JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 421–426 (1993)

REACTIONS OF CYCLOALKYL CHLORIDES AND BROMIDES WITH DIPHENYLPHOSPHIDE IONS IN LIQUID AMMONIA

MÓNICA A. NAZARENO, SARA M. PALACIOS* AND ROBERTO A. ROSSI†

Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Suc. 16, C.C. 61, 5016 Córdoba, Argentina

The reactions of cycloalkyl (butyl, pentyl, hexyl and heptyl) chlorides and bromides with diphenylphosphide ions were studied in liquid ammonia. Cyclobutyl chloride was unreactive, whereas the bromide reacted giving the substitution product cyclobutyldiphenylphosphine (isolated as the oxide) in good yields; this reaction was catalysed by light and partially inhibited by *p*-dinitrobenzene (*p*-DNB). Cyclopentyl, cyclohexyl and cycloheptyl chlorides did not react in the dark, but the substitution products were formed under irradiation, and these reactions were inhibited by *p*-DNB. The bromides reacted in the dark or under irradiation, and these reactions were partially inhibited by *p*-DNB. It can be then concluded that the reactivity of cycloalkyl halides depends on the ring size and the nucleofugal group. In addition, as the overall reactivity decreases, there is an increase in electron transfer reactions.

INTRODUCTION

Nucleophilic substitution reactions of alkyl halides have been known for a long time. The available mechanisms depend on the aliphatic moiety, the nucleophile, the leaving group and the reaction conditions.[1,2]

In addition to the polar mechanisms of nucleophilic substitution reactions (S_N1, S_N2 and related mechanisms), several alkyl halides react with nucleophiles (Nu^-) by an electron-transfer (ET) reaction [equation (1)], and then the alkyl radical intermediate thus formed can react with the $Nu^\cdot$ (cage collapse mechanism)[3] [equation (2)], or it can diffuse and reacts with the nucleophile in a chain process [equation (3)].

$$RX + Nu^- \xrightarrow{ET} (RX)^{-\cdot}\ Nu^\cdot \qquad (1)$$

$$(RX)^{-\cdot}\ Nu^\cdot \longrightarrow [R^\cdot X^- Nu^\cdot]$$

$$[R^\cdot X^- Nu^\cdot] \longrightarrow RNu + X^- \qquad (2)$$

$$[R^\cdot X^- Nu^\cdot] \xrightarrow{\text{diffusion}} R^\cdot \xrightarrow{Nu^-} (RNu)^{-\cdot} \qquad (3)$$

The last reaction mechanism is the radical nucleophilic substitution, or $S_{RN}1$,[4] which is a chain process that requires an initiation step. The main steps are shown in equations (4)–(6).

Initiation step:

$$RX + Nu^- \xrightarrow{ET} R^\cdot + X^- + Nu^\cdot \qquad (4)$$

Propagation steps:

$$R^\cdot + Nu^- \longrightarrow (RNu)^{-\cdot} \qquad (5)$$

$$(RNu)^{-\cdot} + RX \longrightarrow RNu + R^\cdot + X^- \qquad (6)$$

If no spontaneous ET takes place from the nucleophile to the substrate RX [equation (4)], it can occur under photostimulation.[4]

The alkyl halides that react by the $S_{RN}1$ mechanism are those which have an electron-withdrawing group,[5] perfluoroalkyl iodides[4,6] or a relatively low reactivity toward polar nucleophilic substitution due to steric, electronic or strain factors.[4] Hence it has been found that several bridgehead halides,[7] and also neopentyl halides[8] and even *tert*-butyl chlorides,[9] are able to react by the $S_{RN}1$ mechanism.

The nucleophilic substitution of cycloalkyl halides has been studied and different behaviours were found, depending on the ring size, the nucleophile, the leaving group and the reaction conditions, but in general they are less reactive than the non-cyclic substrates.

Cyclopropyl tosylate solvolyses in acetic acid at 170 °C by an S_N1 type of nucleophilic substitution,[10] but a disrotatory opening is necessary to assist the departure of the leaving group (electrocyclic process),[11]

*CEQUIMAP.
†Author for correspondence.

