Synthesis of Several Halobisnoradamantane Derivatives and Their Reactivity through the $S_{RN}1$ Mechanism

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Received February 8, 2001

Several bridgehead halobisnoradamantane derivatives (**5**, **7**, **10**, and **17**) were synthesized from tricyclic diester **1** in good yields using standard methods. The reactivity through the $S_{RN}1$ mechanism of the above compounds and the known halobisethano derivatives **24** and **25a**−**c** was studied. Iodo derivatives **7**, **10**, and **25a** reacted with diphenylphosphide ions in DMSO under irradiation to give the corresponding substitution and reduction products by the $S_{RN}1$ mechanism, while iodo ketone **17** gave a mixture of the rearranged substitution product **36** and the reduction product **18**. Formation of **36** takes place through a 1,5-hydrogen migration of the initially formed radical, a kind of process that has been observed for the first time in the $S_{RN}1$ propagation steps. The diiodo derivative **24** reacted with diphenylphosphide ions under similar reaction conditions to give the substitution and/or reduction products **32**, **31**, **27**, **25a**, and **26**. The intramolecular ET reaction in the monosubstitution radical anion $\mathbf{32}^{\bullet-}$ seems to be faster than the intermolecular ET to the substrate, and the monoiodo derivative **25a** is a reaction intermediate.

Introduction

Several alkyl halides have been found to react with nucleophiles by the radical nucleophilic substitution or $S_{RN}1$ mechanism.[1] When there is not spontaneous electron transfer (ET) from the nucleophile to the substrate, the initiation step can be induced by photostimulation or by $FeBr_2$ (eq 1).[2] The alkyl radical $R^{\bullet}$ thus formed couples with the nucleophile to yield a radical anion $(RNu)^{\bullet-}$ (eq 2), which by an intermolecular ET[3] to the substrate gives the substitution product and the alkyl radical $R^{\bullet}$ that propagates the chain (eq 3).

Initiation	$RX + Nu^-$	$\xrightarrow[(\text{or } FeBr_2)]{h\nu}$	$R\cdot + X^- + Nu\cdot$	(1)
Propagation	$R\cdot + Nu^-$	$\longrightarrow$	$RNu\cdot^-$	(2)
	$RNu\cdot^- + RX$	$\longrightarrow$	$RNu + R\cdot + X^-$	(3)

The alkyl halides that react by the $S_{RN}1$ mechanism are those that have a relatively low reactivity toward polar nucleophilic substitution. For instance, neopentyl halides, cyclohexyl and cyclopropyl halides, and bridgehead halides react with different nucleophiles by the $S_{RN}1$ mechanism.[1]

The $S_{RN}1$ reaction of bridgehead halopolycycloalkanes is of great importance not only from a mechanistic but also from a synthetic point of view. Much of this work has been carried out on adamantane derivatives,[2,4] and less work has been carried out in more strained polycyclic systems: 1-halo- and 1,4-dihalobicyclo[2.2.2]octane derivatives,[5a−e] 1-halo- and 1,4-dihalobicyclo[2.2.1]heptane derivatives,[5f−i] 4-iodo-1,7,7-trimethyltricyclo[2.2.1.$0^{2,6}$]-heptane,[5j] and 1-haloquadricyclane.[5k] It has been suggested that the reactivity of halopolycycloalkanes in ET reactions depends on the nucleofugal group and on the strain energy of the polycycloalkane.[6]

When an aromatic substrate bearing two leaving groups reacts by the $S_{RN}1$ mechanism, either the monosubstitution or disubstitution product can be formed,

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10.1021/jo010159+ CCC: $20.00
Published on Web 07/19/2001

depending on the structure of the substrate, the nature of the nucleofugal groups, the nucleophile, and the reaction conditions.[1b,7] The first reactive intermediate in these reactions is a radical-anion which loses a halide anion to give a haloaryl radical. The coupling reaction of this radical with the nucleophile forms a new radical anion, in which the π^* MO of the aromatic moiety is the bridge that mediates the ET to the σ^* MO of the remaining C−X bond. The rate of the intramolecular ET reaction depends on the energy difference between both MO's.[8]

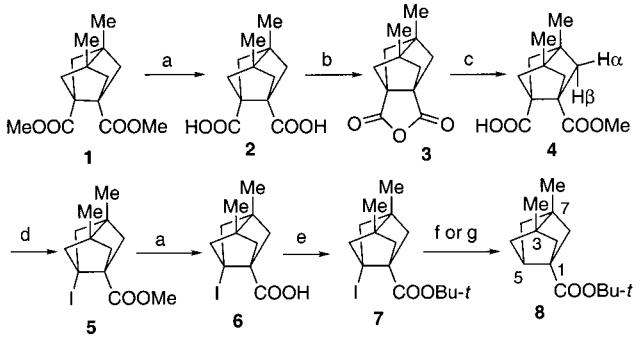
Also, when an alkyl substrate having two leaving groups reacts by the $S_{RN}1$ mechanism, monosubstitution or disubstitution products are formed. The first reactive intermediate is a haloalkyl radical, and in the coupling reaction with the nucleophile a radical-anion is formed.[1,5b,c,9] In this case, intramolecular ET to the σ^* MO of the C−X bond can take place through the σ bonds or through space. The rate of intramolecular ET not only depends on the energy difference between the MO's but also on the number of the intervening bonds, on the distance between the donor and acceptor, and on the flexibility of the bridge.[9−13]

To obtain more insight on the effect of the strain in ET reactions, we decided to study the reactivity of halo- and dihalobisnoradamantane derivatives toward Ph_2P^- ions. To this end, the new iodotricyclo[3.3.0.$0^{3,7}$]octane derivatives **5**, **7**, **10**, and **17** were prepared. These compounds together with the known bisethano derivatives **24**,[14,15] **25a**,[16] **25b**,[16] and **25c**,[16] containing the pentacyclo[6.4.0.0.^{2,10}0.^{3,7}0^{4,9}]dodecane skeleton, are the subject of the present $S_{RN}1$ study.

