necessary to measure radical concentrations at three different temperatures were a negligibly small quantity. The errors given refer to the maximum deviation from the average value.

(26) Kuhn, R.; Trischmann, H. *Monatsh. Chem.* **1964**, *95*, 457–479.

Acknowledgment. We gratefully acknowledge Dr. H. Tanaka of Tokushima University for the measurement of the radical concentrations.

Photostimulated Reaction of 1-Halo- and 1,4-Dihalobicyclo[2.2.2]octanes with Diphenylphosphide Ions by the $S_{RN}1$ Mechanism

Ana N. Santiago,[1] V. Sankar Iyer,[2] William Adcock,*[,2] and Roberto A. Rossi*[,1]

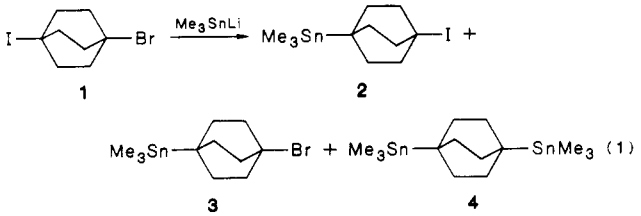
Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Suc. 16, C.C. 61, 5016 Córdoba, Argentina, and School of Physical Sciences, the Flinders University of South Australia, Bedford Park, SA, Australia 5042

Received September 24, 1987

The reaction of 1-iodobicyclo[2.2.2]octane (**5**) with diphenylphosphide ions (**6**) in liquid ammonia gives in 20 min of irradiation and after oxidation of the reaction product good yields of (bicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide (**8**). Although there is some reaction under dark conditions, the reaction is light catalyzed and inhibited by *p*-dinitrobenzene, a good inhibitor of $S_{RN}1$ reactions. However, 1-chlorobicyclo[2.2.2]octane (**9**) does not react under the same reaction conditions (240 min of irradiation). 1-Chloro-4-iodobicyclo[2.2.2]octane (**10**) gives only the monosubstitution product (4-chlorobicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide (**12**), but 1-bromo-4-iodobicyclo[2.2.2]octane (**1**) and 1,4-diiodobicyclo[2.2.2]octane (**15**) give the disubstitution product **14**; the monosubstitution products are not intermediates of these reactions. It is suggested that these reactions occur by the $S_{RN}1$ mechanism of nucleophilic substitution at bridgehead positions.

Radical nucleophilic substitution ($S_{RN}1$ reaction) is a well-established process,[3] and several different types of substrates have been shown to react by this mechanism.[3,4] Among them there are reports in which halo bridgehead compounds substituted at the bridgehead position react with nucleophiles by the $S_{RN}1$ mechanism. For instance, 1-X-adamantanes (X = Cl, Br, I),[5,6] 9-bromotriptycene,[6] and 4-iodotricyclene[7] react with nucleophiles by this mechanism. However, 1-chlorobicyclo[2.2.1]heptane[8] and 4-chlorotricyclene[7] are unreactive under similar experimental conditions.

On the other hand, it has been reported that 1-bromo-4-iodobicyclo[2.2.2]octane (**1**) reacts with (trimethylstannyl)lithium in THF at 0 °C to give the three stannanes **2–4** in the ratio 3:1:3 (eq 1).[9]



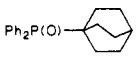
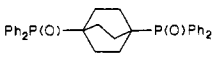
It has been suggested that this reaction, along with others for additional 1,4-dihalobicyclo[2.2.2]octanes, occurs by a chain process similar to the $S_{RN}1$ mechanism but with an additional propagation step involving iodine atom abstraction from **1** by the 4-(trimethylstannyl)bicyclo[2.2.2]oct-1-yl radical intermediate to give **2** as product.[9b]

We now report the photostimulated reaction of 1-halo- and 1,4-dihalobicyclo[2.2.2]octanes with diphenylphosphide ions in order to determine the scope and limitations of these substrates in $S_{RN}1$ reactions.

