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COMPETITIVE REACTIONS OF NUCLEOPHILES—III[1,2]

THE AZIDE PROBE

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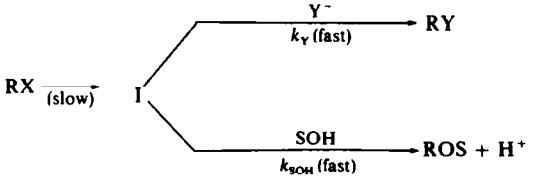
Abstract—The azide competition factors ($k_{N_3^-}/k_{SOH}$) of cyclopentyl mesylate (**1**), 1-methylcyclopentyl chloride (**2**), cyclohexyl brosylate (**3**), benzhydryl chloride (**4**), benzhydryl bromide (**5**), 3β-cholestanyl brosylate (**6**), 3α-cholestanyl brosylate (**7**), 2-methyl-2-adamantyl chloride (**8**), 1-adamantyl bromide (**9**) and 2-adamantyl tosylate (**10**) were determined. Tertiary substrates (**2**, **8**, **9**) invariably gave lower $k_{N_3^-}/k_{SOH}$ values than secondary ones (**1**, **3**, **4**, **5**, **7**); opposite from what is expected on the basis of the stabilities of the respective free carbanium ions. This was explained by the attack of the nucleophile on ion pair(s) rather than on free carbonium ions. The magnitude of the competition factor seems to yield useful mechanistic information only in two extreme cases, i.e. direct displacement (S_N2) and free stable carbonium ions (tertiary aromatic substrates–dissociative S_N1 mechanism). In all other cases, especially with secondary substrates, the mechanistic evaluation of the $k_{N_3^-}/k_{SOH}$ values is ambiguous and in our opinion of doubtful value.

COMPETITIVE REACTIONS OF NUCLEOPHILES have been frequently used in mechanistic studies.[1–6] Thus, Ingold and Hughes studied the effect of added azide ion in competition with solvent in order to determine the susceptibility of a given substrate to direct displacement reactions.[5] More often an added strong nucleophile was used to trap *the first formed* (carbonium-ion type) intermediate(s) in solvolysis reactions[1,2,7–11] Borohydride[7,8,10] and azide ion[5,11] were the most commonly used nucleophiles but reactions with trapping agents[3] such as SCN^-, $S_2O_3^{-2}$, OH^-, amines, AcO^- as well as reactions with bifunctional leaving groups have also been reported.[9]

When a strong nucleophile (Y^-) is added to a solvolysis medium it competes with solvent (SOH) for the cationic intermediate (I) formed in the slow step:



The ratio of second order rate constants k_Y/k_{SOH} is described as *the competition factor*[12] and usually defined for a given substrate and added nucleophile relative to water as the standard nucleophile. If the concentrations of both solvent [SOH] and

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added nucleophile [Y^-] are much greater than the concentration of substrate [RX] the competition factor F_Y can be calculated by the simple formula:*

$$F_Y = \frac{k_Y}{k_{SOH}} = \frac{[RY][SOH]}{[ROS][Y^-]}$$

where RY/ROS is the corresponding products ratio which can be easily determined experimentally.[3]

Swain has determined azide competition factors for solvolysis of the t-butyl, benzhydryl *p,p*-dimethylbenzhydryl and trityl derivatives.[3] The results show an increase in the competition factors with increasing stability of cationic intermediates.[3] This was explained by higher selectivity for nucleophiles of more stable carbonium ions.[13]

The dependence of the product ration RY/ROS on the reaction conditions was used by us to prove the intervention of ion-pair intermediates in the solvolysis of cyclopropylmethyl-, cyclobutyl-, (1-methylcyclopropyl) methyl-, and 1-methylcyclobutyl methanesulphonates[1,10] and dimethylallyl chlorides.[2] The surprising observation was made that secondary substrates showed considerably higher competition factors for borohydride and azide ions than tertiary ones.[1] This was rationalized in terms of preferential attack of the nucleophile on the intimate ion pair rather than on the free solvated ions. Hence, this process is more similar to a direct displacement reaction where primary substrates are more reactive than secondary and tertiary ones. Moreover, Hill[15] has shown that competition factors of the tertiary substrates depend upon the leaving group which indicates that even in these cases the nucleophile does not attack free carbonium ions but rather ion pairs.

