J. Org. Chem. **1995**, *60*, 1000−1004

Intramolecular Electron Transfer Reactions Catalyzed by α-Oxo and β-Oxo Substituents in the 1-Chlorobicyclo[2.2.1]heptane System

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Received August 11, 1994⊗

Efficient intramolecular ET catalysis in $S_{RN}1$ reactions was observed when a carbonyl group is present in 1-chlorobicyclo[2.2.1]heptane in the α or *β* position. 1-Chloro-3,3-dimethyl-2-oxobicyclo-[2.2.1]heptane (**1**) and 4-chloro-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptane (**4**) reacted with diphenylphosphide ion (Ph_2P^-) as nucleophile in liquid ammonia under photostimulation to give the substitution products in good yields, together with very small amounts of the reduction product. The substitution products were not observed in dark conditions, and the photostimulated reactions were inhibited by *p*-dinitrobenzene. These reactions are proposed to proceed via the $S_{RN}1$ mechanism. In competition experiments, the reactivity ratio of **1** to **4** was 2.8, whereas the ratio of 1-chloro-3,3-dimethyl-2-oxobicyclo[2.2.2]octane (**8**) to **4** was 1.1. On the other hand, 1-chloro-2-methylene-3,3-dimethylbicyclo[2.2.1]heptane (**7**) was unreactive under these experimental conditions. It then seems to follow that when there is a carbonyl group in these bicyclic compounds, in the α or *β* position, they react by the $S_{RN}1$ mechanism, and the overall reactivity is similar, but when the C═O is replaced by a C═C, the substrate did not react in these experimental conditions. These results are in agreement with MO calculations, in which the LUMO of compounds **1**, **4**, and **8** belongs to the *π** MO of the C═O group, with similar energies, and is lower than the *π** MO of **7**.

The radical nucleophilic substitution, or $S_{RN}1$, is a chain process in which there are radical and radical anions as intermediates. The main reactions of the propagation steps are outlined in eqs 1−3.[2]

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

$$R^{\bullet} + Nu^{-} \rightarrow (RNu)^{\bullet-} \qquad (2)$$

$$(RNu)^{\bullet-} + RX \rightarrow RNu + (RX)^{\bullet-} \qquad (3)$$

This mechanism requires an initiation step to form one reactive intermediate to enter the propagation cycle. The formation of a radical anion $(RX)^{\bullet-}$ of the substrate is by far the most common process. In a few systems there is a spontaneous (or thermal) electron transfer (ET) from the nucleophile to the substrate to form $(RX)^{\bullet-}$. However, ET can be induced by irradiation when it is not spontaneous.[2]

For aliphatic substrates without electron-withdrawing groups other than the leaving group, such as bridgehead, neopentyl, cyclopropyl, and often cycloalkyl halides, there is no *π** MO to receive the electron. Here the ET reaction places the electron in the C−X *σ** MO, a process that has been proposed to be dissociative, and the reactions indicated in eqs 1 and 3 occur simultaneously (eq 4).[2c,d,f]

$$(RNu)^{\bullet-} + RX \rightarrow RNu + R^{\bullet} + X^{-} \qquad (4)$$

1-Substituted bridgehead compounds react slowly by an S_N1 mechanism of nucleophilic substitution, and the reactivity decreases with increasing strain in the substrate.[3] The reactivity of bridgehead halides by the $S_{RN}1$ mechanism depends not only on the nature of the leaving group (Cl < Br < I), but also on the strain of the bicyclic moiety[4] and on the presence of substituents. Thus, 1-halobicyclo[2.2.2]octanes (Br, I) react with Ph_2P^- ions under irradiation in liquid ammonia to give good yields of the substitution product. However, 1-chlorobicyclo-[2.2.2]octane is unreactive in these experimental conditions.[5] Similarly, 4-iodotricyclane reacts under irradiation with Ph_2P^- ions, whereas 4-chlorotricyclane is completely unreactive under the same experimental conditions.[6]

The presence of a methylene group in the α position with respect to the leaving group such as 2-methylenebicyclo[2.2.2]oct-1-yl triflate changes the rate of solvolysis by $10^{-3.9}$, compared to the unsubstituted substrate.[7] A more important decrease in the reactivity occurs in the presence of a carbonyl group in the α position with respect to the leaving group, such as 3,3-dimethyl-2-oxobicyclo[2.2.2]oct-1-yl triflate, which changes

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⊗ Abstract published in *Advance ACS Abstracts*, January 15, 1995.