(1) Universidad Nacional de Córdoba.
(2) The Flinders University.
(3) For reviews, see: (a) Kornblum, N. *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z, Eds.; Wiley: Chichester, UK, 1982; Supplement F, Chapter 10. (b) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; American Chemical Society: Washington, DC, 1983. (c) Norris, R. K. *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, UK, 1983; Supplement D, Chapter 16.
(4) (a) Feiring, J. *J. Org. Chem.* **1983**, *48*, 347; *J. Fluorine Chem.* **1984**, *24*, 191 and references cited therein. (b) Pierini, A. B.; Peñéñory, A. B.; Rossi, R. A. *J. Org. Chem.* **1985**, *50*, 2739. (c) Ashby, E. C.; Argyropoulos, J. N. *J. Org. Chem.* **1985**, *50*, 3274. (d) Rossi, R. A., Santiago, A. N.; Palacios, S. M. *J. Org. Chem.* **1984**, *49*, 3387. (e) Meijs, G. F. *J. Org. Chem.* **1984**, *49*, 3863; **1986**, *51*, 606.
(5) Rossi, R. A.; Palacios, S. M.; Santiago, A. N. *J. Org. Chem.* **1982**, *47*, 4654.
(6) Palacios, S. M.; Santiago, A. N.; Rossi, R. A. *J. Org. Chem.* **1984**, *49*, 4609.
(7) Santiago, A. N.; Morris, D. G.; Rossi, R. A. *J. Chem. Soc., Chem. Commun.* **1988**, 220.
(8) Santiago, A. N. Ph.D. Thesis, Universidad Nacional de Córdoba, 1986.
(9) (a) Adcock, W.; Iyer, V. S.; Kok, G. B.; Kitching, W. *Tetrahedron Lett.* **1983**, *24*, 5901. (b) Adcock, W., Iyer, V. S.; Kitching, W.; Young, D. *J. Org. Chem.* **1985**, *50*, 3706.

0022-3263/88/1953-3016$01.50/0 © 1988 American Chemical Society

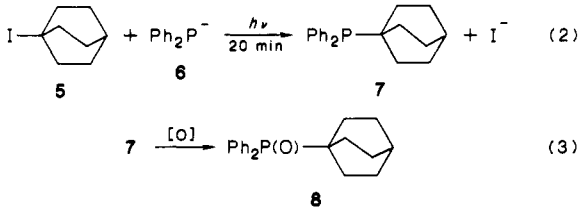
Table I. Reactions of 1-Halo- and 1,4-Dihalobicyclo[2.2.2]octanes with Diphenylphosphide Ions

expt	X	Y	conc × 10^3, M	$[Ph_2P^-] \times 10^3$, M	condition (min)	halide[b]	yield,[a] %		substrate
									
1	I	H	3.42	3.40	$h\nu$ (20)	86	87		c
2	I	H	1.46	1.40	dark (20)	25	24		c
3	I	H	1.19	1.00	dark (20)[d]	15	6		c
4	CI	H	1.74	1.93	$h\nu$ (240)	<5			>95[e]
5	I	CI	1.71	3.33	$h\nu$ (60)	73[f]	63[g]		c,h
6	I	Br	1.58	3.64	$h\nu$ (60)	140	<6	64	13
7	I	Br	0.08	0.17	dark (60)	104	<2	52	47
8	I	Br	0.86	1.86	dark (60)[i]	30	<2	~10[j]	60
9	I	Br	0.07	0.29	$h\nu$ (60)[k]	197	9	83	
10	I	I	1.10	3.33	$h\nu$ (60)	140	17	58	12
11	I	I	0.85	1.78	dark (60)	94	c	46	35

[a] Halide ions determined potentiometrically, and the products are isolated yield, unless otherwise stated. [b] Mol % of halide per mol of substrate. [c] Not quantified. [d] *p*-DNB added (20 mol %). [e] Determined by GLC. [f] Iodide ions, chloride ion, <4%. [g] (4-Chlorobicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide. [h] Small amounts of 1-chloro- and 1-(diphenylphosphinyl)bicyclo[2.2.2]octane were found but not quantified (<3% yield). [i] *p*-DNB added (100 mol %). [j] Contaminated with *p*-DNB. [k] Solvent liquid NH_3–*t*-$BuNH_2$ (2.5:1).

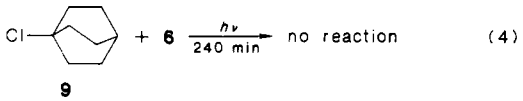
Results

The photostimulated reaction of 1-iodobicyclo[2.2.2]octane (**5**) with diphenylphosphide ions (**6**) in liquid ammonia gave, after 20 min of irradiation, a 86% yield of iodide ion release, and the substitution product 1-bicyclo[2.2.2]octyldiphenylphosphine oxide (**8**) was isolated after oxidation in 87% yield (eq 2 and 3, experiment 1, Table I).

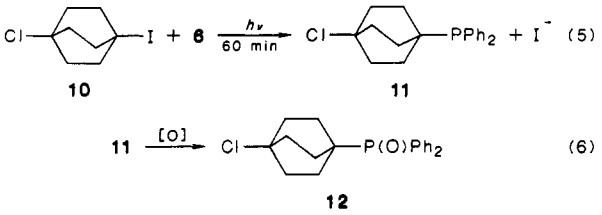


In the dark, **5** together with **6** gave a 25% yield of iodide ion release in 20 min, decreasing to 15% in the presence of *p*-dinitrobenzene, a well-known inhibitor of $S_{RN}1$ reactions (experiments 2 and 3, Table I).