Results and Discussion

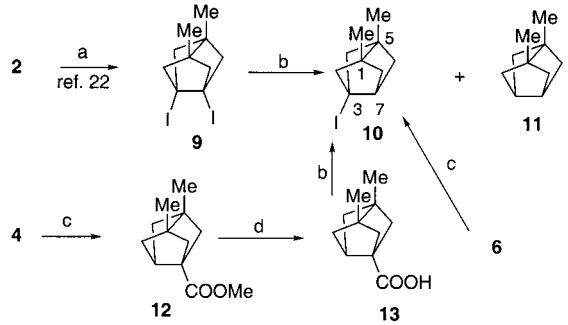
Synthesis. The synthesis of iodo esters **5** and **7** was carried out from the known diester **1**[17] by following standard procedures (Scheme 1). Hydrogenation of **7** at a pressure of 35 atm, using 10% Pd on charcoal as catalyst, was shown to be a very slow process, providing a mixture of starting **7** and *tert*-butyl ester **8** in a ratio of about 1:1 after 1 week of reaction. However, pure *tert*-butyl ester **8** could be obtained as described later on from the $S_{RN}1$ reaction of **7** and diphenylphosphide anion.

Scheme 1[a]



[a] Reagents, conditions, and yields: (a) (1) 10% KOH, MeOH, (2) concentrated HCl, **2** (98%), **6** (66%); (b) Ac_2O, Δ, 88%; (c) MeONa, MeOH, 85%; (d) IBDA, I_2, benzene, *hν*, 73%; (e) 2-methylpropene, concentrated H_2SO_4, CH_2Cl_2, rt, 59%; (f) H_2, 35 atm, 10% Pd/C, Na_2CO_3, EtOH, 7 days, 1:1 mixture of **7** and **8**; (g) Ph_2P^-, *hν*, DMSO, 1.5 h, 70%.

Scheme 2[a]



[a] Reagents, conditions, and yields: (a) IBDA, I_2, benzene, *hν*, 65%; (b) H_2, 1 atm, 10% Pd/C, NaOH, EtOH, 15 h, 70% **10** (14 days **11**, not isolated from the solution; (c) (1) 2,2′-dithiobis(pyridine 1-oxide), Bu_3P, THF, (2) *t*-BuSH, *hν*, **12** (74%) **10,** (70%); (d) (1) 10% KOH, MeOH, (2) concentrated HCl, 72%.

The synthesis of iodo compound **10** (Scheme 2) was first carried out by iododecarboxylation of acid **13**.[18,19] Unfortunately, it could not be separated (column chromatography or distillation) from the iodobenzene formed as a byproduct in this reaction. Alternatively (Scheme 2), iodo compound **10** was prepared by decarboxylation of iodo acid **6** using the Barton procedure.[20] Moreover, iodide **10** was obtained in good isolated yield, by controlled hydrogenation[21] at atmospheric pressure of the known diiodide **9**.[22] Prolonged hydrogenation of diiodide **9** gave the highly volatile alkane **11**, whose volatility precluded isolation from its methanolic solution.

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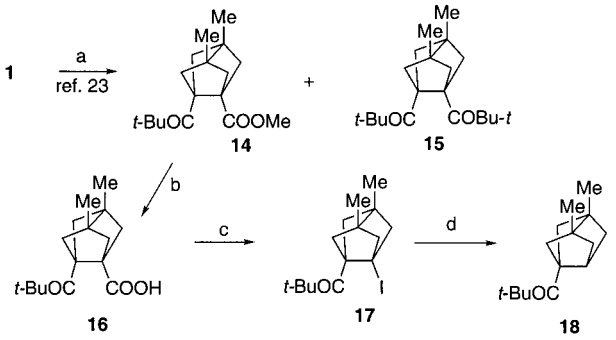
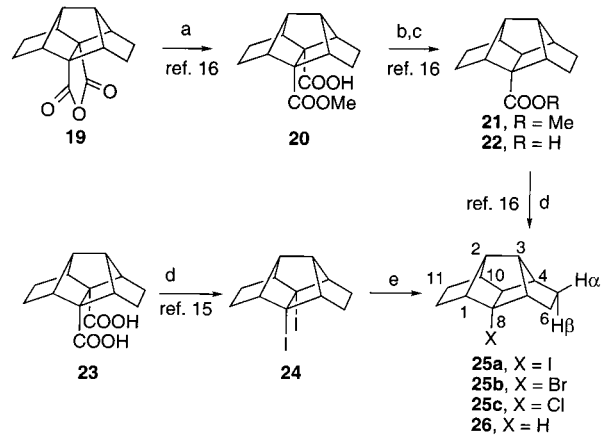
Scheme 3[a]



[a] Reagents, conditions, and yields: (a) *t*-BuLi (1.2 equiv), THF; **14** (72%) **15** (5%); (b) (1) 10% KOH, MeOH, (2) concentrated HCl, 82%; (c) IBDA, I_2, benzene, *hν*, 82%; (d) H_2, 1 atm, 10% Pd/C, NaOH, EtOH, 12 h, 93%.

Scheme 4[a]



[a] Reagents, conditions and yields: (a) (1) NaOMe, MeOH, (2) concentrated HCl, 98%; (b) (1) 2,2′-dithiobis(pyridine 1-oxide), Bu_3P, THF, (2) *t*-BuSH, *hν*, 91%; (c) concentrated H_2SO_4, 50 °C, 30 min, 67%; (d) IBDA, I_2, benzene, *hν*, Δ; **24** (61%), **25a** (82%); (e) H_2, 1 atm, 10% Pd/C, NaOH, EtOH; 15 h, **25a** (65%); 2 weeks, **26** (50%).

Iodo ketone **17** was prepared by following standard procedures from the known keto ester **14**,[23] which on hydrogenation gave ketone **18** (Scheme 3). Although iodo derivative **25a** had been previously prepared[16] from anhydride **19** as shown in Scheme 4, it has now been obtained in a shorter and more convenient way by controlled hydrogenation of the easily available diiodo derivative **24**.[14,15] At longer reaction times, hydrogenation was complete and only the volatile hydrocarbon **26**[14] was obtained.