[1] (a) Universidad Nacional de Córdoba. (b) The University of Glasgow.

[2] For reviews on $S_{RN}1$ see: (a) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS 178; Washington, DC, 1983. (b) Bowman, W. R. *Chem. Soc. Rev.* **1988**, *17*, 283. (c) Rossi, R. A.; Pierini, A. B.; Palacios, S. M. In *Advances in Free Radical Chemistry*; Tanner, D. D., Ed.; JAI Press: New York, 1990; p 193; *J. Chem. Educ.* **1989**, *66*, 720. (d) Savéant, J. M. *Adv. Phys. Org. Chem.* **1990**, *26*, 1. (e) Norris, R. K. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 4, 451. (f) Rossi, R. A.; Santiago, A. N. *Trends in Organic Chemistry* **1992**, *3*, 193. (g) Rossi, R. A.; Pierini, A. B.; Peñéñory, A. B. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1995, in press.

[3] Fort, R. C.; Schleyer, P. v. R. *Adv. Alicycl. Chem.* **1966**, *1*, 283.

[4] Pierini, A. B.; Santiago, A. N.; Rossi, R. A. *Tetrahedron* **1991**, *47*, 941.

[5] Santiago, A. N.; Iyer, V. S.; Adcock, W.; Rossi, R. A. *J. Org. Chem.* **1988**, *53*, 3016.

[6] Santiago, A. N.; Morris, D. G.; Rossi, R. A. *J. Chem. Soc., Chem. Commun.* **1988**, 220.

[7] Takeuchi, K.; Akiyama, F.; Ibai, K.; Shikata, T.; Kato, M. *Tetrahedron Lett.* **1988**, *29*, 873.

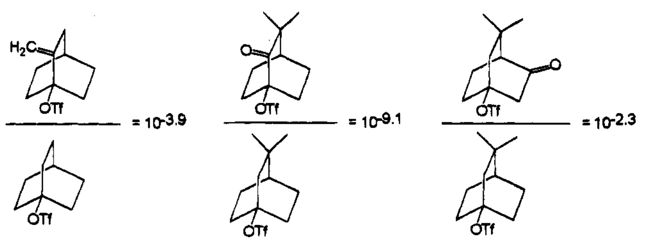
0022-3263/95/1960-1000$09.00/0

Table 1. Reactions of 1, 4, and 7 with Ph_2P^- Ions in Liquid Ammonia

				yields,[b] %		
expt	substrate,[a] 10^3 M	Ph_2P^-, 10^3 M	condns (time, min)	Cl^-	substitutn products	reductn products
1	**1**, 3.32	3.53	*hν*, 80	95	**2−O**, 93	**3**, <1
2[c]	**1**, 3.30	3.50	*hν*, 80	*d*	**2−O**, 21	**3**, <1
3	**1**, 3.27	3.54	dark, 80	12	**2−O**, <1.5	
4	**4**, 3.31	3.40	*hν*, 210	91	**5−O**, 80	**6**, 8
5[c]	**4**, 3.32	3.41	*hν*, 210	56	**5−O**, 11	**6**, 3
6	**4**, 3.35	3.40	dark, 210	13	**5−O**, <1	**6**, <1
7[c]	**4**, 3.22	3.66	dark, 210	17	**5−O**, <1	**6**, <1
8	**4**, 3.30		*hν*, 210	<3		
9	**7**, 3.57	5.73	*hν*, 240	10		

[a] UV spectra of **1** showed a maximum wavelength at 288.5 nm and of **4**, at 286.6 nm, in methanol. [b] Chloride ions determined potentiometrically, and the substitution products **2−O** and **5−O** were obtained after oxidation and together with the reduction products were determined by GLC, using tetraphenyltin and 1-bromoadamantane as internal standards. [c] *p*-DNB (20 mol %) was added. [d] Not determined.

the rate of solvolysis by $10^{-9.1}$ compared to the unsubstituted substrate, indicating that the methylene and oxo substituents decrease the reactivity in solvolytic reactions.[7] Even in the more remote *β* position, such as 5,5-dimethyl-3-oxobicyclo[2.2.2]oct-1-yl triflate, the solvolytic rate decreases by $10^{-2.3}$, compared to the unsubstituted substrate.[8]