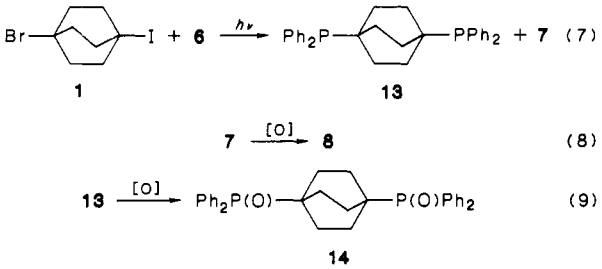
For the photostimulated reaction of 1-chlorobicyclo[2.2.2]octane (**9**), chloride ion was found in less than 6% yield after 240 min of irradiation. No substitution product **8** was found, and the substrate **9** was recovered in more than 95% yield (eq 4, experiment 4, Table I).



In the photostimulated reaction of 1-chloro-4-iodobicyclo[2.2.2]octane (**10**) with **6**, a 73% yield of iodide ion was detected after 20 min; the chloride ion was present in less than 5% yield. The monosubstitution product (4-chlorobicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide (**12**) was isolated after oxidation in 63% yield (eq 5 and 6, experiment 5, Table I).

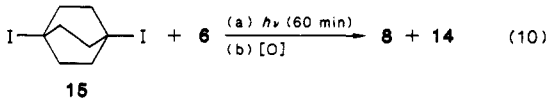


The photostimulated reaction of 1-bromo-4-iodobicyclo[2.2.2]octane (**1**) with **6** gave, after 60 min of irradiation, a 140% yield of halide ions (based on mol % of halide ions per mol of substrate **1**). The disubstitution product 1,4-bis(diphenylphosphinyl)bicyclo[2.2.2]octane (**14**) and the monosubstituted product **8** were formed and isolated in 64% and in less than 6% yields, respectively, after oxidation of the products (eq 7–9, experiment 6, Table I).



However, after 60 min of irradiation the reaction of **1** with **6** is incomplete. We suspected that the poor solubility of **1** in liquid ammonia may be the problem; thus, we performed the same reaction in a solvent mixture of liquid ammonia–*tert*-butylamine (2.5:1) in which both the substrate and the nucleophile were soluble. After 60 min of irradiation we obtained a 197% yield of halide ions, and the disubstitution product **14** was isolated in 83% yield and the monosubstitution product **8** in 9% yield (experiment 9, Table I).

In the dark, the treatment of **1** with **6** gave, after 60 min, a 104% yield of halide ions, **14** (52% yield), and **8** (<2% yield) were isolated (experiment 7, Table I). In the dark and for the same period of time, but with *p*-dinitrobenzene added, the halide ion yield was only 30% (experiment 8, Table I). Almost the same results were obtained with 1,4-diiodobicyclo[2.2.2]octane (**15**) with **6**, either under photostimulation or in the dark (eq 10, experiments 10 and 11, Table I).

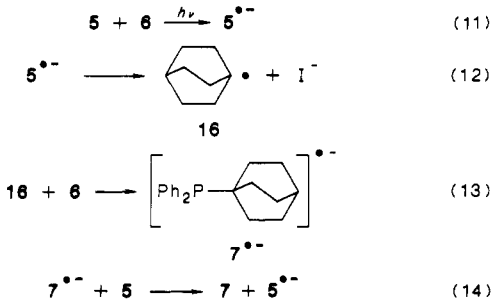


Discussion

The fact that **5** reacts with **6** to give **8** and that this reaction is catalyzed by light and inhibited by the presence of *p*-dinitrobenzene is indicative that **5** reacts with **6** by the $S_{RN}1$ mechanism of nucleophilic substitution (Scheme I).

The nucleophile **6** transfers one electron to **5** to form the radical anion $5^{\bullet-}$ (eq 11) and this reaction is catalyzed by light. Scheme I shows the 1-iodobicyclo[2.2.2]octane

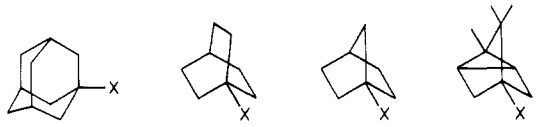
Scheme I



radical anion $5^{\bullet-}$ as an intermediate. Actually, the electron transfer to **5** is believed to be dissociative with eq 11 and 14 of Scheme I occurring in a concerted manner with eq 12.[10]

However, the substrate **9** does not react under these experimental conditions by the $S_{RN}1$ mechanism. The fact that **5** reacts with **6**, is indicative that the radical **16** is able to couple with **6** (eq 13). The lack of reactivity of **9** suggests that there is no formation of the 1-chlorobicyclo[2.2.2]octane radical anion $9^{\bullet-}$.