Reactivity. The $S_{RN}1$ reactivity of the present halopolycyclic compounds was studied with diphenylphosphide ions (Ph_2P^-) in DMSO under irradiation. The phosphane derivatives contained in the initial reaction mixtures were oxidized to the corresponding oxides by reaction with 10% H_2O_2, prior to the isolation or the quantification of the reaction products. The initial studies were carried out on the halopentacyclic derivatives **25a**−**c**. Results are collected in Tables 1 and 2. The photostimulated reaction of iodide **25a** was partially inhibited by *p*-dinitrobenzene (*p*-DNB), a good electron acceptor,[1] while the dark reaction was slow and completely inhibited by *p*-DNB. All these results suggest that iodide **25a** reacts with Ph_2P^- ions by the $S_{RN}1$ mechanism. Worthy of note, the formation of the reduction product **26** was significant. Probably, the coupling reaction between the alkyl radical and the nucleophile is slower in DMSO than in liquid ammonia. Since DMSO is a better hydrogen donor than liquid ammonia,[7d] the reduction of the radical becomes more efficient in the first solvent.

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Table 1. Products and Yields from the Reactions of Different Starting Materials with Diphenyl Phosphide Ions[a]

Starting material	Product (% yield)
5	**12** (80%)
7	**8** (70%) + **39-O** (22%)
10	**11** (40%) + **35-O** (57%)
17	**18** (15%) + **36-O** (83%)
25a (or **25b**) (or **25c**)	**26** (59%) + **27-O** (35%)
28a, X = I **28b**, X = Br	**29-O** (51%) (34%) + **30** (47%) (35%)
25a + **28b**	**25b** + **26** + **27-O** + **29-O** + **30**
24	**25a** (26%) + **26** (6%) + **27-O** (10%) + **31-O** (28%) + **32-O** (5%)[b]

[a] All reaction were carried out in DMSO under photostimulation. For the specific conditions, see the Experimental Section and Tables 2−6. [b] Obtained from a reaction using only 1.1 equiv of diphenylphosphide for 3 min.

Table 2. Reactions of 8-Halopentacyclic Compounds 25a−c with Diphenylphosphide Ions in DMSO

				product yields (%)		
entry	substrate (mmol)	Ph_2P^- (mmol)	conditions	**26**[a]	**27-O**[b]	recovered substrate (%)[c]
1	**25a**, 0.20	0.22	dark, 15 min	9	3	**25a**, 86
2	**25a**, 0.20	0.22	*hν*, 15 min	59	35	**25a**, 5
3	**25a**, 0.20	0.22	*hν*, 15 min[d]	11	9	**25a**, 80
4	**25a**, 0.20	0.22	dark, 15 min[d]			**25a**, 100
5	**25b**, 0.20	0.22	*hν*, 2 h	17	3	**25b**, 80
6	**25c**, 0.20	0.22	*hν*, 2 h			**25c**, 100

[a] Quantified by GLC with biphenyl as internal standard. [b] Quantified by GLC with triphenylphosphine oxide as internal standard. [c] Quantified by GLC with anthracene as internal standard. [d] 20 mol % of *p*-DNB was added.

Table 3. Reactions of 1-Haloadamantanes 28a,b with Diphenylphosphide Ions in DMSO

entry	substrate (mmol)	Ph_2P^- (mmol)	conditions	product yields (%) 29-O[a]	30[b]	recovered substrate (%)[c]
1	**28a**, 0.21	0.23	dark, 10 min	39	43	**28a**, 17
2	**28a**, 0.21	0.23	dark, 10 min[d]	5	24	**28a**, 86
3	**28a**, 0.21	0.23	*hν*, 10 min	51	47	**28a**, −
4	**28b**, 0.20	0.22	dark, 15 min			**28b**, 98
5	**28b**, 0.20	0.22	*hν*, 15 min	34	35	**28b**, 30
6	**28b**, 0.20	0.22	*hν*, 15 min[d]	1	1	**28b**, 98

[a] Quantified by GLC with triphenylphosphine oxide as internal standard. [b] Quantified by GLC with methyl caproate as internal standard. [c] Quantified by GLC with anthracene as internal standard. [d] 20 mol % of *p*-DNB was added.

To know the relative reactivity of iodide **25a** vs 1-iodo- and 1-bromoadamantane (**28a** and **28b**, respectively), the reaction of **28a** and **28b** with Ph_2P^- ions in DMSO was studied. Results, confirming the $S_{RN}1$ mechanism, are collected in Tables 1 and 3. Curiously, bromide **28b** reacts by the $S_{RN}1$ mechanism with Ph_2P^- ions in liquid ammonia to give mainly, after 15 min irradiation and oxidation, the substitution product **29-O**.[4a] As in the case of iodide **25a**, reactions carried out in DMSO gave higher yields of reduction products.

The relative reactivities of pairs of compounds toward the same nucleophile can be established in reactions in which both substrates are present in excess with respect to the nucleophile.[24] In competition reactions between iodide **25a** and bromide **28b**, the radical of the pentacyclic compound abstracts a bromine atom from **28b** to form bromide **25b** (Tables 1 and 4).[25] Thus, the relative reactivity cannot be established quantitatively. **25a** appears as more reactive than **28b** but much less reactive than **28a** (Table 4, entry 4).

There was no reaction of diiodide **24** with 2.2 equiv of Ph_2P^- ions in DMSO,[26] in the dark for 3 min, but it reacted under photostimulation to give, after oxidation, a mixture of products: iodide **25a**, hydrocarbon **26**, the monosubstitution product **27-O**, and the disubstitution product **31-O** in 26, 6, 10, and 28% yields, respectively (Tables 1 and 5). This reaction was partially inhibited by *p*-DNB. At longer reaction times, the yields of the substitution products, **27-O** and **31-O**, and the alkane **26** increased while the yield of **25a** decreased, the substrate being almost completely consumed. The dark reaction of **24** with Ph_2P^- ions for 10 min was sluggish, and the main product was **25a** (5% yield, Table 5, entries 1−3, 5, and 6). All these results agree with an $S_{RN}1$ reaction mechanism and suggest that iodide **25a** is a reaction intermediate.