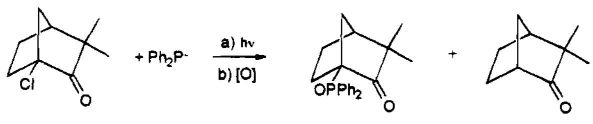


However, the presence of a C=O group in the α position of the chloro-substituted compound *increases* the reactivity in the $S_{RN}1$ mechanism by an *intramolecular* ET from the C=O *π** radical anion to the C−Cl *σ** MO, which leads to the *σ* radical and chloride ions, and thus initiates the nucleophilic substitution (*intramolecular entrainment reactions*). As was demonstrated before, there is no overlapping between the *π* MO of the carbonyl group and the *σ* MO of the C−Cl bond.[4] 1-Chloro-3,3-dimethylbicyclo[2.2.2]octane was unreactive toward Ph_2P^- ions under irradiation in liquid ammonia, but when a carbonyl group is introduced into the α position, the resulting substrate, 1-chloro-3,3-dimethyl-2-oxobicyclo[2.2.2]octane, is much more reactive (>700) toward Ph_2P^- ions than a substrate with less strain such as 1-chloroadamantane and only slightly less reactive (0.40) than a substrate with less strain but with a better leaving group such as 1-bromoadamantane.[9]

1-Chlorobicyclo[2.2.1]heptane, a substrate with more strain than 1-chlorobicyclo[2.2.2]octane, was unreactive toward Ph_2P^- ions under irradiation in liquid ammonia.[10] We therefore feel that methylated derivatives of this compound, but lacking a carbonyl group, will also be unreactive and accordingly were not investigated. Consequently, we thought it of interest to know if the presence of a methylene or a carbonyl group in the α position, or a carbonyl group even in the more remote *β* position, would enhance the rate of nucleophilic substitution with Ph_2P^- ions through the $S_{RN}1$ mechanism. We also investigated how the donor−acceptor distance would affect reactivity in the intramolecular ET.

Results and Discussion

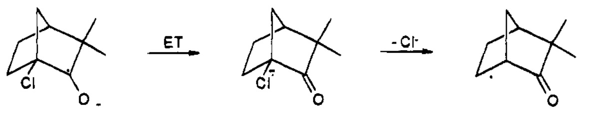
The photostimulated reaction (80 min) of **1** with Ph_2P^- ions in liquid ammonia gave after oxidation the substitution product (3,3-dimethyl-2-oxobicyclo[2.2.1]hept-1-yl)diphenylphosphine oxide (**2-O**) (93%) and mere traces of the reduced product **3** (Table 1, experiment 1) (eq 5).



1 **2-O** **3** (5)

There is no reaction of **1** with Ph_2P^- ions in the dark, and the photostimulated reaction was inhibited by *p*-dinitrobenzene (*p*-DNB) (Table 1, experiments 2 and 3), a well-known inhibitor of $S_{RN}1$ reactions.[2] On the basis of these results, we suggest that **1** reacts with Ph_2P^- ions by the $S_{RN}1$ mechanism and that the presence of a carbonyl group increases reactivity in comparison with the unreactive parent compound without the carbonyl group.

As the LUMO of substrate **1** belongs to the C=O group, it receives the electron to form the radical anion *π** (**1** *π**), which then transfers the odd electron to the C−Cl *σ** bond to form the radical anion *σ** (**1** *σ**) which by a fragmentation process renders chloride ions and the radical **1•** (eq 6). This process probably occurs in a dissociative ET from **1** *π** to give **1•** directly without forming the radical anion **1** *σ**.



1 π* **1 σ*** **1•** (6)

This process is an *intramolecular* ET that catalyses the $S_{RN}1$ reactions.

We studied the reaction of 4-chloro-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptane (4-chlorocamphor, **4**) in order to increase the spatial distance between the leaving group Cl and the C=O moiety, with an extra C−C bond. As the carbonyl group has α-hydrogens and in view of the basicity of our experimental conditions, we were aware of the possibility of deprotonation of **4**, which has acidic

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[8] Yoshida, M.; Takeuchi, K. *J. Org. Chem.* **1993**, *58*, 2566.