0894–3230/93/070421–06$08.00

Received 21 October 1992
Revised 4 March 1993

and it has a high activation energy. Nucleophilic substitution is possible on cyclopropyl halides without ring opening with α-sulphide substituents that stabilize the positive charge.[12]

On the other hand, it has been reported that cyclopropyl bromides react under irradiation with diphenylphosphide and benzenethiolate ions in liquid ammonia by the $S_{RN}1$ mechanism to give the substitution product without ring opening.[13]

gem-Dibromocyclopropanes react under irradiation with different nucleophiles in liquid ammonia[14] and dimethyl sulphoxide[13b] by the $S_{RN}1$ mechanism to give mainly the disubstitution products, but in the reaction with diphenylphosphide (Ph_2P^-) ions as nucleophile it gives in the dark a bromocyclopropane derivative. Hence it has been suggested that *gem*-dibromocyclopropanes undergo a fast nucleophilic attack on the bromine to give the monobromo dehalogenation product.[15] However, *gem*-dichlorocyclopropanes do not react in the dark with Ph_2P^- ions but under irradiation they give good yields of disubstitution product by the $S_{RN}1$ mechanism.[13a]

It is known that the polar substitution reaction of bromocyclobutane is accompanied by a ring opening and rearrangement leading to cyclopropylcarbinyl and butenyl derivatives through an S_N1 mechanism.[16] When the cyclobutane has both the leaving group and a substituent at the same carbon atom that stabilizes the positive charge, such as 1-methyl-1-chlorocyclobutane, it is possible to perform a substitution by the S_N1 mechanism without rearrangement. For instance, the rate of solvolysis[17] or acetolysis[18] is much slower than for the open-chain tertiary chlorides.

Compounds with five-, six and seven-membered rings react with most nucleophiles by an S_N2 mechanism without rearrangement.[2] Five-membered-ring compounds solvolyse 14 times faster than cyclohexyl derivatives, and cyclobutyl derivatives are 11 times more reactive than cyclohexyl derivatives.[19]

It has been reported that cyclohexyl chloride reacts with trimethylstannyl sodium in tetrahydrofuran, and 37% S_N2 substitution and 31% ET was proposed whereas cyclohexyl bromide reacts with 94% ET and 4% halogen–metal exchange.[20]

In this work, we undertook the study of the reactions of cyclobutyl, cyclopentyl, cyclohexyl and cycloheptyl chlorides and bromides with Ph_2P^- ions in liquid ammonia in order to establish the influence of the ring size and nucleofugal groups on the reaction mechanism.

RESULTS AND DISCUSSION

Cyclobutyl halides

There was no reaction, in the dark, nor under irradiation of cyclobutyl chloride (**1-4a**) with Ph_2P^- ions in liquid ammonia, but the bromide (**1-4b**) reacted in the dark in 15 min to give 42% of the substitution cyclobutyldiphenylphosphine, isolated as the oxide (**2-4**) [equations (7) and (8)].

$$\text{cycloalkyl-X} + Ph_2P^- \longrightarrow \text{cycloalkyl-PPh}_2 + X^- \quad (7)$$

1-4, C_4H_7
1-5, C_5H_9
1-6, C_6H_{11}
1-7, C_7H_{13}
a, X = Cl;
b, X = Br

$$\text{cycloalkyl-PPh}_2 \xrightarrow{[O]} \text{cycloalkyl-P(O)Ph}_2 \quad (8)$$

2-4, C_4H_7
2-5, C_5H_9
2-6, C_6H_{11}
2-7, C_7H_{13}

This reaction is catalysed by light (83% of product **2-4** in 15 min, with 100% of bromide ions eliminated), and this photostimulated reaction was partially inhibited by *p*-dinitrobenzene (*p*-DNB), a well known inhibitor of $S_{RN}1$ reactions.[4] In the latter reaction, the amount of product **2-4** obtained (46%) is similar to that obtained in the dark. On the other hand, the reaction in the dark was not inhibited by *p*-DNB (Table 1).

All these reactions were examined for the formation of ring-opened products, but only **2-4** was detected.