Competition factors were found to depend not only upon the structure of the substrate and the attacking nucleophilic reagent but also upon other factors such as the dielectric constant of solvent,[3,14] ionic strength of solution,[11,14] temperature[3,16] and speed of stirring(!).[15] Consequently, values of competition factors reported in the literature for the same substrates are often very different.[3,14,15] These results cast some doubt about the usefulness of competition factors as a mechanistic probe[6,17] and prompted us to conduct experiments which should answer these questions. Since all our previous results were obtained with resonance stabilised intermediates,[1,2,10] in this work we chose systems which solvolyse through classical intermediates. The substrates listed in Tables (1, 2, 3 and 4) were used.

RESULTS

Cyclopentyl mesylate (**1**), 1-methylcyclopentyl chloride (**2**), cyclohexyl brosylate (**3**), benzhydryl chloride (**4**), benzhydryl bromide (**5**), 3β-cholestanyl (**6**) and 3α-cholestanyl brosylates (**7**) were prepared from the corresponding alcohols by the usual methods. 2-Methyl-2-adamantyl chloride (**8**) was prepared from the corresponding alcohol by introducing gaseous HCl at 0°. 1-Adamantyl bromide (**9**) was the commercial product (Fluka) sublimed twice before use. 2-Adamantyl tosylate (**10**)

* However, if concentration of the substrate is comparable to that of the added nucleophile a more complicated equation should be used.[4] The products ratio RY/ROS, as Golomb[14] has shown for trytyl, benzhydryl and *p,p*-dimethylbenzhydryl chlorides in aqueous acetone and dioxane depends upon the water content and, therefore, the water concentration has usually been introduced[1,3,6] in formula I.

was obtained from Professor P. v. R. Schleyer. The purities and identities of compounds **1–10** were determined by NMR, IR, TLC, GLC and/or microanalyses. Details are given in the experimental section.

Compounds **1–10** were solvolysed for approximatively 8 halflives in the presence of sodium azide (Tables 1–4). The acid formed was potentiometrically titrated with an automatic recording titrator. The yield of the alcohol (ROH) and/or the ether (ROS) produced, was calculated from the titer. The difference between the initial amount of the substrate and experimental titer gave the yield of the azide (RN_3) produced.* From these data using eq. 1 the competition factors for azide ion were calculated in cases where concentrations of substrate were low as compared with the concentrations of both water and added azide.

It is important to point out that this equation is based on the assumption that solvolysis occurs *via* one intermediate and that no S_N2 reaction is included. If this is not the case the "competition factors" cannot be easily explained. This argument is not necessarily of equal importance for different substrates. However, the substrates we chose are known to solvolyse *via* the S_N1 mechanism. All experiments were performed under conditions as identical as possible and with the azide concentration much greater than the starting concentration of the substrate. Therefore, the competition factors obtained may be compared.

The results obtained with cyclopentyl mesylate and 1-methylcyclopentyl chloride are given in Table 1.

TABLE 1. AZIDE COMPETITION FACTORS OF CYCLOPENTYL MESYLATE (1) AND 1-METHYLCYCLOPENTYL CHLORIDE (2) IN 66·7% AQUEOUS DIGLYME IN THE PRESENCE OF ADDED 0·5 M NaN_3

Compound[a]	Temp. °C	% product of elimination[b]	$k_{N_3^-}/k_{H_2O}$[c]
1	40	22·9 ± 0·4	237 ± 4
	90	38·0 ± 0·4	226 ± 2
2	40	65·0 ± 0·5	24 ± 2

[a] [RX] = 0·010 0·025 mol/li

[b] Determined in 66·7% aq diglyme by potentiometric titration.

[c] Corrected for elimination products by eq. 2.† Mean values from 3–5 runs, uncertainties are standard errors.

The assumption was made that the ratio of elimination product and alcohol remains essentially the same regardless of whether azide is present or not, since the ratio of the corresponding activation energies should be independent of added azide. Also, it was shown that under the conditions used the double bond in cyclohexene is

* The azide incorporations determined[6] by gas chromatography were in good agreement with those measured titrimetrically.