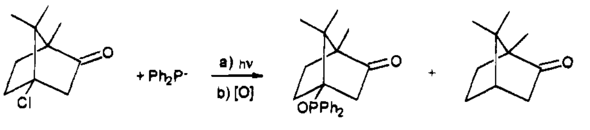
[9] Santiago, A. N.; Takeuchi, K.; Ohga, Y.; Nishida, M.; Rossi, R. A. *J. Org. Chem.* **1991**, *56*, 1581.

[10] Santiago, A. N. *Study of New Substrates and Nucleophiles by the $S_{RN}1$ Mechanism*; Ph. D. Thesis, Universidad Nacional de Córdoba, 1986.

α hydrogens; the carbanion so formed would be unreactive under our $S_{RN}1$ conditions.

Although the basicity of the reacting species is not known, we were able to estimate it on the basis of the pK_a in DMSO reported by Bordwell.[11] The pK_a of diphenylamide[11] is 24.95, and is should be lower for a similar phosphorus derivative.[12] The pK_a of camphor[13] is 30.4, and it should be at least two units lower for a similar chloride derivative. However, in our experimental conditions we used sodium *tert*-butoxide ($pK_a = 32.2$) which could deprotonate the substrate. We therefore attempted to form the anion of **4** with excess of sodium *tert*-butoxide in liquid ammonia and tried to trap the carbanion with methyl iodide but no methylation occurred. This suggests that substrate **4** is not deprotonated under these experimental conditions.

The photostimulated reaction of **4** with Ph_2P^- ions was complete after 210 min. After oxidation of the product mixture we obtained (1,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-4-yl)diphenylphosphine oxide (**5-O**) (80%) derived from the substitution product and the primary reduction product **6** (8%) of the reaction (Table 1, experiment 4) (eq 7).

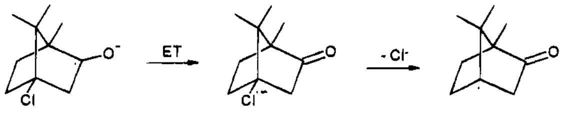


4 **5-O** **6** (7)

In dark conditions there was almost no reaction (the yield of **5-O** was <1%), although 13% yield of chloride ions was found. In dark conditions and in the presence of *p*-DNB the same results were obtained (Table 1, experiments 6 and 7). The photostimulated reaction with *p*-DNB gave 11% yield of **5-O** and 3% yield of **6**, but chloride ions were formed in 56% yield. No other products could be determined, and the origin of this dehalogenation reaction is unknown to us. The irradiation of **4** for 210 min without the nucleophile gave less than 3% of chloride ions, indicating that the dehalogenation reaction is not due to a photolysis of the substrate (Table 1, experiment 8).

On the other hand, the UV spectra of compounds **1** and **4** in methanol showed an absorption at a wavelength <290 nm shorter than the 350 nm wavelength (Pyrex filtered) of the irradiation experiments.

From all these results we suggest that substrate **4** also reacts with Ph_2P^- ions by the $S_{RN}1$ mechanism and that the β-oxo substituent catalyzes these reactions, forming radical anion **4** π*, analogous to that for the α-oxo substrate **1** (eq 8), although in substrate **4** the carbonyl group is spatially more distant than in **1**.



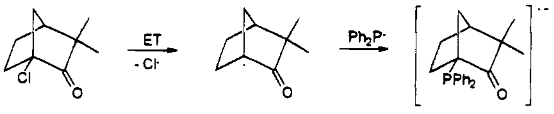
4 π* **4 σ*** **4·** (8)

If we compare the separate photostimulated reaction of **1** and **4** with Ph_2P^- ions, qualitatively **1** is more reactive than **4**, because the reaction is completed in less irradiation time.

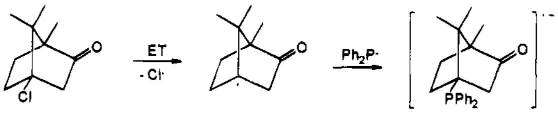
There was no photostimulated reaction (240 min) of 1-chloro-2-methylene-3,3-trimethylbicyclo[2.2.1]heptane (**7**) with Ph_2P^- ions (10% of chloride ions, Table 1, experiment 9).