It has been reported that 1-chloroadamantane (**17a**) reacts in 105 min of irradiation with **6** in liquid ammonia to give a 40% yield of chloride ion elimination.[6] On the other hand, 1-chlorobicyclo[2.2.1]heptane (**18a**)[8] and 4-chlorotricyclene[7] (**19a**) do not react under these experimental conditions.



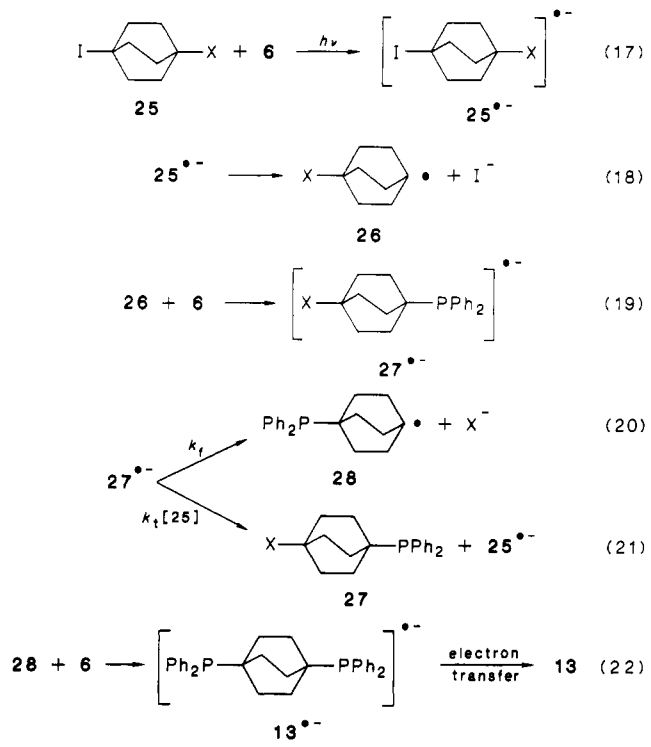
17a, X = Cl; **b**, X = I; **9**, X = Cl; **5**, X = I; **18a**, X = Cl; **19a**, X = Cl; **b**, X = I

It is known that as the bond angle of the bridgehead position decreases with increasing strain energy,[11] there is an increase in the reduction potential of 1-halo-substituted bridgehead compounds with the same halogen.[12] Since electron transfer from the nucleophile to the substrate depends on the ionization potential of the donor and the electron affinity of the acceptor, the latter being related to the reduction potential, the observed relative reactivity of the substrates **17a**, **9**, **18a**, and **19a** with the same nucleophile **6** (constant ionization potential), is in agreement with the expected reduction potential trends of the bridgehead compounds (**19a** ≃ **18a** > **9** > **17a**).

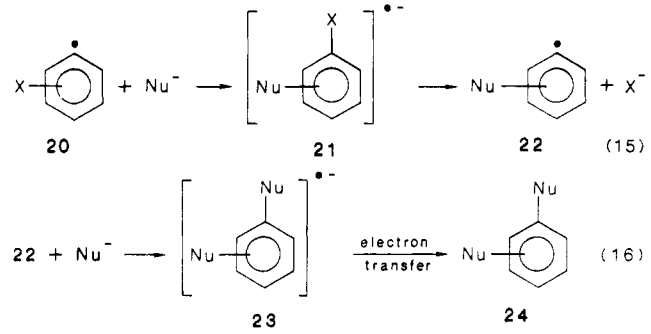
Reduction potentials also depend on the leaving group, thus, in these cases, on the halogen bonded to the bridgehead position. The ease of reduction is known to be R–I > R–Br > R–Cl, and the bridgehead iodides studied, **17b**, **5**, and **19b**, react with **6** by the $S_{RN}1$ mechanism.