† $$k_{N_3}/k_{H_2O} = \frac{[RN_3][H_2O]}{\{[ROH] - p[ROH]\}[NaN_3]}; [N_3^-]_0 \gg [RX]_0 \quad (2)$$

where p is the percentage of the elimination product as determined by potentiometric titration with 0·1 N $KBr/KBrO_3$ using platinum and calomel electrodes.

not attacked by HN_3 (Experimental). However, even in the case of a change of the olefin/alcohol ratio due to the presence of azide, the direction of the change should be approximately the same for all substrates investigated. Therefore, the relative ratios of their competition factors should not change significantly.

It does not seem that the S_N2 reaction interferes significantly in the case of **1** since a tenfold *decrease* in azide concentration more than doubles the $k_{N_3^-}/k_{H_2O}$ ratio (Table 2). Moreover, the secondary α-deuterium isotope effect in solvolysis of cyclopentyl-1-d mesylate was practically the same without (k_H/k_D = 1·16) or with (k_H/k_D = 1·15) added NaN_3 (0·5 mole/l), another indication that the direct displacement reaction is insignificant.

TABLE 2. AZIDE COMPETITION FACTORS IN CYCLOPENTYL MESYLATE (**1**) IN 66·7% AQUEOUS DIGLYME AT 40°

Substrate[a]	$[NaN_3]$ mole/l	$[H_2O]$ mole/l	$k_{N_3^-}/k_{H_2O}$[b]
1	0·05	18·54	632 ± 24
	0·5	18·54	242 ± 10

[a] $[ROMs]_0$ = 0·01 – 0·025 mole/l.

[b] Calculated from eq. 3 since $[ROMs]_0 \approx [NaN_3]_0$, $k_{N_3^-}/k_{H_2O} = F$

$$F = \frac{[H_2O]}{[ROH]} \ln \frac{(1+q)[H_2O] + F[NaN_3]_0}{(1+q)[H_2O] + F\{[NaN_3]_0 - [ROMs]_0\}} \qquad (3)$$

where $q = \frac{\%\ \text{product of elimination}}{\%\ \text{alcohol}}$ and $[ROMs]_0$ and $[NaN_3]_0$ are corresponding starting concentrations.

The results obtained with other substrates are given in Tables 3 and 4.

TABLE 3. AZIDE COMPETITION FACTORS IN SOLVOLYSIS OF 2-ADAMANTYL TOSYLATE (**10**), 2-METHYL-2-ADAMANTYL CHLORIDE (**8**), 1-ADAMANTYL BROMIDE (**9**), BENZHYDRYL BROMIDE (**5**) AND BENZHYDRYL CHLORIDE (**4**)

Compound[a]	Solvent	Temp. °C	$[NaN_3]$ mole/l	$k_{N_3^-}/k_{H_2O}$[b]
10	70·0% aq acetone	76·6	0·5	6·6 ± 0·5
	66·7% aq EtOH	76·6	0·5	3·3 ± 0·1[c]
	80·0% aq EtOH	75	0·04	2·5[c,d]
8	66·7% aq diglyme	80·0	0·5	4·9 + 0·2
	70·0% aq acetone	76·6	0·5	3·3 ± 0·3
	66·7% aq EtOH	76·6	0·5	3·9 ± 0·1[c]
9	66·7% aq EtOH	76·6	0·5	2·7 ± 0·3[c]
	66·7% aq EtOH	76·6	0·05	11 ± 1[c]
	66·7% aq EtOH	76·6	0·01	233[c]
	80·0% aq EtOH	75·0	0·04	2·5[c,d]
5	70·0% aq acetone	25·0	0·04	100 ± 3
	70·0% aq acetone	25	0·02	170[e]
4	66·7% aq acetone	50·0	0·5	96 ± 6

[a] $[RX]_0$ = 0·001–0·02 mole/l. [b] Mean values from 3–4 runs. [c] $k_{N_3^-}/k_{SOH}$, $k_{SOH} = k_{H_2O} + k_{EtOH}$. [d] Calculated from ref. 6. [e] Values from ref. 3; the azide competition factors we obtained were about 30% lower from those reported by Swain[3] but his experimental procedure was slightly different from ours (titration in the presence of bromothymolblue *vs.* potentiometric titrations).