The facts that this reaction was catalysed by light and that it was partially inhibited by *p*-DNB suggests that the mechanism of the reaction is in part $S_{RN}1$. On the other hand, there was an important thermal (dark) reaction that was not inhibited by *p*-DNB, and no cyclopropylcarbinyl and butenyl derivatives were found. The facts that the cyclic substitution product was obtained and also that the reaction rate was fast at low temperature (−33 °C, b.p. of ammonia) suggest that this is not a polar nucleophilic substitution, where rearranged products are formed with high activation energy.

Cyclopentyl halides

Cyclopentyl chloride (**1-5a**) reacts with Ph_2P^- ions under irradiation in 60 min to give the substitution product [isolated as the oxide (**2-5**) in 70% yield and 95% of chloride ions]. However, in the dark there was only 4% yield of **2-5** (although there was 22% yield of chloride ion eliminated), and the photostimulated reaction was almost completely inhibited by *p*-DNB (8% yield of **2-5**).

All these results suggest that substrate **1-5a** reacts with Ph_2P^- ions mainly by the $S_{RN}1$ mechanism. The facts that the yield of the substitution product is lower than that of the chloride ion eliminated and that no other products were found under experimental conditions used may indicate that a minor reaction such as

Table 1. Reactions of halocycloalkanes with Ph_2P^- ions in liquid ammonia[a]

Entry	Cycloalkyl-X	Conditions		X^- (%)	Substitution products (%)[b]
		Irradiation	Time (min)		
1	C_4H_7Cl	*hν*	180	5	[c]
2	C_4H_7Br	*hν*	15	100	83
3	C_4H_7Br	Dark	15	47	42
4[d]	C_4H_7Br	*hν*	15	46	46
5[d]	C_4H_7Br	Dark	15	45	43
6	C_5H_9Cl	*hν*	60	95	70
7	C_5H_9Cl	Dark	60	22	4
8[d]	C_5H_9Cl	*hν*	60	14	8
9	C_5H_9Br	*hν*	30	100	94
10[d]	C_5H_9Br	*hν*	30	70	65
11	C_5H_9Br	Dark	30	100	96
12[d]	C_5H_9Br	Dark	30	75	72
13[e]	$C_6H_{11}Cl$	*hν*	180	[c]	33
14[e]	$C_6H_{11}Cl$	Dark	180	[c]	2
15[d,e]	$C_6H_{11}Cl$	*hν*	180	[c]	0·5
16[e]	$C_6H_{11}Br$	*hν*	10	[c]	30
17[e]	$C_6H_{11}Br$	Dark	10	[c]	4
18[e]	$C_6H_{11}Br$	*hν*	30	[c]	93
19[e]	$C_6H_{11}Br$	Dark	30	[c]	21
20[d,e]	$C_6H_{11}Br$	*hν*	30	[c]	25
21[d,e]	$C_6H_{11}Br$	Dark	30	[c]	21
22	$C_7H_{13}Cl$	*hν*	180	64	56
23	$C_7H_{13}Cl$	Dark	180	18	0·5
24[d]	$C_7H_{13}Cl$	*hν*	180	4	0·5
25	$C_7H_{13}Br$	*hν*	15	100	94[f]
26[d]	$C_7H_{13}Br$	*hν*	15	65	55
27	$C_7H_{13}Br$	Dark	15	100	96[f]
28[d]	$C_7H_{13}Br$	Dark	15	52	52

[a] Reactions carried out in *ca* 300 ml of liquid ammonia with 1 mmol of substrate and 1 mmol of nucleophile.
[d] Determined by GC (internal standard method), unless specified otherwise.
[c] Not determined.
[d] *p*-Dinitrobenzene (20 mol%) added.
[e] From Ref. 21.
[f] Isolated product.

elimination is also occurring, and in this case the cyclopentene formed could be lost in the work-up.

On the other hand, cyclopentyl bromide (**1-5b**) reacts almost quantitatively in only 30 min with Ph_2P^- ions in the dark or under irradiation. However, both reactions were inhibited by *p*-DNB to 72% and 65% of **2-5**, respectively. These results suggest that **1-5b** reacts in part by a polar nucleophilic substitution reaction and in part by the $S_{RN}1$ mechanism.