It is known in $S_{RN}1$ reactions that a more reactive substrate can induce a less reactive one to react faster (*intermolecular* entrainment reactions).[3] For instance, *p*-bromotoluene is induced to react *faster* in the presence of *p*-iodotoluene with **6** as nucleophile.[13] On the other hand, **19a** was not induced to react with **6** by intermolecular entrainment in the presence of **19b**.[7]

Scheme II



It is known that certain dihalo aromatic compounds react with nucleophiles to give the disubstitution product and that the monosubstitution product is not an intermediate of the reaction. These facts can be readily explained by the $S_{RN}1$ mechanism. Thus, in these reactions, when the intermediate haloaryl radical **20** couples with a nucleophile, a new radical anion **21** is formed which fragments to give the aryl-substituted radical **22**, which, in turn, reacts with the nucleophile to give the disubstitution product **24** (eq 15 and 16).[3b,14]



Although an intermolecular entrainment reaction was not observed for **19a** with **19b**, we felt that an *intramolecular* entrainment reaction might be a possibility for the 1-chloro-4-iodo derivative **10** as substrate (Scheme II, X = Cl) given the reactivity of the 1-iodo derivative **5** (see above).

It is important to note, however, that there is a significant difference between dihalo-substituted aliphatic and aromatic systems as substrates for the $S_{RN}1$ reaction. Whereas in the latter the haloaryl radical (e.g., **20**) couples with the nucleophile to generate a radical anion intermediate (e.g., $21^{\bullet-}$) in which the π system "connects" the

(10) Andrieux C. P.; Saveant, J. M.; Su, K. B. *J. Phys. Chem.* **1986**, *90*, 3835 and references cited therein.

(11) (a) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. A. *J. Am. Chem. Soc.* **1987**, *109*, 985 and references cited therein. (b) Lomas, J. S.; Dubois, J. E. *Tetrahedron Lett.* **1983**, *24*, 1161.

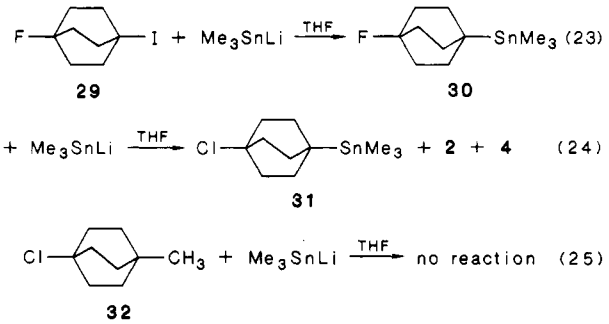
(12) (a) Sease, J. W.; Chang, P.; Groth, J. L. *J. Am. Chem. Soc.* **1964**, *86* 3154. (b) Lambert, F. L.; Albert, A. H.; Hardy, J. P. *J. Am. Chem. Soc.* **1964**, *86*, 3155.

(13) Swartz, J. E.; Bunnett, J. F. *J. Org. Chem.* **1979**, *44*, 340.

(14) Rossi, R. A. *Acc. Chem. Res.* **1982**, *15*, 164.

coupling–fragmentation process (eq 15); in the former the haloalkyl radical (e.g., **26**) combines with the nucleophile to form a radical anion species (e.g., $\mathbf{27}^{\bullet-}$) which fragments by dissociative intramolecular electron transfer to the C–X bond (intramolecular entrainment reaction) (eq 20).

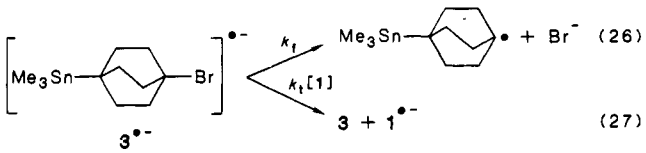
There are precedents for such an intramolecular entrainment reaction. It has been reported that 1-fluoro-4-iodobicyclo[2.2.2]octane (**29**) reacts with Me_3SnLi in THF at 0 °C to give the monosubstitution product **30**, in which only the iodine is replaced (eq 23).[15] On the other hand, **10** reacts with Me_3SnLi to give the monosubstitution products (chloro tin **31** and iodo tin **2**) as well as the disubstitution product **4** (eq 24).[9] These results constrast markedly with the fact that 1-chloro-4-methylbicyclo[2.2.2]octane (**32**) does not react with Me_3SnLi under the same experimental conditions (eq 25).[16]



In the reaction of **10** with **6**, the only product obtained was **12**. These results suggest that in this system $k_f \ll k_t[\mathbf{25}]$ (eqs 20 and 21, X = Cl). In other words, the intermolecular electron transfer to the substrate **10** is faster than the intramolecular electron transfer to the C–Cl bond.