The nucleophile transfers one electron to diiodide **24** to give the radical **33** (Scheme 5), which is either reduced to give the iodide **25a** that enters into a new $S_{RN}1$ cycle to give finally the reduction (**26**) and monosubstitution (**27**) products or reacted with the nucleophile to give the radical anion intermediate **32**$^{\bullet-}$. This radical-anion would have two competing reaction pathways: (1) intermolecular ET to diiodide **24** to afford the iodo phosphine **32** and the radical **33** that propagates the chain reaction or (2) an intramolecular ET to the C−I bond to give the radical **34** that is reduced to give the phosphine **27** or reacts with the nucleophile to afford the diphosphine **31**. Also, the iodo phosphine **32** can react with the nucleophile to give the radical **34** that enters into a new cycle of the $S_{RN}1$ mechanism. Since the iodo phosphine **32** was not observed, the intramolecular ET should be faster than the intermolecular ET to diiodide **24**. However, in the photostimulated reaction of diiodide **24** with 1.1 equiv of Ph_2P^- for 3 min, iodo phosphine oxide **32-O** was isolated in low yield (5%) (Table 5, entry 4). Under these experimental conditions, the intermolecular ET to diiodide **24** could compete with the intramolecular ET because the concentration of the acceptors (diiodide **24** and iodide **25a**) is higher than that in the reaction of diiodide **24** with 2.2 equiv of Ph_2P^- ions. In the photostimulated reaction in the presence of *p*-DNB, iodo phosphine oxide **32-O** was not observed, meaning that the initiation step is inhibited more efficiently than the propagation ones (Table 5, entry 3). It is remarkable that the diiodide **24** gave the disubstitution product **31**. In similar systems, such as 1,2-dichloroadamantane[13] or *o*-dichlorobenzene,[27] the photostimulated reaction with diphenylphosphide ions in liquid ammonia gave only the monosubstitution products.

About the reactions of several iodotricyclo[3.3.0.$0^{3,7}$]-octane derivatives (iodo esters **5** and **7**, iodide **10**, and iodo ketone **17**), the results collected in Tables 1 and 6 suggest that the reaction proceeds in all cases by the $S_{RN}1$ mechanism.

Worthy of note, both the dark and the photostimulated reaction of iodo ketone **17** with Ph_2P^- ions gave, after oxidation, the reduction product **18** and the rearranged substitution product **36-O** (Tables 1 and 6).

The ET from the nucleophile to **17** gives the bridgehead radical **37**. This radical rearranges by an intramolecular substitution (S_Hi) or 1,5-hydrogen migration to afford the methylene radical **38** which couples with Ph_2P^- ion to give the observed substitution product **36** (eq 4). This is the first time an intramolecular hydrogen atom abstraction is observed in the propagation steps of a $S_{RN}1$ reaction. Reduction of radicals **37** or **38** would give ketone **18**.

No similar rearranged substitution products were obtained from the reaction of iodo esters **5** and **7**. Probably, the bridgehead radicals **40** and **42** do not rearrange to the methyl radicals **41** and **43**, respectively (eqs 5 and 6). It is known that the 1,5-hydrogen migration is more favorable than the corresponding 1,6-process. This could explain the absence of rearrangement of radical **42** to **43** (1,6-hydrogen migration) but not the absence of rearrangement of radical **40** to **41** (1,5-hydrogen migration).

To explain the obtained results, we performed a theoretical study with the MOPAC program using the

(24) Bunnett, J. F. In *Investigation of Rates and Mechanisms of Reaction*, 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part 1, pp 158−165.

(25) There are precedents for the abstraction of iodine by bridgehead radicals in the propagation cycle of the $S_{RN}1$ mechanism,[5a,b] but the corresponding bromine abstraction has not been described yet. The preferential abstraction of iodine vs bromine by a carbon radical is reflected in the values of the rate of abstraction of iodine from Me_3CI or bromine from Me_3CBr by octyl radicals: ca. 2×10^6 M^{-1} s^{-1} and ca. 4.6×10^3 M^{-1} s^{-1}, respectively.[25b] Probably, in our system, the 1-adamantyl radical is more stable than the radical derived from iodide **25a**, and its coupling with the nucleophile competes with the bromine abstraction from 1-bromoadamantane. (b) Newcomb, M.; Sánchez, R. M.; Kaplan, J. *J. Am. Chem. Soc.* **1987**, *109*, 1195−1199.

(26) The photostimulated reaction of the diiodide **24** with diphenylphosphide ion in liquid ammonia was attempted but **24** is quite insoluble in this solvent and most of the starting compound was recovered unchanged.

(27) Santiago, A. N.; Rossi, R. A., unpublished results.

Table 4. Competition Reactions of Halides 25a and 28b with Diphenylphosphide Ions in DMSO[a]

	substrates/reagent (mmol)			products (mmol)						
entry	**25a**	**28b**	Ph_2P^-	**25a**	**25b**	**26**	**27-O**	**28b**	**29-O**	**30**
1[b]	0.240	0.244	0.278	0.035	0.012	0.140	0.054	0.228	0.008	0.008
2[c]	0.215	0.669	0.232	0.056	0.018	0.072	0.017	0.540	0.017	0.006
3[b]	0.252	2.527	0.278	0.061	0.061	0.092	0.038	2.252	0.068	0.018
4[b]	0.307	0.322[d]	0.280	0.306					0.160	0.160

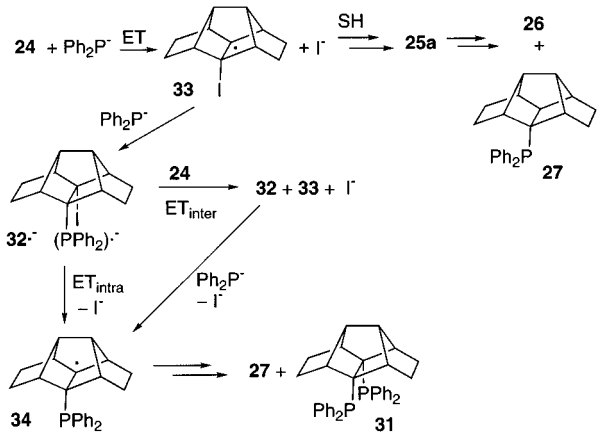
[a] All reactions were performed under irradiation for 15 min. The products were quantified as indicated in Tables 2 and 3. [b] 12.5 mL of DMSO. [c] 10 mL of DMSO. [d] 1-Iodoadamantane **28a** was used.

