The Reactivity of 1-Chloro-3,3-dimethylbicyclo[2.2.2]octan-2-one in the Radical Mechanism of Nucleophilic Substitution

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1-Chloro-3,3-dimethylbicyclo[2.2.2]octan-2-one (**5**) does not react with diphenyl phosphide ions (**4**) in liquid ammonia in the dark in 240 min, but under irradiation (30 min) it gives good yields of the substitution product (**10**) isolated as the oxide **12** (69% yield) and 3% yield of the reduction product 3,3-dimethylbicyclo[2.2.2]octan-2-one (**11**). This photostimulated reaction is inhibited by *p*-dinitrobenzene and 2,2,6,6-tetramethyl-1-piperidinyloxy. In competition experiments **5** is more reactive (≥700) than 1-chloroadamantane (**3a**) and only slightly less reactive than 1-bromoadamantane (**3b**) (0.40) toward diphenyl phosphide ions. On the other hand, 1-chloro-3,3-dimethylbicyclo[2.2.2]octane (**6**) was completely unreactive toward **4** under irradiation. We suggest that the bridgehead chloride **5** reacts by the $S_{RN}1$ mechanism of nucleophilic substitution and that the 2-oxo substituent increases the reactivity of the chloride due to the LUMO of the carbonyl group.

The radical mechanism of nucleophilic substitution, or $S_{RN}1$, is a well-known process by which a substitution is produced on adequately substituted substrates.[3] This nucleophilic substitution mechanism is a chain process which involves radicals and radical anions as intermediates. The main steps of this mechanism are sketched in Scheme I.

Scheme I

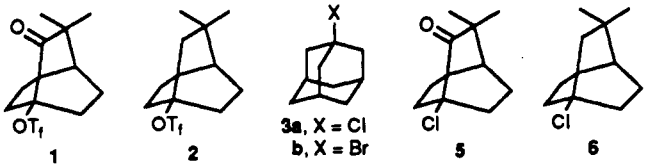
$$(RX)^{\bullet-} \rightarrow R^{\bullet} + X^{-} \quad (1)$$

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

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

This mechanism of nucleophilic substitution has been proposed with several alkyl halides,[4,5] and it has been suggested that these halo aliphatic compounds without electron-withdrawing groups react with nucleophiles by the $S_{RN}1$ mechanism because they react slowly or do not react at all by the polar mechanisms of nucleophilic substitution.[4]

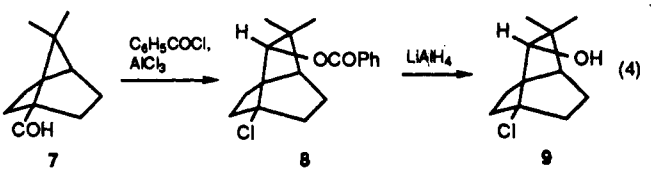
In general, 1-substituted bicyclic compounds are known to have low reactivity toward nucleophilic substitution reactions. Moreover, it has been recently reported that 2-oxo-3,3-dimethylbicyclo[2.2.2]oct-1-yl triflate (**1**) solvolyzes 4.34×10^{-9} times more slowly than the 3,3-dimethylbicyclo[2.2.2]oct-1-yl triflate (**2**) in ethanol at 25 °C.[6] The presence of a carbonyl group in the α-position of the carbocationic center makes it even less reactive toward solvolysis due to the inductive effect of the oxo substituent at the C(2) position.