As the $S_{RN}1$ mechanism is a chain process with initiation, propagation, and termination steps, the overall reactivity depends on the efficiency of the photostimulated initiation step, the individual rates of the propagation steps, and the termination steps. To compare the reactivity of different substrates, the *relative* reactivity was studied by competition experiments with a nucleophile. In this competition reaction the relative rates of the ET reactions of eq 3 can be determined.

When a solution containing substrates **1** and **4** in excess is allowed to compete for Ph_2P^- ions under irradiation, the radicals **1·** and **4·** are formed and react with Ph_2P^- ions forming the radical anion intermediates $\mathbf{2}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$, respectively (eq 9a,b).



1 **1·** $\mathbf{2}^{\bullet-}$ (9a)



4 **4·** $\mathbf{5}^{\bullet-}$ (9b)

These radical anions $\mathbf{2}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ transfer their odd electron either to substrate **1** or **4**, giving the substitution products **2** and **5**, and the radicals **1·** and **4·** which follow the chain reaction of the $S_{RN}1$ mechanism (eq 10).

$$\mathbf{2}^{\bullet-} \text{ or } \mathbf{5}^{\bullet-} + \mathbf{1} \rightarrow \mathbf{2} \text{ or } \mathbf{5} + \mathbf{1}^{\bullet} + \mathrm{Cl}^- \quad (10a)$$

$$\mathbf{2}^{\bullet-} \text{ or } \mathbf{5}^{\bullet-} + \mathbf{4} \rightarrow \mathbf{2} \text{ or } \mathbf{5} + \mathbf{4}^{\bullet} + \mathrm{Cl}^- \quad (10b)$$

If there is no other competing reaction (or if the reduction processes of the radicals **1·** and **4·** are similar), all the radicals will end in the substitution products **2** and **5**, and the reduction products **3** and **6**, and from the amount of products obtained it is possible to estimate the relative rates of eq 10. The relative reactivities were estimated as in previous works.[14]

In the photostimulated reaction of **1** and **4** in excess over Ph_2P^- ions it was possible to estimate the relative reactivity, and it was found to be 2.8 (Table 2, experiments 1 and 2).

We also studied the competition experiments between 1-chloro-3,3-dimethyl-2-oxobicyclo[2.2.2]octane **8** *vs* **4**, and it was found that both substrates have almost the same reactivity (Table 2, experiments 3–5). On the basis

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[11] Bordwell, F. G.; Cheng, J. P.; Ji, G. Z.; Satish, A. V.; Zhang, Y. *J. Am. Chem. Soc.* **1991**, *113*, 9790.

[12] Approximately, the pK_a for Ph_2PH is 22: Issielb, K.; Kümmel, R. *J. Organomet. Chem.* **1964**, *86*, 5633.

[13] Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

[14] The equation used in the relative reactivity determination of substrates **1** and **4** in excess *vs* Ph_2P^- ions is:

$$\frac{k(\mathbf{1})}{k(\mathbf{4})} = \frac{\ln [\mathbf{1}]_0/[\mathbf{1}]_t}{\ln [\mathbf{4}]_0/[\mathbf{4}]_t}$$

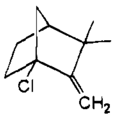
where $[\mathbf{1}]_0$ and $[\mathbf{4}]_0$ are initial concentrations and $[\mathbf{1}]_t$ and $[\mathbf{4}]_t$ are concentrations at time *t* of both substrates. This equation is based on a first-order reaction of both radical anions intermediates with substrates **1** and **4**; see: Bunnett, J. F. *Investigation of Rates and Mechanisms of Reactions*, 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part 1, p 159.

Table 2. Competition Reactions of 1 and 8 *vs* 4 toward Ph_2P^- Ions in Liquid Ammonia

expt	**1** or **8**, 10^3 M	**4**, 10^3 M	Ph_2P^-, 10^3 M	yield[a] % **2–O**	**3**	**5–O**	**6**	rel reactivity
1[b]	**1**, 3.77	15.11	3.85	30.9	5.9	49.5	11.8	2.8
2[b]	**1**, 3.69	11.32	3.85	34.2	3.2	37.7	10.3	2.8
						average		2.8
3[c]	**8**, 3.34	6.70	3.56	27.2[d]	11.1[e]	52.5	11.9	1.3
4[c]	**8**, 3.34	6.05	3.70	25.2[d]	7.0[e]	55.9	7.2	0.9
5[c]	**8**, 3.25	4.77	3.41	26.4[d]	8.9[e]	4.3	6.2	1.1
						average		1.1 ± 0.2