Table 5. Reactions of Diiodo Compound 24 with Diphenylphosphide Ions in DMSO[a]

		product yields (%)				
entry	conditions	**24**[b]	**25a**[c]	**26**[d]	**27-O**[b]	**31-O**[e]
1	dark, 3 min	99				<1
2	*hν*, 3 min	25	26	6	10	28
3	*hν*, 3 min[f]	50	21	2	3	13
4	*hν*, 3 min[g]	28	40	3	3	10
5	dark, 10 min	91	5	1	1	<1
6	*hν*, 10 min	3	3	26	24	40

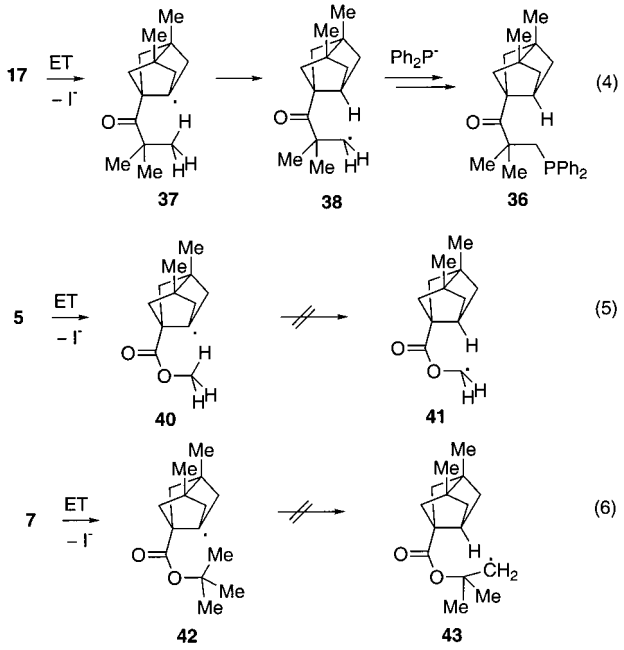
[a] 0.20 mmol of **24**, 0.45 mmol Ph_2P^-. [b] Quantified by GLC with triphenylphosphine oxide as internal standard. [c] Quantified by GLC with anthracene as internal standard. [d] Quantified by GLC with biphenyl as internal standard. [e] Quantified by ^1H NMR with *cis*-cyclooctene as internal standard. [f] 20 mol % of *p*-DNB was added. [g] 0.20 mmol of **24**, 0.22 mmol of Ph_2P^-, 5% yield of **32-O** (isolated).

Scheme 5



AM1 method. As expected, in the halo compounds **5**, **7**, **10**, **17**, **25a**, **25b**, and **25c**, the more reactive iodo derivatives in ET reactions show lower LUMO (σ^* C−halo bond) energies (SI, Table 1). The enthalpy of formation (ΔH_f) of the methylene radicals **38**, **41**, and **43** are lower than the corresponding bridgehead radicals **37**, **40**, and **42**, respectively (SI, Table 1). However, small differences are observed for the SOMO energies of the isomeric radical pairs, although the SOMO of the bridgehead radicals are always lower in energy than their methylene isomers. Consequently, the rearrangement of the bridgehead radical **37** to the methylene radical **38**, not observed for the related radicals **40** and **42**, might be due to the fact that, only in this case, there is a minimum energy conformation in which the migrating hydrogen atom is close enough to the bridgehead radical center (2.72 Å).

In conclusion, we have synthesized several bridgehead halobisnoradamantane derivatives and established that they react with diphenylphosphide ions in DMSO through the $S_{RN}1$ mechanism. The order of reactivity for different halo derivatives follows the order iodide > bromide > chloride, which correlates well with their LUMO energies. The expected substitution products were formed, although in low yield as compared with similar reactions carried out in liquid ammonia. At the same time, the corresponding reduction products were formed in higher yields. This may be due to a comparatively slower coupling of the intermediate alkyl radical and the nucleophile in DMSO and the better hydrogen-donating ability of the DMSO, which would favor the reduction of the radical. In competition experiments between iodide **25a** and bromide **28b**, a bromine abstraction reaction from **28b** by the radical derived from **25a** was observed. This is the first example of a bromine atom abstraction through the chain propagation of the $S_{RN}1$ mechanism. Also, for the first time, a 1,5-hydrogen shift has been observed in an $S_{RN}1$ reaction, which may be explained by taking into account the close proximity between the migrating hydrogen atom and the radical center. From the reaction of the double bridgehead 1,2-diiodo derivative **24**, monoreduction, direduction, monosubstitution plus reduction, and disubstitution products, **25a**, **26**, **27** and **31**, respectively, were mainly formed. The monoreduction product **25a** appeared as an intermediate in the formation of the direduction and monosubstitution plus reduction products, **26** and **27**. Intramolecular ET from the monosubstitution radical-anion $\mathbf{32}^{\bullet-}$ seems to be faster than the intermolecular process.



Experimental Section

3,7-Dimethyltricyclo[3.3.0.0^{3,7}]octane-1,5-dicarboxylic Anhydride (3). A solution of diacid **2** (3.7 g, 16.5 mmol) in acetic anhydride (20 mL) was heated under reflux for 1.5 h.