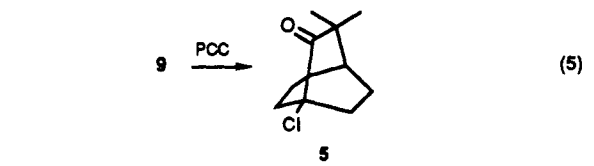


We have found that 1-bromo or 1-iodo bicyclic compounds react under irradiation in liquid ammonia with nucleophiles by the $S_{RN}1$ mechanism of nucleophilic substitution, but there is no reaction with the 1-chloro bicyclic compounds.[4,7] One exception was 1-chloroadamantane (**3a**) that reacts under irradiation (2 h) with diphenyl phosphide ions (**4**) to give 40% yield of reaction.[8] We then thought of interest to study 1-chloro-3,3-dimethylbicyclo[2.2.2]octan-2-one (**5**) in comparison with 1-chloro-3,3-dimethylbicyclo[2.2.2]octane (**6**) in order to see if the 2-oxo substituent which *remarkably decreases* the rate of the polar reaction *increases* the rate of the radical reaction. On the other hand, it is well known that aliphatic substrates with electron-withdrawing groups, such as *p*-nitrocumyl substrates[3,9] and halonitropropanes,[3,10] react with nucleophiles by the $S_{RN}1$ mechanism, but in competition with the S_N2 process. In the case of substrate **5**, there would be no competition with polar substitutions.

Results

Synthesis. 1-Chloro-3,3-dimethylbicyclo[2.2.2]octan-2-one (**5**) was prepared following eqs 4 and 5.





The acylative ring expansion of 7,7-dimethylbicyclo-[2.2.1]heptane-1-carbaldehyde (**7**) by using benzoyl chloride and aluminum chloride in carbon disulfide afforded 1-chloro-3,3-dimethylbicyclo[2.2.2]oct-2-yl benzoate (**8**).[11,12]

(1) Universidad Nacional de Córdoba.
(2) Kyoto University.
(3) For reviews, see: (a), Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; Washington, D.C., 1983. (b) Bowman, W. R. *Chem. Soc. Rev.* **1988**, *17*, 283. (c) Kornblum, N. *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1982; Supplement F, Chapter 10.
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(9) Kornblum, N.; Michel, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5662.
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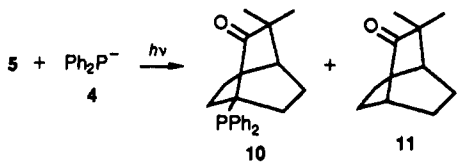
Table I. Photostimulated Reaction of 1-Chloro-3,3-dimethylbicyclo[2.2.2]octan-2-one (5) with Ph_2P^- ions (4) in Liquid Ammonia

expt	5, M × 10^3	4, M × 10^3	hν, min	yields, %[a] Cl⁻	11	12
1	1.43	1.41	30	91	3	69
2	0.97	0.95	240[b]	≤5		
3	0.93	-	30	≤2	-	-
4[c]	1.40	1.45	30	17[d]	4	8
5[e]	1.52	1.65	120	52[f]	9	24
6[g]	1.14	1.14	45	63	h	35
7	1.20[i]	0.57	30	h	h	97.7[j]
8	1.20[k]	1.20	30	h	h	20[l]
9	0.97[m]	0.97	120	≤3		

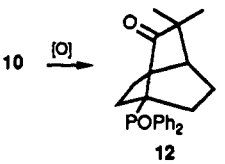
[a] Chloride ions were determined potentiometrically. The products 11 and 12 were determined after oxidation by GLC by the internal standard method. [b] Dark reaction. [c] p-Dinitrobenzene (27 mol %) was added. [d] Starting chloride 5 was recovered (79%). [e] p-Dinitrobenzene (12 mol %) was added. [f] The starting chloride 5 was recovered (37%). [g] TEMPO (30 mol %) was added. [h] Not quantified. [i] 1-Chloroadamantane (0.021 M) was added. [j] Relative yield compared with 1-adamantyldiphenylphosphine oxide (2.3%). [k] 1-Bromoadamantane (1.20 × 10^{-3} M) was added. [l] Based on the concentration of 4. 1-Adamantyldiphenylphosphine oxide (43%) was also formed. [m] 1-Chloro-3,3-dimethylbicyclo[2.2.2]octane.

The benzoate 8 was reduced with lithium aluminum hydride to 1-chloro-3,3-dimethylbicyclo[2.2.2]octan-2-ol (9), which was then converted to 5 by oxidation with pyridinium chlorochromate (PCC) in an overall yield of 46% based on 7.

Reactions. Substrate 5 does not react with 4 in liquid ammonia in the dark (Cl^- ion ≤ 5% yield in 240 min, Table I, experiment 2), but under irradiation it gives 91% of Cl^- ion, 69% yield of the substitution product 10 isolated as the oxide 12,[13] and 3% yield of the reduced product 11, in only 30 min (Table I, experiment 1, eqs 6–7).