[a] Substitution products were determined by GLC, using tetraphenyltin, or by HPLC, using diphenyl disulfide as internal standard. The reduction products were determined by GLC, using 1-bromoadamantane or 1-bromonaphthalene as internal standard. [b] Irradiation time for 10 min. [c] Irradiation time for 30 min. [d] (3,3-Dimethyl-2-oxobicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide. [e] 3,3-Dimethylbicyclo[2.2.2]octan-2-one.

of these results, we suggest that **1** is more reactive than **8** with Ph_2P^- ions through the $S_{RN}1$ mechanism and that the structure of the bicyclic system changes the relative reactivity of substrates.



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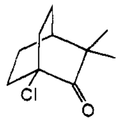

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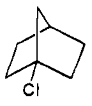

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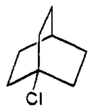

10

To estimate the values of the LUMO MO of the substrates, we studied theoretically **1**, **4**, **7**, **8**, and the parent compounds 1-chlorobicyclo[2.2.1]heptane (**9**) and 1-chlorobicyclo[2.2.2]octane (**10**). The calculations were done with the AM1 method as implemented in AMPAC.[15]

In substrates **1**, **4**, and **8** the LUMO belongs to the π^* MO of the C=O groups, and the σ^* MO of the C–Cl bonds are always higher in energy. The fact that the three compounds have similar LUMO values makes their relative reactivities similar, following the trend **1** ≥ **8** ≥ **4** (Table 3).

The reactivity of compounds **1**, **4**, and **8** correlates with the π^* MO order of the C=O groups and does not follow the σ^* MO order of the C–Cl bond probably due to the fact that once the π^* radical anions are formed, there is a fast intramolecular ET to the σ^* MO of the C–Cl bonds and there is no competition with an intermolecular ET. However, this should be supported by experimental evidence.

Although the LUMO value of **7** belongs to π^* MO of the C=C group, it is much higher in energy than the previous substrates with a C=O group. This high energy LUMO close to the σ^* MO of the C–Cl bonds explains the lack of reactivity of this substrate.

In the parent compounds **9** and **10** the LUMOs belong to the σ^* MO of the C–Cl bonds and are close in energy to the σ^* MO of the C–Cl bonds of compounds **1**, **4**, **7**, and **8** (Table 3). By considering that the parent compounds and **7** were unreactive in our experimental conditions, but **1**, **4**, and **8** reacted easily and with similar reactivities, it is suggested that the C=O groups receive the electron to increase the reactivity of the compounds.

Experimental Section

General Methods. NMR spectra were recorded on a Bruker FT-200 nuclear magnetic resonance spectrometer. Mass Spectra (MS) and high-resolution mass spectra (HRMS) were obtained with a Finnigan MAT-90 mass spectrometer of The University of Illinois at Chicago, USA. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument with a flame-ionization detector and a data system Hewlett-Packard 3396 Series II, using a column HP5 (5% methyl silicone, 0.5 m × 0.53 mm). High-pressure liquid chromatography (HPLC) was performed on an LKB Bromma 2249 instrument with a UV–vis LKB Bromma 2141 detector, Spherisorb ODS2 column (5 μm, 4 × 250 mm) (methanol–water, 70:30) and a data system LKB Bromma 2221. Irradiation was conducted in a reactor equipped with two 400-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water-refrigerated). UV spectra were recorded on a Shimadzu UV-2101 PC UV–vis scanning spectrophotometer. Column chromatography was performed on silica gel (70–270 mesh ASTM). Potentiometric titration on halide ions was performed in a pH meter (Seybold Wien), using an Ag/Ag^+ electrode and $AgNO_3$ as standard. Melting points were obtained with a Büchi 510 apparatus and are not corrected.