Table 6. Reactions of Iodobisnoradamantane Derivatives with Diphenylphosphide Ions in DMSO

				product yields (%)		
entry	substrate (mmol)	Ph_2P^- (mmol)	conditions	substitution	reduction	recovered substrate (%)
1	**5**, 0.23	0.23	*hν*, 10 min		**12**,[a] 80	
2	**7**, 0.21	0.23	*hν*, 10 min	**39-O**,[a] 22	**8**,[a] 70	
3	**7**, 0.21	0.23	dark, 10 min		**8**, 5	**7**,[b] 93
4	**10**, 0.20	0.22	dark, 10 min	**35-O**,[c] 7	**11**,[d] 8	**10**,[e] 85
5	**10**, 0.20	0.22	*hν*, 3 min	**35-O**, 55	**11**, 41	**10**, 4
6	**10**, 0.20	0.22	*hν*, 10 min[f]	**35-O**, 15	**11**, 5	**10**, 80
7	**10**, 0.20	0.22	dark, 10 min[f]	**35-O**, <1	**11**, −	**10**, 99
8	**10**, 0.20	0.22	*hν*, 15 min	**35-O**, 57	**11**, 40	**10**, 3
9	**17**, 0.21	0.23	dark, 5 min	**36-O**,[c] 19	**18**,[g] 3	**17**,[g] 78
10	**17**, 0.21	0.23	*hν*, 5 min	**36-O**, 83	**18**, 15	**17**, 2
11	**17**, 0.21	0.23	*hν*, 5 min[f]	**36-O**, 8	**18**, 2	**17**, 90
12	**17**, 0.21	0.23	dark, 5 min[f]	**36-O**, 2	**18**, 3	**17**, 95

[a] Isolated yield. [b] Quantified by GLC with anthracene as internal standard. [c] Quantified by GLC with triphenylphosphine oxide as internal standard. [d] Quantified as the difference between starting **10** and recovered **10** plus **35-O**. [e] Quantified by GLC with biphenyl as internal standard. [f] 20 mol % of *p*-DNB was added. [g] Quantified by GLC with anthrone as internal standard.

Evaporation of the volatile materials at reduced pressure gave a residue (3.6 g) that was sublimed at 200−220 °C/2 Torr to afford anhydride **3** (3.0 g, 88% yield), mp 233−234 °C.

5-Methoxycarbonyl-3,7-dimethyltricyclo[3.3.0.0^{3,7}]-octane-1-carboxylic Acid (4). To a solution of anhydride **3** (1.80 g, 8.7 mmol) in anhydrous MeOH (130 mL) was added solid MeONa (2.40 g, 44 mmol), and the mixture was heated under reflux for 18 h in a dry ($CaCl_2$ tube) atmosphere. The solvent was evaporated to dryness under reduced pressure, and the residue was taken in H_2O (70 mL) and washed with EtOAc (35 mL). The aqueous phase was made acidic with concentrated HCl, and the precipitated solid was filtered, washed with H_2O (2 × 6 mL), and dried in vacuo to a constant weight to give hemiester **4** (1.50 g). The combined filtrate and washings were extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo to give, after crystallization from a mixture of CH_2Cl_2 and *n*-hexane, additional solid **4** (0.27 g) (total yield 1.77 g, 85%). An analytical sample was obtained by crystallization from EtOAc (286 mg/mL), mp 154−155 °C.

Methyl 5-Iodo-3,7-dimethyltricyclo[3.3.0.0^{3,7}]octane-1-carboxylate (5). A suspension of hemiester **4** (714 mg, 3.0 mmol), iodosobenzene diacetate (IBDA) (974 mg, 3.0 mmol), and iodine (762 mg, 3.0 mmol) in anhydrous benzene (55 mL) was irradiated under reflux with a 60 W tungsten lamp for 4 h.[19,20] Then, the solution was allowed to cool to room temperature, more IBDA (974 mg, 3.0 mmol) and iodine (762 mg, 3.0 mmol) were added, and irradiation under reflux was continued for an additional 18 h. The cold solution was washed with a 10% aqueous solution of sodium thiosulfate (2 × 20 mL), brine (2 × 20 mL), and an aqueous solution of saturated $NaHCO_3$ (20 mL). The organic phase was dried (Na_2SO_4) and concentrated at reduced pressure, affording a liquid residue (2.30 g) of iodobenzene and **5**. Part of the iodobenzene was removed by microdistillation, and the residue (1.60 g) was submitted to column chromatography [silica gel, 66 g, mixtures of *n*-hexane and EtOAc in the ratio of 90:10] to give pure **5** (700 mg, 73% yield) as a white solid. After acidification of the basic aqueous extracts with concentrated HCl and extraction with CH_2Cl_2, **4** (70 mg) was recovered. An analytical sample of **5** was obtained by sublimation (50 °C/1 Torr), mp 49−50 °C.

5-Iodo-3,7-dimethyltricyclo[3.3.0.0^{3,7}]octane-1-carboxylic Acid (6). Ester **5** (3.50 g, 10.9 mmol) was added to a solution of KOH in MeOH (10%, 40 mL), and the mixture was stirred at room temperature for 24 h. The solvent was evaporated to dryness under reduced pressure, and the residue was taken in H_2O (80 mL) and washed with diethyl ether (2 × 50 mL). The organic phase was dried (Na_2SO_4) and concentrated in vacuo to give ester **5** (0.60 g). The aqueous phase was cooled to 0−5 °C, was made acidic with concentrated HCl, and was evaporated in vacuo to dryness. The residue was extracted with warm diethyl ether (4 × 45 mL), and the combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo to give **6** (2.20 g, 66% yield) as a white solid. An analytical sample was obtained by crystallization from diethyl ether (129 mg/mL), mp 179−180 °C.

***tert*-Butyl 5-Iodo-3,7-dimethyltricyclo[3.3.0.0^{3,7}]octane-1-carboxylate (7).** A solution of iodo acid **6** (527 mg, 1.72 mmol) in CH_2Cl_2 (3.8 mL) was cooled to −5 °C (ice−salt bath), and concentrated H_2SO_4 (0.02 mL) was added. Isobutene (450 mg, 8.0 mmol) was added, and the mixture was stirred at room temperature for 48 h.[28] Excess isobutene was removed at reduced pressure. The organic layer was washed with water (2 × 4 mL), 5% aqueous $NaHCO_3$ (2 × 4 mL), and water (2 mL) and dried (Na_2SO_4). The solvent was removed at reduced pressure to give a yellow residue (470 mg), which was submitted to column chromatography [silica gel (9 g), mixture of *n*-hexane and EtOAc in the ratio of 95:5], affording pure **7** (370 g, 59% yield) as a colorless oil. An analytical sample was obtained by sublimation (80 °C/1 Torr), mp 33−34 °C.