(6)



(7)

This photostimulated reaction was inhibited by p-dinitrobenzene (p-DNB) (in 30 min it gives 17% of Cl^- ion and 8% of 12 and 4% of 11, whereas in 120 min 52% yield of Cl^- ion was found, Table I, experiments 4–5), and slightly by 30 mol % of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (Table I, experiment 6), well-known inhibitors of $S_{RN}1$ reactions.[3] The irradiation of substrate 5 in liquid ammonia without the nucleophile 4 did not give any reaction (Table I, experiment 3).

On the other hand, 1-chloro-3,3-dimethylbicyclo-[2.2.2]octane (6) was completely unreactive with nucleophile 4 in 2 h of irradiation under the same experimental conditions (Table I, experiment 9).

Competition Experiments. We intended to study the relative reactivity of 5 vs 6, but it was not possible due to the lack of reactivity of 6. We chose to study the relative reactivity of 5 to be compared with 1-chloroadamantane (3a) which reacts under these experimental conditions.[8] Once the yields of substitution products 1-adamantyldiphenylphosphine oxide and 12 were determined in the photostimulated reaction of 3a and 5 with nucleophile 4 followed by oxidation, it was possible to calculate k_5/k_{3a} by using eq 8.[14b] $[5]_0$ and $[3a]_0$ are initial concentrations,

$$\frac{k_5}{k_{3a}} = \frac{\ln [5]_0/[5]_t}{\ln [3a]_0/[3a]_t} \quad (8)$$

and $[5]_t$ and $[3a]_t$ are concentrations at time t. This equation is based on a first-order reaction of both substrates with the nucleophile 4.[14b]

In the competition experiment (Table I, experiment 7) the obtained relative yield of 12 was 97.7%, whereas of 1-adamantyldiphenylphosphine oxide,[8] it was 2.3%. We roughly estimate that 5 is ≥700 times more reactive than 3a.[14a]

We studied also the relative reactivity of 5 compared with 1-bromoadamantane (3b), which has been shown to be more reactive than 3a in the photostimulated reaction with 4 in liquid ammonia.[8] In the competition experiment we found the substitution product 12 (20% yield) and 1-adamantyldiphenylphosphine oxide (43% yield) (Table I, experiment 8). The relative reactivity found for k_5/k_{3b} is 0.40.

Discussion

The fact that 5 reacts under irradiation with nucleophile 4, that its photostimulated reaction was inhibited by p-DNB and TEMPO, and that the reaction does not occur in the dark suggests that 5 reacts with 4 by the $S_{RN}1$ mechanism of nucleophilic substitution.

According to the results of the competition reactions, 5 has a reactivity greater than 3a and similar to 3b. This enhancement in the reactivity cannot be attributed to an increase of the initiation steps of the $S_{RN}1$ mechanism due to the photolysis of 5.[15]

It was calculated that as the angular strain increases in the bicyclic halides studied, their reduction potentials are more negative (higher values of their C-X LUMO's σ* values), with a decrease in their reactivity in $S_{RN}1$ reactions.[16] According to MNDO calculations,[17] the presence

(11) This method is an extension of the acylative ring expansion of bridgehead aldehydes by using benzoyl triflate and triflic acid to form bicyclic 1,2-diols; see ref 12.

(12) Takeuchi, K.; Kitagawa, I.; Akiyama, F.; Shibata, T.; Kato, M.; Okamoto, K. *Synthesis* **1987**, 612.

(13) (a) The substitution product 10 was oxidized with H_2O_2 (15%).[13b] (b) Denniston, M. L.; Martin, D. R. *Inorg. Synth.* **1977**, *17*, 183.

(14) (a) Due to the high difference in reactivity of both substrates, the relative reactivity is only approximate. (b) Bunnett, J. F. In *Investigation of Rates and Mechanisms of Reactions*, 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part I, p 159.