Cyclohexyl halides[21]

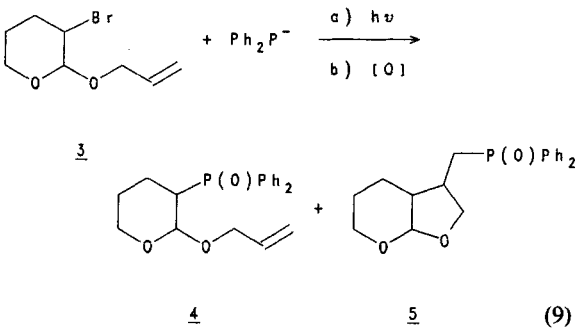
Cyclohexyl chloride (**1-6a**) gave only 3% of the substitution product, isolated as the oxide (**2-6**) in 180 min. Under irradiation the yield of **2-6** increased to 33%, but this photostimulated reaction was strongly inhibited by *p*-DNB (less than 0·5% yield), suggesting that substrate **1-6a** reacts exclusively by the $S_{RN}1$ mechanism.

With cyclohexyl bromide (**1-6b**) there was a fast reaction under irradiation. Thus, in only 10 min it gave the substitution product, isolated as the oxide (**2-6**) in 30% yield, which increased to 93% in 30 min of irradiation. In the dark the yields of **2-6** were 4% and 21% in 10 and 30 min, respectively. The photostimulated reaction was partially inhibited by *p*-DNB (from 93% to 25% yield in 30 min). The dark reaction was not inhibited by *p*-DNB.

All these results suggest that substrate **1-6b** reacts mostly by the $S_{RN}1$ mechanism under irradiation. The dark reaction may be due to a polar reaction because *p*-DNB did not affect the rate of reaction.

In order to establish whether all the reaction occurs by the $S_{RN}1$ mechanism or partially by a polar nucleophilic substitution, the photostimulated reaction of the radical probe[22] 3-bromo-2-tetrahydropyranyl allyl ether (**3**) with Ph_2P^- ions in liquid ammonia was

studied. This reaction afforded both the substitution product **4** and the cyclized substitution product **5** [equation (9)].[21]



3 4 5 (9)

The relative yields of **4** and **5** depend on the concentration of the nucleophile. Thus, in more concentrated solutions (*ca* 0·080 M) the yield of **4** was 61% and that of the cyclized product **5** was 39%, whereas in more dilute solutions (*ca* 0·0024 M) the yield of **4** was only 5% with a 93% yield of **5**. The fact that up to 93% of cyclized product was obtained suggests that free cyclohexyl radicals were intermediates as the major reaction pathway, and that after cyclization the rearranged radical reacted with Ph_2P^- ions by the $S_{RN}1$ mechanism.

Cycloheptyl halides

Cycloheptyl chloride (**1-7a**) and Ph_2P^- ions did not give substitution products in 180 min, although there was a slight elimination of chloride ion, but under irradiation it gave 56% of the substitution product, isolated as the oxide (**2-7**), and the photostimulated reaction was completely inhibited by *p*-DNB (see Table 1). These results clearly agree with the $S_{RN}1$ mechanism.

On the other hand, cycloheptyl bromide (**1-7b**) reacts very fast (15 min) in the dark and under irradiation to give the substitution product **2-7** in high yields, but both reactions are partially inhibited by *p*-DNB (52% and 55% of **2-7**, respectively), indicating that this substrate reacts partially by both polar and $S_{RN}1$ reactions.

CONCLUSIONS

The main conclusion drawn from these reactions is that the reaction mechanism of cycloalkyl halides with Ph_2P^- ions in liquid ammonia depends on the ring size and the leaving group.

Thus, cyclobutyl chloride does not react either in the dark or under irradiation, whereas with the bromide the reaction is catalysed by light and partially inhibited by *p*-DNB, which suggests an $S_{RN}1$ mechanism [The photolysis of cycloalkyl chlorides and bromides is easily discarded because they do not show light absorption between 270 and 500 nm (Pyrex flasks were used)]. However, the dark reaction is neither inhibited by *p*-DNB nor were rearranged substitution products observed, which suggests the participation of the radicals as intermediates, since an S_N2 reaction is unlikely owing to the low temperature of the reaction and the steric hindrance of the cyclobutyl system for the simultaneous attack of the nucleophile and departure of the leaving group. On the other hand, the S_N1 mechanism is not compatible with unrearranged products.