Materials. Reagents were commercially available and used as received: 1-bromoadamantane (98%) (Aldrich Chem. Co.), *p*-dinitrobenzene, 1-bromonaphthalene, diphenyl disulfide (Fluka), sodium diphenylphosphide was prepared from triphenylphosphine (Bayer), and sodium metal in liquid ammonia;[5] 2-methyl-2-propanol (Carlo Erba) and tetraphenyltin (Research Chemicals). 1-Chloro-3,3-dimethyl-2-oxobicyclo[2.2.1]heptane **1**,[16] 4-chloro-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptane (**4**),[17] and 1-chloro-3,3-dimethyl-2-methylenebicyclo[2.2.1]heptane (1-chlorocamphene, **7**)[18] were synthesized as reported. 1-Chloro-3,3-dimethyl-2-oxobicyclo[2.2.2]octane (**8**) and (3,3-dimethyl-2-oxobicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide were obtained from another study.[9]

Photostimulated Reaction of 1-Chloro-3,3-dimethyl-2-oxobicyclo[2.2.1]heptane (1) or 4-Chloro-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptane (4) with Ph_2P^- Ions in Liquid Ammonia. The following procedure is representative of all the 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 were condensed 300 mL of ammonia previously dried with Na metal under nitrogen. Triphenylphosphine (1 mmol) and Na metal (2 mmol) were added to form sodium diphenylphosphide, and *t*-BuOH (1 mmol) was added to neutralize the amide ions formed. To this solution 1 mmol of substrate (**1** or **4**) in 3 mL of anhydrous diethyl ether was added and then irradiated for 80 or 210 min. The reaction was quenched by adding ammonium nitrate in excess, and the ammonia was allowed to evaporate. The residue was dissolved with water and then extracted with diethyl ether. The products were oxidized with H_2O_2 and then quantitatively analyzed by CGL with the internal standard method. In another experiment the product was oxidized with H_2O_2, (3,3-dimethyl-2-oxobicyclo[2.2.1]hept-1-yl)diphenylphosphine oxide (**2-O**) or (1,7,7-trimethyl-2-oxobicyclo[2.2.1]hept-4-yl)diphenylphosphine oxide (**5-O**) was isolated as a white solid after chromatography on silica gel, elution was achieved with diethyl ether, and the oxides were recrystallized from petroleum ether–methylene chloride.

(3,3-Dimethyl-2-oxobicyclo[2.2.1]hept-1-yl)diphenylphosphine oxide (2-O): mp 146–149 °C; ^{1}H NMR δ 0.95 (3 H, s), 1.05 (3 H, s), 2.5 (7 H, m), 7.5 (6 H, m), 7.9 (4 H, m); ^{13}C NMR δ 21.33, 22.87, 24.26 ($^3J_{C-P}$ = 8.09 Hz), 27.31, 37.35 ($^2J_{C-P}$ = 1.46 Hz) 45.95 ($^3J_{C-P}$ = 11.57 Hz), 49.43 ($^3J_{C-P}$ = 6.05 Hz), 60.46 ($^1J_{C-P}$ = 81.66 Hz), 128.27 ($^3C_{C-P}$ = 12.08 Hz), 128.37 ($^2J_{C-P}$ = 7.37 Hz), 131.39, 131.58, 132.46 ($^2J_{C-P}$ = 10 Hz), 217.71; mass spectrum *m/e* (relative intensity) 339 (24.9),

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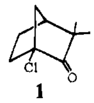
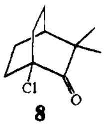
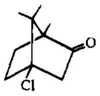
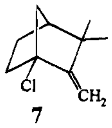
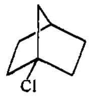
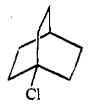
[15] The calculations were carried out with the semiempirical AM1 method available from the QCPE, program 506. For the sake of simplicity compounds 1, 4, and 7 were calculated without the methyl groups, which will not affect the LUMO energy order. We thank Professor A. B. Pierini for here advice in these calculations.

[16] Paukstelis, J. V.; Macharia, B. W. *J. Org. Chem.* **1973**, *38*, 646. Brown, F. C.; Morris, D. G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 125.

[17] Houben, J.; Pfankuch, E. *Ann.* **1933**, *501*, 219. Morris, D. G.; Murray, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1579.

[18] Joshi, C. G.; Warnhoff, E. W. *J. Org. Chem.* **1972**, *37*, 2383.