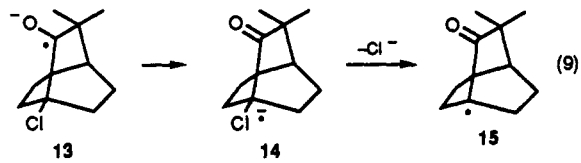
(15) (a) It is known the photolytic cleavage of α-chloro ketones in other experimental conditions.[15b] (b) Morrison, H; de Cardenas, L. *J. Org. Chem.* **1987**, *52*, 2590 and references cited therein.

(16) Pierini, A. B.; Santiago, A. N.; Rossi, R. A. *Tetrahedron*, in press.

(17) The calculations were carried out with the semiempirical MNDO method as implemented in AMPACK, available from the Quantum Chemistry Program Exchange (QCPE), program 506.

of a 2-oxo substituent in substrate **5** decreases the antibonding σ^* MO of the C–Cl bond. For instance, compound **6** has a C–Cl antibonding σ^* MO value of 0.84 eV,[18] compound **3a** has a C–Cl σ^* MO value of 0.81 eV, whereas **5** has the antibonding σ^* MO of the C–Cl value of 0.59 eV. However, the LUMO of this molecule belongs to the carbonyl group (0.45 eV),[19] similar to the LUMO value (0.49 eV) of the antibonding σ^* of the C–Br in 1-bromoadamantane, **3b**.

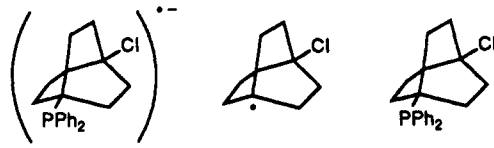
In order to rationalize the high reactivity of **5**, we suggest that it receives the electron in the antibonding π^* MO of the carbonyl group to form the π^* radical anion **13**, which by an intramolecular reaction transfers its extra electron to the antibonding σ^* MO C–Cl to form the radical anion **14**, which then fragments to give the radical **15** and chloride ions to propagate the chain reaction of Scheme I (eq 9).



(9)

Another possibility is that the radical anion intermediate has an in-phase mixing of the antibonding π^* orbital of the carbonyl group and of the antibonding orbital σ^* C–Cl, and once formed fragments into radical **15** and chloride ions.[20] It has been shown by ab initio calculations that the radical anion of chloronitromethane fragments spontaneously, and this process is exothermic due to an in-phase mixing of the antibonding π^* orbital of the NO_2 group and the antibonding orbital σ^* of the C–Cl bond.[21] Our calculations show mixing of the antibonding orbitals leading to the most stable σ^* radical anion intemediate **14**.

According to our results, we suggest that the 2-oxo substituent enhances the reactivity of 1-chloro bicyclic compounds in $S_{RN}1$ reactions. It is interesting to note that a very close radical anion of the bicyclo[2.2.2]oct-1-yl system, such as the radical anion **16** formed in the coupling of the radical **17** with **4** in liquid ammonia, does not transfer its odd electron to the antibonding σ^* of the C–Cl bond, and only the monosubstitution product **18** is formed.[7b]



16 17 18

Experimental Section

General Method. IR spectra were recorded on a Hitachi 215 spectrophotometer. ^1H NMR spectra were recorded on a Hitachi R-24, JEOL FX90A, or JEOL GSX270 spectrometer. ^{13}C NMR spectra were obtained on a JEOL FX90A or JEOL GSX270 spectrometer. In all NMR measurements TMS was used as an internal standard. Mass spectra were obtained with a Finnigan 3300 f-100 mass spectrometer. Gas chromatographic analyses were performed on a Shimadzu GC-8A or Konik instruments with a flame ionization detector and data system Shimatzu CR-3A or Spectra Physics SP-2400, using a column packed with 5% OV17 on Chromosorb G (1.5 m × 3 mm). Column chromatography was performed on silica gel (70–270-mesh ASTM). Irradiation was conducted in a reactor equipped with four 250-W lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated). Potentiometric titration of halide ions was performed in a PH meter (Seybold Wien) using Ag/Ag^+ electrode and $AgNO_3$ standard. Melting points were obtained with a Büchi 510 apparatus and are not corrected. Elemental analyses were performed in the Microanalytical Center, Kyoto University.