***tert*-Butyl 3,7-Dimethyltricyclo[3.3.0.0^{3,7}]octane-1-carboxylate (8). Method a.** The iodo derivative **7** (260 mg, 0.22 mmol) was dissolved in ethanol (45 mL), sodium carbonate (76 mg) and 10% Pd on charcoal (300 mg) were added, and the resulting mixture was hydrogenated at 35 atm for 1 week. The suspension was filtered, and the solvent was evaporated at atmospheric pressure to give a mixture of **7** and **8** (220 mg) in a ratio of about 1:1 (GC).

Method b. Compound **8** was obtained as an oil from the $S_{RN}1$ reaction of compound **7** and Ph_2P^- using the general procedure described later on. The reaction should be carried out until completion (1.5 h) to avoid obtaining a difficult to separate mixture of **7** and **8**. In this way, **8** was isolated as a colorless oil in 70% yield after silica gel column chomatography [mixture of *n*-hexane and EtOAc in the ratio of 95:5]. An analytical sample was obtained by microdistillation (coldfinger, 60 °C/1 Torr).

3-Iodo-1,5-dimethyltricyclo[3.3.0.0^{3,7}]octane (10). Method a. To a solution of iodo acid **6** (2.00 g, 6.53 mmol) and 2,2′-dithiobis(pyridine 1-oxide) (2.10 g, 8.3 mmol) in dry THF (62 mL) protected from sunlight was added tri-*n*-butylphosphane (2.2 mL, 8.9 mmol) dropwise at 0 °C, and the solution was stirred at room temperature for 2 h, taking a lemon-yellow color characteristic of the thiohydroxamic esters. Freshly distilled *tert*-butanethiol (3.7 mL, 32.5 mmol) was added to the solution, and it was irradiated with a 60 W tungsten lamp for 2 h.[20] Diethyl ether was added (60 mL), and the organic solution was successively washed with a saturated aqueous solution of $NaHCO_3$ (3 × 20 mL), aqueous 5 M HCl (3 × 20 mL), water (3 × 15 mL), and brine (3 × 15 mL). The organic phase was dried (Na_2SO_4) and concentrated at atmospheric pressure to give a green oil (3.0 g), which was submitted to column chromatography [silica gel (66 g), *n*-hexane], affording **10** (1.20 g, 70% yield) as a colorless oil. An analytical sample was obtained by microdistillation (coldfinger) (50 °C/40 Torr).

(28) Valerio, R. M.; Alewood, P. F.; Johns, R. B. *Synthesis* **1988**, 786−789.

Method b. Diiodo derivative **9** (112 mg, 0.29 mmol) was dissolved in methanol (3 mL), sodium hydroxide (36 mg, 0.9 mmol) and 10% Pd on charcoal (23 mg) were added, and the resulting mixture was hydrogenated at atmospheric pressure for 15 h. When the hydrogenation was over (GC control), water (6 mL) was added and the suspension was extracted with CH_2Cl_2 (5 × 3 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated at atmospheric pressure to give **10** (53 mg, 70% yield).

After 14 days of hydrogenation, 1,5-dimethyltricyclo[3.3.0.0^{3,7}]-octane (**11**) was the only remaining product, which could not be isolated from the solution due to high volatility. GC/MS (EI), t_r = 5.11 min, significant ions, *m*/*z* (%): 121 [(M − CH_3)$^+$, 15], 107 [(M − C_2H_5)$^+$, 40], 95 (42), 94 (89), 93 [(M − C_3H_7)$^+$, 88], 79 [(M − C_4H_9)$^+$, 100].

Method c. A procedure similar to that used for the conversion of hemiester **4** to iodo ester **5** was followed, except that the solvent was removed at atmospheric pressure. From acid **13** (302 mg, 1.66 mmol), a mixture of **8** and iodobenzene, which could not be separated either by column chromatography or by distillation, was obtained.

Methyl 3,7-Dimethyltricyclo[3.3.0.0^{3,7}]octane-1-carboxylate (12). A procedure similar to that used for the decarboxylation of iodo acid **6** to iodo derivative **10** was followed. From hemiester **4** (1.40 g, 5.9 mmol), ester **12** was obtained as a colorless oil (0.85 g, 74% yield), after column chromatography [silica gel (4 g), mixtures of *n*-hexane and diethyl ether]. An analytical sample was obtained by distillation (40 °C/2 Torr) on a rotary microdistillation equipment.

3,7-Dimethyltricyclo[3.3.0.0^{3,7}]octane-1-carboxylic Acid (13). A mixture of ester **12** (770 mg, 4.0 mmol) and a solution of KOH in MeOH (10%, 10 mL) was heated under reflux for 3 h. Water (10 mL) was added, and the solution was heated under reflux for an additional 3 h. The mixture was cooled at 0−5 °C, was made acidic with concentrated HCl (2 mL), and was evaporated to dryness in vacuo, and the residue was extracted with warm diethyl ether (4 × 40 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated at reduced pressure to give **13** (520 mg, 72% yield) as a white solid. An analytical sample was obtained by crystallization from diethyl ether (100 mg/mL), mp 109−110 °C.

3,7-Dimethyl-5-pivaloyltricyclo[3.3.0.0^{3,7}]octane-1-carboxylic Acid (16). A mixture of ester **14** (2.30 g, 8.3 mmol) and a solution of KOH in MeOH (10%, 20 mL) was stirred at room temperature for 24 h. The solvent was evaporated to dryness at reduced pressure, and the residue was taken up in H_2O (50 mL) and washed with diethyl ether (2 × 15 mL). The aqueous phase was cooled at 0−5 °C, was made acidic with concentrated HCl, and was evaporated to dryness in vacuo. The residue was extracted with warm diethyl ether (5 × 70 mL), and the combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo to give **16** (1.80 g, 82% yield) as a white solid. An analytical sample was obtained by crystallization from *n*-hexane (20 mg/mL), mp 158−160 °C.