A similar behaviour is found with cyclohexyl halides: the chloride occurs only by an $S_{RN}1$ reaction and the bromide by an $S_{RN}1$ reaction accompanied in part probably by a polar substitution reaction.

On the other hand, cyclopentyl and cycloheptyl chlorides react exclusively by an $S_{RN}1$ reaction, but the bromides by a competition between polar nucleophilic substitution and an $S_{RN}1$ substitution.

Another important feature of this study concerns the possibility of a nucleophilic substitution by ET on cyclobutyl bromide without ring opening. This reaction opens up an interesting synthetic route to cyclobutyl systems.

EXPERIMENTAL

General methods. ^{1}H NMR spectra were recorded on a Bruker FT-80 or FT-200 nuclear magnetic resonance spectrometer, and all spectra are reported in parts per million relative to tetramethylsilane (δ) using Cl_3CD as the solvent. Mass spectra were measure on a Finnigan 3300 f-100 mass spectrometer. Gas chromatographic (GC) analyses were performed on a Shimadzu GC8A gas chromatograph equipped with a Shimadzu CR-3A data system or a Spectra-Physics SP-2400 gas chromatograph equipped with a flame ionization detector or a Konik 3000HRGC provided with a flame ionization detector and a column packed with 3% OV-17 on Chromosorb P (1·8 m × 3 mm i.d.). Irradiation was conducted on a reactor equipped with four 250 W UV lamps emitting maximally at 350 nm (Philips, Model HPT, water refrigerated). Quantitative analysis was done by the internal standard method. The potentiometric titration of halide ions was performed with a pH meter (Seybold, Wien) equipped with an Ag/Ag^+ electrode and $AgNO_3$ standard solution. Melting points were measured with a Büchi 510 apparatus and are uncorrected.

Materials. Commercial reagents were used without purification. Compounds **1-5a**, **1-6a** and **1-7a** were prepared by the reaction of the corresponding alcohol and concentrated hydrochloric acid, and **1-5b**, **1-6b** and **1-7b** by reaction of the alcohol with hydrobromic acid according to a previous procedure.[23] Cyclobutyl chloride and bromide (Aldrich) were used as received.

Photostimulated reaction of cyclobutyl bromide with diphenylphosphide ions in liquid ammonia. The reaction of **1-4b** and diphenylphosphide ions is representative. Into a three-necked 500 ml round-bottomed flask, equipped with a cold-finger condenser charged with CO_2 and ethanol, a nitrogen inlet and a magnetic stirrer, were condensed approximately 300 ml of ammonia. To the ammonia 262 mg (1 mmol) of triphenylphosphine were added, together with 48 mg (2 mmol) of sodium metal, and allowed to react until the solution became dark orange. Then 0·1 ml of *tert*-butanol was added to neutralize the sodium amide generated. Finally 0·090 ml (1 mmol) of cyclobutyl bromide (**1-4b**) was added and the resulting solution was irradiated for 15 min. Then the reaction was quenched by the addition of NH_4NO_3 and the ammonia was allowed to evaporate. The residue was partitioned between 70 ml of water and 3 × 50 ml portions of dichloromethane. The aqueous extract was diluted to 100 ml and a 1 ml aliquot was titrated with $AgNO_3$ solution, showing 100% of bromide release. The organic extract was treated with 20 ml of 10% hydrogen peroxide solution and then was analysed by GC and the cyclobutyldiphenylphosphine oxide (**2-4**) was detected and quantified by the internal standard method (83% yield), m.p. 155–158 °C (lit.[24] m.p., 173–174 °C [recrystallized from light petroleum–benzene (*ca* 90:10)]. ^{1}H NMR ($CDCl_3$), δ 2·01–3·50 (broad peak, 7H), 7·50–7·90 (m, 10 H). ^{13}C NMR ($CDCl_3$), δ 19·92 (d, C_3, $^3J_{C-P}$ = 15 Hz), 21·16 (d, C_2, C_4, $^2J_{C-P}$ = 6 Hz), 32·62 (d, C_1, $^1J_{C-P}$ = 73 Hz), 132·61 (d, C_i, $^1J_{C-P}$ = 97 Hz), 130·79 (d, C_o, $^2J_{C-P}$ = 9 Hz), 128·29 (d, C_m, $^3J_{C-P}$ = 12 Hz), 131·27 (d, C_p, $^4J_{C-P}$ = 3 Hz). Mass spectrum, *m/z* (relative intensity) 256 (33), 255 (28), 227 (8), 202 (100), 183 (5·4), 155 (5), 125 (4·04), 77 (33·6).