Materials. Diphenyl phosphide ions were prepared from triphenylphosphine (Aldrich) and sodium metal in liquid ammonia, and the amide ion formed was neutralized with *tert*-butyl alcohol.[3a] 7,7-Dimethylbicyclo[2.2.1]heptane-1-carbaldehyde (**7**) was prepared as described previously.[12] 1-Chloro-3,3-dimethylbicyclo[2.2.2]octane (**6**)[22] and bicyclo[2.2.2]octanone[23,24] were prepared following reported methods. Carbon disulfide was dried over calcium chloride and distilled. Methylene chloride was distilled from phosphorus pentoxide.

1-Chloro-3,3-dimethylbicyclo[2.2.2]oct-2-yl Benzoate (8). To a stirred suspension of pulverized aluminum chloride (6.79 g, 50.9 mmol) in carbon disulfide (50 mL) was added a solution of 7,7-dimethylbicyclo[2.2.1]heptanecarbaldehyde (**7**)[12] (2.28 g, 15.0 mmol) and benzoyl chloride (2.91 g, 20.7 mmol) in carbon disulfide (21 mL) at 3–4 °C over 14 min under nitrogen, and then stirring was continued at room temperature for 90 min. The reaction mixture was poured into ice and extracted with ether. The combined extract was washed with a saturated $NaHCO_3$ aqueous solution and dried ($MgSO_4$). Evaporation of the solvents afforded crude **8** (4.6 g). An analytical sample was obtained by recrystallization from hexane as a colorless solid: mp 96.5–97.0 °C; ^1H NMR (60 MHz, CCl_4) δ 1.00 (s, 3 H), 1.36 (s, 3 H), 1.4–2.8 (m, 9 H), 4.94 (br s, 1 H), 7.3–8.2 (m, 5 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 39.1, 69.4 (C), 35.3, 82.3 (CH), 24.2, 24.6, 28.8, 34.0 (CH_2), 23.2, 29.1 (CH_3), 128.3, 129.6, 130.0, 132.8 (Ph), 166.0 (C=O); IR (CCl_4) 2970, 1730, 1600, 1450, 1395, 1370, 1280, 1180, 1120, 1030, 710 cm^{-1}. Anal. Calcd for $C_{17}H_{21}ClO_2$: C, 69.73; H, 7.23. Found: C, 69.85; H, 7.46.

1-Chloro-3,3-dimethylbicyclo[2.2.2]octan-2-ol (9). An ether solution of crude 1-chloro-3,3-dimethylbicyclo[2.2.2]oct-1-yl benzoate (**8**) (4.68 g) was added dropwise to $LiAlH_4$ (0.76 g, 20 mmol) in ether with stirring. The reaction mixture was further stirred for 30 min at room temperature and then worked up in a usual manner. Separation of **9** from benzyl alcohol by medium-pressure liquid chromatography (MPLC) on silica gel gave pure **9** (1.33 g, 7.07 mmol) in an overall yield of 47% based on aldehyde **7**: mp 43.5–44.0 °C; ^1H NMR (60 MHz, CCl_4) δ 1.05 (s, 3 H), 1.10 (s, 3 H), 1.2–2.6 (m, 9 H), 3.37 (s, 1 H, OH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 38.8, 75.8 (C), 35.6, 81.0 (CH), 24.6, 24.9, 27.6, 34.1 (CH_2), 22.7, 30.1 (CH_3); IR (CCl_4) 3600, 2950, 1460, 1325, 1270, 1080, 970, 910 cm^{-1}. Anal. Calcd for $C_{10}H_{17}ClO$: C, 63.65; H, 9.08. Found: C. 63.37; H, 9.16.