TABLE 4. AZIDE COMPETITION FACTORS[a] OF CYCLOPENTYL MESYLATE (1), CYCLOHEXYL (3), 3α-CHOLESTANYL (7) AND 3β-CHOLESTANYL (6) BROSYLATES

Compound	Temp. °C	% Product of elimination	$k_{N_3^-}/k_{SOH}$[d]
1[b]	40·0	23[e]	200 ± 3
3[b]	40·0	57[f]	107 ± 2
	76·6		72 ± 3
7[c]	76·6	69[g]	99 ± 10
6[c]	76·6	17[g]	5 ± 1

[a] In 0·5 mole/l NaN_3 in 66·7% aq EtOH.
[b] $[RX]_0$ = 0·013 mole/l.
[c] $[RX]_0$ = 0·001 mole/l.
[d] $k_{SOH} = k_{H_2O} + k_{EtOH}$, with correction for elimination (see Table 1, *c*).
[e] Experimentally obtained in 66·7% aq diglyme and ref. 18.
[f] Value from ref. 19.
[g] Value from ref. 20.

DISCUSSION

The original application of the azide probe as a measure of relative carbonium ion stability[13, 21] seem to be useful only for simple aromatic, highly resonance stabilized and sterically unhindered carbonium ions such as the trityl and benzhydryl cations. Even in these cases, as Hill,[15] Swain,[3] Golomb[14] and Brown[8] have shown, competition factors depend upon the leaving group.

With alicyclic and polycyclic secondary and tertiary substrates the azide competition factors, as shown in the course of this work, cover a rather wide range and cannot be rationalized in terms of a simple structure-reactivity relationship.*

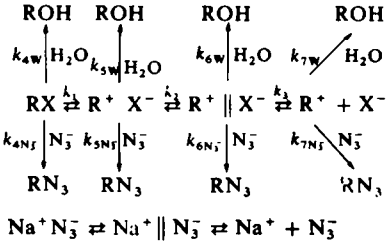
Tertiary substrates (**2**, **8**, **9**) invariably gave *lower* $k_{N_3^-}/k_{SOH}$ values than secondary ones (**1**, **3**, **4**, **5**, **7**) which is opposite from what should be expected on the basis of the stabilities of the respective free ions.

Since it appears reasonable to assume that in the case of **1** a competing direct displacement reaction does not interfere significantly† (*vide supra*) the most probable explanation of these results is that the attack of the azide ion occurs on the intimate or solvent separated ion pair(s).

* This holds also for resonance stabilized systems as we have shown previously.[1, 2]

† α-Deuterium isotope effect measurements in the presence of azide ions can be considered as a sufficiently reliable measure of a possible intervention of direct displacement reaction as was shown with dimethylallyl chlorides,[22] and in this paper in the solvolysis of cyclopentyl-1-d mesylate.

SCHEME 1



However, the general mechanism of solvolytic reactions can be even more complex.[23] Recent results[24] support concurrent S_N1 and S_N2 reactions contrary to the unified theory of nucleophilic substitution suggested by Sneen[11] but do not exclude a more complex scheme like I.

Competition factors are higher for ion pairs than for free ions.[4] This ion pairing is important not only for the substrate as shown on numerous examples but also for sodium azide.[25,26] The increased factors obtained with cyclopentyl mesylate and 1-adamantyl bromide when decreasing the concentration of sodium azide (Table 2 and 3) support this reasoning. On the other hand, decrease of the sodium azide concentration decreases the ionic strength of the solution and attack probably occurs on more tight ion (pair(s). The character of ion pairs may be modified either by varying the solvent medium or the solution temperature.[27] Azide bound to different counter-ions could be expected[23] to give rise to different values of competition factors under otherwise identical conditions.

Thus, only in the two extreme cases, i.e. direct displacement (S_N2) and free stable carbonium ions (tertiary aromatic substrates-dissociative S_N1 mechanism) can competition factors yield useful mechanistic information. In all other cases, especially with secondary substrates, the qualitative evaluation of the azide-water rate ratio is hardly possible and in our opinion of doubtful value.*

An illustration of a possible relation of azide competition factors and the reaction mechanism for primary, secondary and tertiary substrates is given in Fig 1.

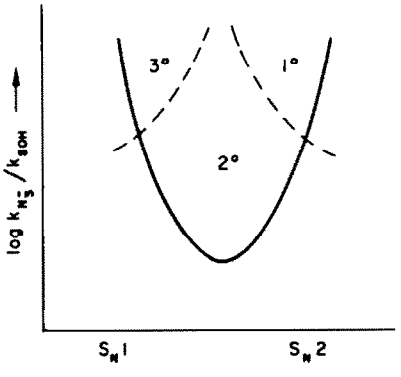


FIG 1.