Cyclopentyldiphenylphosphine oxide (**2-5**). M.p. 120–122 °C [recrystallized from hexane–dichloromethane (*ca* 90:10)] (lit.[25] m.p. 126–128 °C). ^{1}H NMR ($CDCl_3$), δ 1·41–3·13 (broad peak, 9 H), 7·16–7·95 (m, 10 H). ^{13}C NMR ($CDCl_3$), δ 26·42, 26·68, 26·86 (d, C_3, and s, C_2), 37·08 (d, C_1, $^1J_{C-P}$ = 75 Hz), 133·49 (d, C_i, $^1J_{C-P}$ = 96 Hz), 130·88 (d, C_o, $^2J_{C-P}$ = 9 Hz), 128·34 (d, C_m, $^3J_{C-P}$ = 10 Hz), 131·38 (d, C_p, $^4J_{C-P}$ = 3 Hz). Mass spectrum, *m/z* (relative intensity) 270 (20), 269 (30), 229 (100), 202 (86), 183 (12), 108 (1), 77 (21).

Cyclohexyldiphenylphosphine oxide (**2-6**). M.p. 166–168 °C [recrystallized from hexane–dichloromethane (*ca* 90:10)] (lit.[26] m.p. 168–169 °C). ^{1}H NMR ($CDCl_3$), δ 1·26–2·43 (broad peak, 11 H), 7·28–7·90 (m, 10 H). ^{13}C NMR ($CDCl_3$), δ 24·70, (d, C_2, $^2J_{C-P}$ = 3 Hz) 25.66 (C_4), 26·00 (d, C_3, $^3J_{C-P}$ = 24 Hz) 37·14 (d, C_1, $^1J_{C-P}$ = 73 Hz), 131·89 (d, C_i, $^1J_{C-P}$ = 95 Hz), 131·00 (d, C_o, $^2J_{C-P}$ = 9 Hz), 128·42 (d, C_m, $^3J_{C-P}$ = 11 Hz), 131·30 (d, C_p, $^4J_{C-P}$ = 3 Hz). Mass spectrum, *m/z* (relative intensity) 284 (25), 283 (30), 229 (28), 202 (100), 183 (8), 155 (17), 135 (12), 125 (11), 77 (60).

Cycloheptyldiphenylphosphine oxide (**2-7**). M.p. 134·5–135 °C [recrystallized from hexane–dichloromethane (*ca* 90:10)]. ^{1}H NMR ($CDCl_3$), δ 1·32–2·52 (broad peak, 13 H), 7·34–7·89 (m, 10 H). ^{13}C NMR ($CDCl_3$), δ 26·56 (d, C_2, $^2J_{C-P}$ = 2 Hz), 27·99 (C_4), 28·04 (d, C_3, $^3J_{C-P}$ = 15 Hz), 37·55 (d, C_1, $^1J_{C-P}$ = 70 Hz), 132·48 (d, C_i, $^1J_{C-P}$ = 94 Hz), 130·96 (d, C_o, $^2J_{C-P}$ = 9 Hz), 128·52 (d, C_m, $^3J_{C-P}$ = 11 Hz), 131·37 (d, C_p, $^4J_{C-P}$ = 3 Hz). Analysis: calculated for $C_{19}H_{23}OP$, C 76·51, H 7·72; found, C 76·24, H 8·03%. Mass spectrum, *m/z* (relative intensity) 298 (43), 297 (11), 229 (20), 202 (100), 183 (7), 155 (16), 125 (16), 77 (32).

Compounds **4** *and* **5**. These have been reported previously.[21]

ACKNOWLEDGEMENTS

M. A. N. acknowledges the receipt of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). This work was supported in part by the Consejo de Investigaciones de la Provincia de Córdoba (CONICOR), CONICET and the Antorchas Foundation, Argentina.

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