1-Chloro-3,3-dimethylbicyclo[2.2.2]octan-2-one (5). To a suspension of pyridinium chlorochromate (2.29 g, 10.6 mmol) in methylene chloride (13 mL) was added a solution of 1-chloro-3,3-dimethylbicyclo[2.2.2]octan-2-ol (**9**) (1.33 g, 7.07 mmol) in methylene chloride (13 mL), and the mixture was magnetically stirred under nitrogen at room temperature for 11 h. The reaction mixture was passed through a column of Florisil (13 g), and the residue was well washed with ether and passed through the same column. Evaporation of the solvents afforded a colorless solid (1.33 g), which was purified by MPLC over silica gel (hexane–ether, 9:1) to give pure **5** (1.29 g, 6.93 mmol, 98%): mp 46.0–47.0 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 1.21 (s, 6 H), 1.6–2.5 (m, 9 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 47.5, 72.1 (C), 37.3 (CH), 23.8, 33.3 (CH_2), 24.0 (CH_3), 211.3 (C=O); IR (CCl_4) 2950, 1730, 1460, 1380, 970 cm^{-1}. Anal. Calcd for $C_{10}H_{15}ClO$: C, 64.34; H, 8.10; Cl, 18.99.

(18) The compound studied was 1-chlorobicyclo[2.2.2]octane for the sake of simplicity.

(19) The compound studied was 1-chlorobicyclo[2.2.2]octan-2-one for the sake of simplicity.

(20) Depending on the substrate the electron-transfer reaction to an alkyl halide is dissociative leading straightforward to a radical and the halide ion, see: (a) Symons, M. C. R. *Pure Appl. Chem.* **1981**, *53*, 223. (b) Andrieux, C. P.; Saveant, J. M.; Su, K. B. *J. Phys. Chem.* **1986**, *90*, 3815 and references cited therein.

(21) Bigot, B.; Roux, D.; Salem, L. *J. Am. Chem. Soc.* **1981**, *103*, 5271.

(22) Wnuk, T. A.; Kovacic, P. *J. Am. Chem. Soc.* **1975**, *97*, 5807.

(23) Freeman, P. K.; Balls, D. M.; Brown, D. J. *J. Org. Chem.* **1968**, *33*, 2211.

(24) Mislow, K.; Berger, J. G. *J. Am. Soc. Chem.* **1962**, *84*, 1956.

Found: C, 64.25; H, 8.40; Cl, 18.69.

3,3-Dimethylbicyclo[2.2.2]octan-2-one (11). To a solution of lithium diisopropylamide (4.43 mmol) in THF (4.4 mL) and hexane (4.4 mL) was added a solution of bicyclo[2.2.2]octanone (mp 175–179 °C; lit.[24] mp 175.5–177.5 °C) (0.500 g, 4.03 mmol) in THF (2.0 mL) at −78 °C, and the mixture was stirred for 30 min. HMPA (0.72 g, 4.0 mmol) and methyl iodide (0.63, 4.4 mmol) were added in this sequence, and stirring was continued for 20 min. After stirring at room temperature for 15 min, the reaction mixture was poured into 10% NH_4Cl aqueous solution and extracted with ether. The ether solution was washed with a saturated NaCl aqueous solution and dried ($MgSO_4$). Evaporation of the ether afforded a brown solid (0.573 g) which was then subjected to MPLC over silica gel by using hexane–ether (95:5) to give 11 (76 mg, 12%) and 3-methylbicyclo[2.2.2]octan-2-one (216 mg, 39%). The latter was again methylated as above to give 11 (71 mg). The two yellowish crops of 11 were combined and further purified by preparative GLC to give 11 (68 mg) of 99% purity: mp 92.5–94.0 °C (lit.[25] mp 97 °C); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 45.9 (C), 38.4, 42.7 (CH), 22.3, 23.3 (CH_2), 23.6 (CH_3), 228.9 (C=O). ^1H NMR spectra agreed with reported data.[25]