EXPERIMENTAL

M.ps were determined using a Koffer hot stage microscope and a Thiele apparatus and are uncorrected. For potentiometric titrations and measurements a Radiometer, Copenhagen, SBR 2c Titrigraph with PHM 25 and TTT 11 was used. NMR spectra were recorded on a Varian A-60A spectrometer. Diglyme was commercial product (Fluka) which was purified according to the published procedure.[30] Sodium azide

* Low competition factors observed with adamantyl derivatives (Table 3) and considered by Schleyer[6] as indicative of strongly hindered backside solvent attack do not seem to be due to unique structural feature of the adamantyl skeleton, because similar effects were also observed with 3β-cholestanyl brosylate (Table 4). The low $k_{N_3^-}/k_{SOH}$ ratio with this substrate did not preclude a backside solvent attack yielding solvolysis products of inverted configuration.[28,29].

(Fluka 99%) was recrystallized from 50% aqueous EtOH and dried at 110°. All other reagents were analytical grade.

Cyclopentyl mesylate (1). Cyclopentanol (purity 99·5% by GLC) was obtained in 97% yield (20 g), b.p. 139–140°, by LAH reduction (0·5 M in ether) of cyclopentanone (20 g, 0·24 mole). The methanesulfonate, pale yellow viscous oil, 1·96 g (69%); n_D^{23} = 1·4507 was prepared[31] by reacting the alcohol (1·5 g, 17·4 mmoles) in CH_2Cl_2 in the presence of dry pyridine with the theoretical amount of MsCl. According to "infinity" titers, NMR and IR spectra it was 90–95% pure. The impurities were free methanesulfonic acid, pyridine and CH_2Cl_2.

1-*Methylcyclopentyl chloride* (2). 1-Methylcyclopentanol (6·5 g; 65%) m.p. 29–30°, (lit.[32] m.p. 32–34°) b.p. 60°/20 mm was prepared[33] by the Grignard reaction from cyclopentanone (8·4 g, 0·1 mole) and MeMgI (18·8 g, 0·132 mole of MeI and 3·28 g, 0·135 mol of Mg). 2 was obtained by introducing gaseous HCl into the alcohol (2·4 g, 24 mmoles) at 0°. Water was removed and the crude product dried over $CaCl_2$ and K_2CO_3 and distilled *in vacuo*. The yield of the chloride was 1·6 g (56·8%) and according to IR and NMR spectra it was more than 96% pure; n_D^{22} = 1·445 (lit.[34] n_D^{25} = 1·446).

Cyclohexyl brosylate (3). Cyclohexanol (2 g, 20 mmoles, b.p. 161·5°) was treated with *p*-BsCl (6·1 g, 24 mmoles) in the presence of anhydrous pyridine at 0° for 48 hr. The mixture was treated according to the published procedure.[35] The crude product was recrystallized at low temp. from ether–hexane mixture. The yield was 2·8 g (46%), m.p. 45–46°, (lit.[35] m.p. 48·1–48·6°). (Found: C, 44·79; H, 4·56. $C_{12}H_{15}BrO_3S$ requires: C, 45·15; H, 4·73%).

Benzhydryl chloride (4). Benzhydrol (17·6 g, 80% yield, recrystallized from pentane m.p. 68–69°) was prepared by LAH (1·36 g, 35·8 mmoles in 100 ml ether) reduction of benzophenone (21·7 g, 0·119 mole). Treatment of pentane solution of benzhydrol (2 g, 10·8 mmoles) with dry gaseous HCl for 4 hr gave the crude chloride (1·6 g, 75%) which was dried over $CaCl_2$ and recrystallized from pentane at low temp.; m.p. 14° (lit.[36] m.p. 12–14°).

Benzhydryl bromide (5). PBr_3 (3·4 g, 12·7 mmoles) in CCl_4 was added dropwise into benzhydrol (5 g, 27·2 mmoles) in CCl_4 with stirring. The mixture was allowed to stand for 24 hr, heated to 60–70° for 6 hr and treated as described in the literature.[3] The crude benzhydryl bromide (4·3 g, 65% yield) was recrystallized at low temp. from pentane–ether mixture; m.p. 38·5–39·5° (lit.[37] m.p. 45°).