1-Iodo-3,7-dimethyl-5-pivaloyltricyclo[3.3.0.0^{3,7}]-octane (17). A procedure similar to that used for the iododecarboxylation of hemiester **4** to iodo ester **5** was followed. From keto acid **16** (900 mg, 3.4 mmol) a red liquid residue (2.60 g), mixture of iodobenzene and **17**, was obtained. After column chromatrography [silica gel (82 g), mixture of *n*-hexane and EtOAc in the ratio of 98:2], pure **17** (960 mg, 82% yield) was obtained as a white solid. A small amount of **16** (50 mg) was also recovered. An analytical sample of **17** was obtained by sublimation (60 °C/0.5 Torr), mp 67−68 °C.

1,5-Dimethyl-3-pivaloyltricyclo[3.3.0.0^{3,7}]octane (18). Iodo ketone **17** (100 mg, 0.29 mmol) was dissolved in absolute ethanol (3 mL), NaOH (25 mg, 0.6 mmol) and 5% Pd on charcoal (10 mg) were added, and the mixture was hydrogenated at atmospheric pressure for 12 h. When the hydrogenation was over (GC control), water (7 mL) was added and the suspension was extracted with CH_2Cl_2 (3 × 7 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo to give **18** (59 mg, 93% yield) as a colorless oil. An analytical sample was obtained by microdistillation (cold-finger) (30 °C/1 Torr).

8-Iodopentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodecane (25a)[16] and Pentacyclo[6.4.0.0^{2,10}.0^{3,7}.0^{4,9}]dodecane[14] (26). The pentacyclic diiodo derivative **24** (412 mg, 1.0 mmol) was dissolved in absolute ethanol (10 mL), sodium hydroxide (152 mg, 3.8 mmol) and 5% Pd on charcoal (70 mg) were added, and the resulting solution was hydrogenated at atmospheric pressure. After 15 h of reaction, **24** had been consumed and GC control showed the solution to contain a mixture of **25a** and hydrocarbon **26** in an area ratio of 75:25.

The suspension was filtered, washing the solid with ethanol (2 mL). The combined filtrate and washings were divided into two equal portions. (a) Water (6 mL) was added to the first portion, and the suspension was extracted with CH_2Cl_2 (5 × 7 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated at reduced pressure. The residue was kept in vacuo for 24 h to eliminate the volatile hydrocarbon **26**, giving the known **25a** (94 mg, 65% yield) as a colorless oil. (b) More sodium hydroxide (140 mg) and 5% Pd on charcoal (100 mg) were added to the second portion, and hydrogenation was continued for 2 weeks until no more **25a** was detected by GC analysis. After a workup similar to that described above, concentration of the dried organic extracts at reduced pressure gave the known **26** (40 mg, 50% yield) as a colorless oil. ^{1}H NMR (200 MHz) δ: 1.47 (s, 10H), 2.11 (s, 6H).

Photostimulated Reaction of Polycyclic Halides with Ph_2P^- in DMSO. The following procedure is representative of all the $S_{RN}1$ reactions. A solution of potassium *tert*-butoxide (50 mg, 0.45 mmol) in anhydrous DMSO (20 mL) was prepared in a 50 mL three-necked round-bottomed flask equipped with a reflux condenser, an argon inlet, and a magnetic stirrer. Diphenylphosphane (75 mg, 70 μL, 0.40 mmol) was added, and after 10 min at room temperature, the polycyclic halide (0.4 mmol) was added and then the solution was irradiated for 15 min with a 125 W mercury lamp. The reaction was quenched by addition of water (10 mL) after addition of diethyl ether (10 mL), and the solution was allowed to cool to room temperature. Water (90 mL) and solid NaCl (2 g) were added, and the mixture was extracted with dichloromethane (4 × 20 mL). The combined organic extracts were treated with aqueous 10% H_2O_2 (20 mL) to oxidize the phosphane products, and after washing with water (2 × 50 mL) the mixture was quantitatively analyzed by GC using the internal standard method.

The same procedure was followed when the reaction was performed in the presence of *p*-DNB, except that *p*-DNB (0.2 equiv) was added to the solution of the nucleophile prior to the substrate addition.

Photostimulated Competition Reaction of a Polycyclic Halide and Adamantyl Bromide with Ph_2P^- in DMSO. The procedure was similar to that previously described, except that a solution of both substrates in DMSO was added to the solution of the nucleophile in DMSO.

Photostimulated Reaction of Diiodide 24 with Ph_2P^- in DMSO. The procedure was similar to that previously described, except that potassium *tert*-butoxide (100 mg, 0.90 mmol) and diphenylphosphane (161 mg, 150 μL, 0.86 mmol) were added, the solution was stirred for 10 min, and then the diiodide **24** (165 mg, 0.4 mmol) was added. After the oxidation step, the combined organic extracts were transferred to a 100 mL volumetric flask which was completed with dichloromethane. *cis*-Cyclooctene was added to a 20 mL portion and the resulting solution was concentrated at reduced pressure. The thus obtained mixture was quantified by ^{1}H NMR. The internal standards were added to the main portion of the reaction mixture that was quantified by GC.

Isolation of Diphenylphosphorylpolycycloalkanes. The procedure was similar to that previously described, but the reaction was performed on a larger scale using the following: substrate (0.5 mmol) and Ph_2P^- ions (0.55 mmol) in DMSO (25 mL). After oxidation of the products, the organic phase was concentrated at reduced pressure, and the residue was submitted to column chromatography [silica gel (40−50 g)/g of residue]. See Supporting Information.

Acknowledgment. A fellowship from Consejo Nacional de Investigaciones Científicas y Técnicas

(CONICET) (Argentina) to A.E.L. and financial support from Comissionat per a Universitats i Recerca of the Generalitat de Catalunya (Project 1999-SGR-00080) are gratefully acknowledged. We also thank the Serveis Científico-Tècnics of the University of Barcelona and particularly Dr. M. Feliz and Dr. A. Linares for recording de NMR spectra and P. Domènech from the Centro de Investigación y Desarrollo (C.I.D.) (Barcelona, Spain) for carrying out the elemental analyses.

Supporting Information Available: General experimental part, characterization data for all new compounds, isolation of the $S_{RN}1$ reaction products, and Table 1: formation entalpies (ΔH_f, kcal/mol) and LUMO or SOMO energies (eV) for several halopolycyclic compounds and radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

JO010159+