Photostimulated Reaction of 1-Chloro-3,3-dimethylbicyclo[2.2.2]octan-2-one (5) with Ph_2P^- Ions in Liquid Ammonia. The following procedure is representative of all 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 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 diphenyl phosphide ions, and *t*-BuOH (1 mmol) was added to neutralize the amide ions formed. To this solution substrate 5 (1 mmol) was added and then irradiated for 30 min. The reactions 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, and the products were oxidized with H_2O_2[13b] and then quantified by GLC with the internal standard method. In another experiment the substitution product 10 was oxidized with H_2O_2, and (2-oxo-3,3-dimethylbicyclo[2.2.2]oct-1-yl)diphenylphosphine oxide (12) was isolated as a white solid after chromatography on silica gel, eluted with diethyl ether, and recrystallized from hexane–benzene: mp 188–189 °C; ^1H NMR ($CDCl_3$) δ 1.10 (6 H, s), 1.69 (3 H, m), 1.88 (4 H, m), 2.48 (2 H, m), 7.38 (6 H, m), 7.97 (4 H, m): ^{13}C NMR ($DCCl_3$ relative to TMS) δ 22.23 ($^2J_{C-P}$ = 9.8 Hz, C_6), 23.40 (C_5), 23.84 (Me), 37.88 (C_4), 47.05 ($^2J_{C-P}$ = 4.9 Hz, C_3), 50.91 ($^1J_{C-P}$ = 77.3 Hz, C_1 bridgehead), 128.09 ($^3J_{C-P}$ = 11.7 Hz, C_m), 131.2 ($^1J_{C-P}$ = 97.8 Hz, C_i), 131.5 ($^4J_{C-P}$ = 2.9 Hz, C_p), 132.7 ($^2J_{C-P}$ = 9.8 Hz, C_o), 218.95 ($^2J_{C-P}$ = 2.9 Hz, C_2=O). Mass spectrum, *m/e* (relative intensity) 352 (41), 337 (14), 324 (66), 283 (27), 255 (74), 202 (73), 201 (100), 184 (23), 155 (23), 125 (19), 77 (25). Anal. Calcd for $C_{22}H_{25}PO_2$: C, 74.98; H, 7.15; P, 8.79. Found: C, 74.75; H, 7.09; P, 8.72.

Reaction of 5 with Ph_2P^- Ions in Liquid Ammonia in the Dark. With the same procedure as before Ph_2P^- ions (1 mmol) and 5 were added and the solution in the reaction flask was wrapped with aluminum foil. After 240 min the reaction was quenched and analyzed as before. No substitution product was found (chloride ions were found in ≤5% yield).

Photolysis of 5 in Liquid Ammonia. To 300 mL of dry liquid ammonia was added 0.28 mmol of 5, the mixture was irradiated during 30 min, diethyl ether (100 mL) was then added and the ammonia was allowed to evaporated, and the workup was similar as before. In the aqueous solution no chloride ions were found (≤3%).

Reaction of 1-Chloro-3,3-dimethylbicyclo[2.2.2]octane (6) with Ph_2P^- Ions in Liquid Ammonia. With the same procedure was prepared 0.29 mmol of Ph_2P^- ions in 300 mL of liquid ammonia, and substrate 6 (0.29 mmol) was added; after 120 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. In the aqueous layer chloride ion was found in ≤3% yield.

Competition Experiments: 1-Chloro-3,3-dimethylbicyclo[2.2.2]octan-2-one (5) vs 1-Chloroadamantane (3a). To a solution of 250 mL of liquid ammonia with 0.17 mmol of Ph_2P^- ions prepared as before were added **3a** (5.3 mmol) and 5 (0.30 mmol), and after 30 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 ether extract was oxidized with H_2O_2 and then analyzed by GLC with the internal standard method.

Competition Experiments: 1-Chloro-3,3-dimethylbicyclo[2.2.2]octan-2-one (5) vs 1-Bromoadamantane (3b). To a solution of 250 mL of liquid ammonia with 0.30 mmol of Ph_2P^- ions prepared as before were added **3b** (0.30 mmol) and 5 (0.30 mmol), and after 30 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 ether extract was oxidized with H_2O_2 and then analyzed by GLC with the internal standard method.

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Registry No. **3a**, 935-56-8; **3b**, 768-90-1; **5**, 131437-02-0; **6**, 57422-54-5; **7**, 110977-32-7; **8**, 131437-03-1; **9**, 131437-04-2; **11**, 50682-96-7; **12**, 131437-05-3; Ph_2P^-, 6396-02-7; bicyclo[2.2.2]octanone, 2716-23-6; 3-methylbicyclo[2.2.2]octan-2-one, 26051-25-2.

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