In the photostimulated reaction of **1** and **15** with **6**, only the disubstitution product was obtained. These results suggest that with these substrates the intermolecular electron transfer to the substrates is slower than the intramolecular electron transfer to the C–X bonds ($k_f \gg k_t$[substrate]; Scheme II, X = Br, I). As pointed out previously,[9b] the mechanism of intramolecular electron transfer to the C–X bond ("through-bond" or "through-space" σ electron delocalization or an electron tunneling mechanism) is unknown.[9b]

In the reaction of **1** with Me_3SnLi in THF at 0 °C, the monosubstitution product **3** was found as product together with the disubstitution product **4**, which suggests that the radical anion intermediate $\mathbf{3}^{\bullet-}$ has the two competing reactions with fairly similar rates, $k_f \simeq k_t[\mathbf{1}]$ (eqs 26 and 27).[9b]



These facts suggest a relatively slow intramolecular electron transfer to the C–Br bond or a slow fragmentation rate of radical anion $\mathbf{3}^{\bullet-}$ (eq 26). We also have to consider the different temperature and solvent used in both systems.

In the reactions under dark conditions of **1** with **6** or in the presence of *p*-dinitrobenzene there was a decrease in the yield of the disubstitution product **3**, but the presence of halo-substituted compounds such as **27** (X = Br, I) as intermediates were not detected. These results suggest that indeed the disubstitution product **3** is obtained without the formation of **27** as an intermediate in these reactions and also that another competing reaction such as halide abstraction by the nucleophile did not occur.

Finally, in view of the well-known fact that liquid ammonia and *tert*-butylamine are very poor hydrogen atom donors, it is of interest to point out that the formation of significant amounts of **8** in the reactions of **1** and **15** with **6** (see experiments 6–11, Table I) is probably not the result of hydrogen atom abstraction from the solvent by the intermediate bridgehead radical species **28**. A more likely possibility is that **8** in a consequence of a carbanion intermediate derived from the reduction of **28**.

Experimental Section

General Methods. The ^1H and broad-band proton-decoupled ^{13}C NMR spectra were recorded in the pulse Fourier transform mode on a JEOL FX-90Q spectrometer operating at 89.56 and 22.53 MHz, respectively. A ^{13}C NMR spectrum of one of the compounds (1,4-bis(diphenylphosphinyl)bicyclo[2.2.2]octane) was also recorded on a Bruker spectrometer operating at 100.40 MHz. We thank Dr. W. Kitching for access to this instrument at the University of Queensland, Australia. The ^{31}P NMR spectra were recorded at 36.2 MHz (JEOL FX-90Q). Mass spectral measurements were obtained with a Finnigan Model 3300 mass spectrometer, and gas chromatographic analyses were performed on a Varian Aerograph Series 1400 instrument with a flame ionization detector by using a column packed with 3% SE 30 on Chromosorb P or 5% OV 17 on Chromosorb P. Irradiation was conducted in a reactor equipped with four 250-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated).

Materials. Diphenylphosphide ions were prepared from triphenylphosphine (Sigma) and 2 equiv of sodium metal in liquid ammonia,[5] and the amide ion formed was neutralized with 1 equiv of *tert*-butyl alcohol. 1-Iodo-, 1-chloro-4-iodo-, and 1-bromo-4-iodobicyclo[2.2.2]octanes were obtained as previously described.[17] 1,4-Diiodobicyclo[2.2.2]octane was obtained by treatment of 1-acetoxy-4-methoxybicyclo[2.2.2]octane in acetic anhydride with freshly distilled 55% aqueous hydroiodic acid.[16] 1-Chlorobicyclo[2.2.2]octane was obtained from the corresponding iodo derivative following the procedure outlined for the preparation of methyl 4-chlorobicyclo[2.2.2]octane-1-carboxylate.[18] *tert*-Butylamine was dried over potassium hydroxide and distilled immediately before performing the reactions.[19]

Photostimulated Reactions of 1-Iodobicyclo[2.2.2]octane with Diphenylphosphide Ions. The following procedure is representative of these reactions: into a three-necked, 500-mL, round-bottomed flask, equipped with a cold finger condenser charged with dry ice–ethanol, a nitrogen inlet, and a magnetic stirrer, was condensed 250 mL of ammonia previously dried under nitrogen. To the ammonia was added triphenylphosphine (1 mmol) and sodium metal (2 mmol) to form the diphenylphosphide ions, and then *tert*-butyl alcohol (1 mmol) was added to neutralize the amide ions formed. A solution of 1-iodobicyclo[2.2.2]octane (1 mmol) dissolved in 2 mL of diethyl ether was added, and the solution irradiated for 20 min. The reaction was quenched by the addition of excess ammonium nitrate, and the ammonia was then allowed to evaporate. Water (100 mL) was added to the residue, and the mixture was extracted with diethyl ether. The iodide ions in the aqueous phase were determined potentiometrically. The ether extract was analyzed by GLC and then oxidized with hydrogen peroxide. Removal of the ether by distillation gave a residue from which, after column chromatography on silica gel (elution with diethyl ether), bicyclo[2.2.2]oct-1-yldiphenylphosphine oxide was isolated as a white solid. Recrys-