Table 3. Relative Reactivities in Photostimulated Reactions toward Ph_2P^- Ions in Liquid Ammonia, LUMO, and σ^* MO C−Cl Bonds of Substrates 1, 4, 7, and 8 and the σ^* MO C−Cl Bonds of 9 and 10

Substrate	Relative Reactivity	LUMO π^* (eV)	σ^* MO C-Cl Bond (eV)
 **1**	2.8	(C=O) 0.678	1.305
 **8**	1.1	(C=O) 0.723	1.161
 **4**	1.0	(C=O) 0.713	1.196
 **7**	Unreactive	($C{=}CH_2$) 1.107	1.607
 **9**	Unreactive	-	1.589
 **10**	Unreactive	-	1.439

338 (100.0), 310 (18.7), 309 (12.0), 295 (16.1), 282 (12.0), 269 (34.1), 267 (14.9), 243 (5.6), 242 (20.4), 241 (13.9), 227 (14.4), 219 (4.6), 203 (22.2), 202 (39.7), 201 (47.1), 185 (7.4), 183 (11.3), 155 (6.8), 154 (5.0), 141 (4.9), 137 (4.8), 133 (4.7), 124 (4.9), 125 (14.0), 123 (5.5), 119 (5.5), 109 (10.8), 107 (4.7); HRMS calcd 338.143 557, found 338.143 608. Anal. Calcd for $C_{21}H_{23}O_2P$: C, 74.54; H, 6.85. Found: C, 74.30; H, 7.16.

(1,7,7-Trimethyl-2-oxobicyclo[2.2.1]hept-4-yl)diphenylphosphine oxide (5-O): mp 183−185 °C; ^{1}H NMR δ 0.8 (3 H, s), 0.9 (3 H, s), 1.0 (3 H, s), 1.8 (4 H, m), 2.05 (1 H, d), 2.55 (1 H, m), 2.92 (1 H, m), 7.5 (6 H, m), 8.0 (4 H, m); ^{13}C NMR δ 8.91, 18.17, 19.06, 29.55 ($^3J_{C-P}$ = 12.85 Hz), 29.7 ($^2J_{C-P}$ = 5.16 Hz), 44.74 ($^2J_{C-P}$ = 2.31 Hz), 49.95 ($^1J_{C-P}$ = 79.58 Hz), 52.12, 60.51 ($^3J_{C-P}$ = 6.78 Hz), 128,56 ($^3C_{C-P}$ = 11.38 Hz), 131.52 ($^2J_{C-P}$ = 8.53 Hz), 131.74, 132.46 ($^2J_{C-P}$ = 10 Hz), 133.49, 215.83 ($^3J_{C-P}$ = 13.85 Hz); mass spectrum *m/e* (relative intensity) 352 (6.6), 339 (16.4), 338 (71.9), 324 (11.8), 310 (12.3), 309 (11.2), 295 (11.2), 269 (26.5), 242 (19.9), 241 (14.2), 227 (11.5), 203 (50.1), 202 (100.0), 201 (64.8), 183 (10.9), 155 (10.8); HRMS calcd 352.159 219, found 352.158 326. Anal. Calcd for $C_{22}H_{25}O_2P$: C, 74.98; H, 7.15. Found: C, 74.68; H, 7.08.

Competition Experiments. 1-Chloro-3,3-dimethyl-2-oxobicyclo[2.2.1]heptane (**1**) or 1-chloro-3,3-dimethyl-2-oxobicyclo[2.2.2]octane (**8**) *vs* 4-chloro-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptane (**4**). To a solution of 300 mL of liquid ammonia with 1.00 mmol of sodium diphenylphosphide prepared as before were added **1** (1.00 mmol) and **4** (4.00 mmol), and after 10 min of irradiation the reaction was quenched by adding ammonium nitrate in excess and the ammonia was allowed to evaporate. The residue was dissolved with water and then extracted with diethyl ether. The products were oxidized with H_2O_2 and then quantitatively analyzed by GLC or HPLC with the internal standard method.

Photostimulated Reaction of Substrates 1 or 4 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.

Acknowledgment. This work was supported in part by the Consejo de Investigaciones de la Provincia de Córdoba (CONICOR), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Antorchas Foundation (Argentina), and Stiftung Volkswagenwerk (Germany). D.G.M. wishes to thank the Royal Society (London) for support. A.E.L. gratefully acknowledges receipt of a fellowship from CONICET (Argentina).

Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra for **2-O** and **5-O** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO941396Y