3β-*Cholestanyl brosylate* (6). Partially acetylated 3β-cholestanol (25 g) was obtained[38] by catalytic hydrogenation over Pt (0·12 g PtO_2) of 3β-cholesterol (25 g, 64 mmoles) in glacial AcOH at 65° for 24 hr. The product was purified by removal of the remaining cholesterol with conc. H_2SO_4, hydrolysis with NaOH in EtOH, filtration through Al_2O_3 column (II/III) and recrystallization from anhydrous EtOH. The 3β-cholestanol was obtained in 56% yield (14 g), m.p. 139–140°. 3β-Cholestanyl brosylate (1·7 g, 88% yield) was prepared[39] by treatment of the alcohol (1·24 g, 3·18 mmoles) in dry pyridine with BsCl (1·24 g, 4·84 mmoles) at 0° for 48 hr. The mixture was then treated as usual.[39] The crude product was recrystallized at low temp. from ether–pentane mixture, m.p. 130–132°, (lit.[40] m.p. 120–122°). According to NMR and TLC it was 97% pure.

3α-*Cholestanyl brosylate* (7), was prepared from 3α-cholestanol[28] (1·1 g, 2·83 mmoles; $[\alpha]_D^{25}$ + 32·9° ($CHCl_3$); m.p. 184·0–185·5, lit.[40] m.p. 184–186°; 95% pure according to NMR and TLC in the same manner as described for the 3β-epimer. The crude product contained about 30% (NMR) of unreacted alcohol. 7 was purified by SiO_2 column chromatography with C_6H_6–EtOAc (9:1). Low temp. recrystallization from ether–pentane gave 907 mg (53%) of product with m.p. 132–133°. NMR spectra and TLC showed the presence of only about 5% alkenes.

2-*Methyl*-2-*adamantyl chloride* (8). 2-Methyl-2-adamantol (995 mg, 60% yield) was prepared by the Grignard reaction from adamantanone (1·5 g, 0·01 mole) and MeMgI (1·21 g, 0·05 mole of Mg and 7·1 g, 0·05 mole of MeI). Low temp. recrystallization from pentane gave 800 mg of pure compound, m.p. 205–206° (lit.[41] m.p. 207·8–209·0°). 8 was obtained by introducing dry HCl into a pentane solution of the alcohol (800 mg, 4·82 mmoles) at room temp. for 2 hr. Water was removed and the pentane solution dried over K_2CO_3 and $CaCl_2$. The solvent was evaporated *in vacuo* and the crude product subjected to low temp. recrystallization from pentane. The yield was 920 mg (98%), m.p. 176–176·5° (sealed capillary). According to IR spectra the product was free from the starting material. (Found: C, 71·59; H, 9·24. $C_{11}H_{17}Cl$ requires: C, 71·54; H, 9·21%).

1-*Adamantyl bromide* (9) (Fluka purum) was sublimed twice at 80°/15 mm; m.p. 118–119° (lit.[42] m.p. 119·0–120·0°). (Found: C, 55·82; H, 7·27. $C_{10}H_{15}Br$ requires: C, 55·83; H, 6·98%).

2-*Adamantyl tosylate* (10). M.p. 80·0–80·2° (lit.[41] m.p. 82·7–83·7°).

Competition factors. About 0·3–0·1 mmole of the corresponding derivative was weighed to a precision

of ±0·1 mg and introduced together with the weighing container into 20 ml of a sodium azide solution (the cholestanyl derivatives were dissolved in 50 ml). After closing the reaction flask or sealing it (as required), stirring was started and continued for about 8 solvolysis half-lives. After cooling, an aliquot was taken and the liberated hydrazoic acid titrated potentiometrically. Another sample of the substrate from the same batch was solvolyzed for 8 half-lives in the same solvent without added NaN_3 and the amount of liberated acid determined by titration.

Reaction of cyclohexene with hydrazoic acid. A solution of cyclohexene (0·13 mole/l) and *p*-TsOH (0·12 mole/l) in 66·7% diglyme–D_2O containing NaN_3 (0·5 mole/l) was heated at 76° for 24 hr in a sealed NMR tube. The intensity of the signals for vinylic protons remained unchanged.

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