(15) Adcock, W.; Abeywickrema, A. N. *J. Org. Chem.* **1982**, *47*, 2951.
(16) Adcock, W.; Iyer, V. S., submitted for publication in *J. Org. Chem.*
(17) Adcock, W.; Gangodawila, H.; Kok, G. B.; Iyer, V. S.; Kitching, W.; Drew, G. M.; Young G. *Organometallics* **1987**, *6*, 155.
(18) Adcock, W.; Kok, G. B. *J. Org. Chem.* **1985**, *50*, 1079.
(19) Perrin, D. D.; Armarengo, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, Great Britain, 1980; p 146.

tallization from acetone gave colorless crystals, mp 206–208 °C. Bicyclo[2.2.2]oct-1-yldiphenylphosphine oxide (8): MS, m/e (relative intensity) 311 (9), 310 (4), 297 (3), 282 (8), 201 (3), 109 (23), 77 (44), 67 (100), 55 (37), 47 (38), 41 (39), 27 (10), 18 (15); ^{1}H NMR ($CDCl_3$) δ 1.67 (13 H, m), 7.50 (6 H, m), 7.92 (4 H, m); ^{13}C NMR ($CDCl_3$, relative to TMS) δ 34.21 (J_{C-P} = 78.21 Hz, C_1), 24.89 (C_2), 25.15 (J_{C-P} = 11.59 Hz, C_3), 23.73 (C_4), 131.26 (J_{C-P} = 91.56 Hz, C_i), 132.29 (J_{C-P} = 7.93 Hz, C_o), 128.20 (J_{C-P} = 10.98 Hz, C_m), 131.32 (J_{C-P} = 2.44 Hz, C_p); ^{31}P NMR δ (ppm, relative to external 85% H_3PO_4) 35.30 (positive sign–downfield). Anal. Calcd for $C_{20}H_{33}PO$: C, 77.4; H, 7.5. Found: C, 77.3; H, 7.4.

Photostimulated Reaction of 1-Iodobicyclo[2.2.2]octane with Ph_2P^- Ions in the Presence of *p*-Dinitrobenzene. The procedure was similar to that for the previous reaction, except that 20 mol % of *p*-dinitrobenzene was added.

Photostimulated Reaction of 1-Iodobicyclo[2.2.2]octane with Ph_2P^- Ions in Liquid Ammonia–*tert*-Butylamine. To the 200 mL of freshly distilled liquid ammonia was added 80 mL of dry *tert*-butylamine, and the procedure was similar to that described above.

Photostimulated Reaction of 1-Bromo-4-iodobicyclo[2.2.2]octane and 1,4-Diiodobicyclo[2.2.2]octane with 6 in Liquid Ammonia. The procedure was similar to that described above except that the irradiation time was 60 min. The residue was chromatographed on a column of silica gel. Elution with diethyl ether and then ethanol afforded the monosubstitution and the disubstitution products, respectively. The 1,4-bis(diphenylphosphinyl)bicyclo[2.2.2]octane was recrystallized from benzene, mp 313 °C (hot plate mp apparatus). 1,4–Bis(diphenylphosphinyl)bicyclo[2.2.2]octane (14): MS, m/e (relative intensity) 509 (6), 508 (6), 386 (3), 325 (3), 309 (47), 281 (12), 201 (100), 183 (12), 108 (4), 107 (23), 91 (8), 77 (26), 47 (3); ^{1}H NMR ($CDCl_3$) δ 1.82 (12 H, t), 7.48 (12 H, m) 7.86 (8 H, m); ^{13}C NMR ($DCCl_3$, relative to Me_4Si)[20] δ 34.48 ($^1J_{C-P}$ = 79.35 Hz, $^4J_{C-P}$ = 1.52 Hz, $C_1 + C_4$), 24.51 ($C_2 + C_3$), 130.49 (J_{C-P} = 93.08 Hz, C_i), 132.14 (C_o), 128.37 (C_m), 131.64 (C_p); ^{31}P NMR δ (ppm, relative to external 85% H_3PO_4) 34.80 (positive sign—downfield shift). Anal. Calcd for $C_{32}H_{32}P_2O_2$; C, 75.3; H, 6.3. Found C, 75.6; H, 6.2.

Photostimulated Reaction of 1-Chloro-4-iodobicyclo[2.2.2]octane with 6 in Liquid Ammonia. The procedure was similar to that described above, except that the irradiation time was 240 min. The residue from the ether extract was chromatographed on a column of silica gel (elution with diethyl ether) afforded (4-chlorobicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide as a white solid, which was recrystallized from diethyl ether/benzene (1:1), mp 212 °C. (4-Chlorobicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide (12): MS, m/e (relative intensity) 344.6 (23), 309.4 (100), 281 (23), 237 (4), 201 (76), 183 (14), 107 (18), 91 (14), 77 (39), 67 (6), 51.1 (12), 47 (10); ^{1}H NMR ($CDCl_3$) δ 1.98 (12 H, br s), 7.51 (6 H, m), 7.89 (4 H, m); ^{13}C NMR ($DCCl_3$, relative to Me_4Si) δ 33.33 (J_{C-P} = 77.15 Hz, C_1), 27.48 (C_2), 35.29 (J_{C-P} = 11.23 Hz, C_3), 65.78 (J_{C-P} = 2.44 Hz, C_4), 130.41 (J_{C-P} = 92.77 Hz, C_i), 132.02 (J_{C-P} = 8.3 Hz, C_o), 128.4 (J_{C-P} = 11.23 Hz, C_m), 131.74 (J_{C-P} = 4.4 Hz, C_p); ^{31}P NMR δ (ppm, relative to external 85% H_3PO_4) 34.38 (positive sign—downfield shift). Anal. Calcd for $C_{20}H_{22}POCl$: C, 69.7; H, 6.4. Found: C, 70.0; H, 6.1.

Acknowledgment. ANS gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina. This work is partially supported by the CONICET and the Consejo de Investigaciones de la Provincia de Córdoba.

Registry No. 1, 89566-55-2; 5, 931-98-6; 8, 114378-27-7; 9, 2064-03-1; 10, 89566-54-1; 12, 114378-28-8; 14, 114378-29-9; 15, 10364-05-3; *p*-DNB, 100-25-4; $Ph_2P^-Na^+$, 15205-59-1; triphenylphosphine, 603-35-0.

(20) Resonances for C_2, C_3, C_o, and C_m of compound 14 exhibit second-order characteristics even at 100.4 MHz (X parts of ABX spin systems; see ref 21 and 22 for examples).

(21) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 2361.
(22) Olah, G. A.; Shih, J. G.; Krishnamurthy, V. V.; Singh, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4492.

Selective Cross Diels–Alder Reactions of 2-(Phenylsulfonyl) 1,3-Dienes

Ta-shue Chou* and Su-Chun Hung

Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, Republic of China

Received January 6, 1988

2-Sulfonylated 1,3-dienes have been prepared by way of their stable precursors, 3-sulfonylated 3-sulfolenes. These dienes underwent clean cross Diels–Alder reactions with Danishefsky diene, cyclopentadiene, cyclohexadiene, 6,6-dimethylfulvene, and norbornadiene at 130 °C. In the cross cycloaddition reactions, the sulfonylated 1,3-dienes may react as both the dienes and the dienophiles. When the sulfonylated 1,3-dienes were reacted with Danishefsky diene, they behaved as the dienophiles. When the sulfonylated 1,3-dienes were reacted with cyclopentadiene at room temperature, mixtures containing the cycloadducts from the reactions of sulfonylated dienes as the dienes with cyclopentadiene as the dienophile and those from the reactions of cyclopentadiene as the diene with the sulfonylated dienes as the dienophiles were obtained. The latter cycloadducts, being the major products of the reactions, could be converted completely to the former adducts by a sigmatropic rearrangement process at 130 °C. Thus, this paper illustrates successful examples of a cross Diels–Alder reaction between two different dienes where only one of the possible isomeric cycloadducts was obtained cleanly.

Although the Diels–Alder dimerization reactions of conjugated dienes are frequently observed, the cross Diels–Alder (CDA) reactions between two different conjugated dienes have not been systematically studied,[1] and their synthetic applications remain essentially unexplored so far. The major reason is that the CDA reactions usually nonselectively produce mixtures of all possible structural, stereoisomeric, and regioisomeric cycloadducts in addition to the dimers of each diene so they are synthetically useless. For example, there are four possible isomers in eq 1. Nevertheless, each of the four cycloadducts shown in eq 1 is suitably functionalized (if X is a heteroatom functionality), and they may be transformed into many mono- and multicyclic molecules that are not easily ac-

(1) For examples, see: (a) Johnstone, R. A. W.; Quan, P. M. *J. Chem. Soc.* **1963**, 935. (b) Stewart, C. A., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4815. (c) Houk, K. N.; Luckus, L. J. *J. Org. Chem.* **1973**, *38*, 3836. (d) Franck-Neumann, M.; Martina, D.; Brion, F. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 864. (e) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665.

0022-3263/88/1953-3020$01.50/0 © 1988 American Chemical Society