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$S_{RN}1$ Reactions of 7-Iodobicyclo[4.1.0]heptane with Carbanions. A Novel Stereoselective C-C Bond Formation on Cyclopropane Rings

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Abstract: The photostimulated reaction of 7-iodobicyclo[4.1.0]-heptane (7-iodonorcarane, **1**, a mixture of *ca.* 1:1 of the *exo:endo* isomers) with acetophenone enolate ion **2** in DMSO at 60°C gave the substitution products **3a** (*exo*) and **3b** (*endo*) in 87% yield (with an *exo:endo* ratio of 16). In the dark at 60°C, not only the *ipso* substitution products **3a** and **3b** (51%), but also the *cine* substitution product **4** were formed (20%) by an elimination-addition reaction. In the dark and at room temperature there is no reaction. It is suggested that **1** reacts with **2** by a photostimulated as well as a thermal (60°C) $S_{RN}1$ reaction to give the *ipso* products **3**, with a **3a**:**3b** ratio of *ca.* 15-23, showing a stereoselectivity of the 7-norcaranyl radicals in the coupling reaction with **2**. More selectivity of **1** with **2** was found in the photostimulated reaction in liquid ammonia (at -33°C), with a **3a**:**3b** ratio of *ca.* 55, although in lower yields (37%). The photostimulated reaction of **1** with 2-acetonaphthone **7** gave only the *ipso* products (with an *exo:endo* ratio of 45) and in dark conditions at 60°C there is no reaction with **7**. There was no photostimulated reaction of **1** with the anion of nitromethane **9** in DMSO. However, the photostimulated reaction of **1** with **9** in presence of acetone enolate ion **10**, the *ipso* substitution products derived from **9** were formed (entrainment $S_{RN}1$ reaction), with an *exo:endo* ratio of *ca.* 7.3. From competition experiments, **9** was *ca.* 6.4 times more reactive than **2**.

Substituted cyclopropanes react by the S_N1-type nucleophilic substitution, but a disrotatory opening is necessary to assist the departure of the leaving group (electrocyclic process).[1] This process has a relative high activation energy due to the fragmentation of two bonds in a concerted process. When the cyclopropane has the leaving group as well as a substituent at the same carbon atom of the ring, it stabilizes the positive charge and it is possible to perform a substitution by the S_N1 mechanism without ring opening.[2] On the other hand, halocyclopropanes do not usually suffer nucleophilic substitution by the S_N2-type reaction.[3]

Gem-dihalocyclopropanes have a similar reactivity because nucleophilic substitution normally involves an elimination-addition sequence.[4,5] When substitution by the S_N1 mechanism was attempted, it usually led to a fissure of the ring, whereas substitution by the S_N2 mechanism is considered geometrically unfavorable.[6] However, it has been found that halo- and dihalocyclopropanes react with nucleophiles by the $S_{RN}1$ mechanism.[7]

The main reaction steps proposed for the $S_{RN}1$ mechanism involve the fragmentation of the radical anion of the substrate to give a radical intermediate and the nucleofugal group (eq. 1); the reaction of the radical with the nucleophile to give the radical anion of the substitution product (eq. 2) which by an electron transfer (ET) to the substrate completes the chain propagation cycle of the proposed mechanism (eq. 3). In aliphatic systems without a low lying π^* MO, the radical anion $(RX)^-$ probably is not an intermediate and equations (1) and (3) occur simultaneously (eq. 1,3).[7]

$$(RX)^- \longrightarrow R + X^- \quad (1)$$

$$R + Nu^- \longrightarrow (RNu)^- \quad (2)$$

$$(RNu)^- + RX \longrightarrow RNu + (RX)^- \quad (3)$$

$$(RNu)^- + RX \longrightarrow RNu + R + X^- \quad (1,3)$$

This mechanism requires an initiation step; one of them may involve the ET from a suitable electron donor such as the nucleophile present in the reaction media, and this ET can be thermal (spontaneous ET), or stimulated by light.

The photostimulated reaction by the $S_{RN}1$ mechanism of 7-bromonorcarane (7-bromobicyclo [4.1.0]heptane) with several nucleophiles has been reported. Thus the photostimulated reaction of Ph_2P^- ions in liquid ammonia afforded, after oxidation, (7-norcaranyl)diphenylphosphine oxide in 87% yield. The photostimulated reaction is inhibited by di-*tert*-butyl nitroxide and *p*-dinitrobenzene (*p*-DNB), well known inhibitors of $S_{RN}1$ reactions, suggesting that it reacts by this mechanism.[8] Similar behavior was observed with other nucleophiles, such as Ph_2As^- [8a] and PhS^- ions.[8b]

Pinacolone enolate ion did not react with 7-bromonorcarane in liquid ammonia in the dark, but reacted under irradiation to give 18% yield of the substitution product.[9]

We have reported that carbanions, such as acetophenone enolate ions and other stabilized carbanions, react with 1-iodoadamantane,[10] neopentyl iodide[11] and iodobenzene[12] in DMSO by the $S_{RN}1$ mechanism of nucleophilic substitution. As the reactivity in $S_{RN}1$ reactions of bridgehead halides, and other alkyl halides with nucleophiles is similar,[7] we studied the reaction of 7-iodo-norcarane **1** with carbanions in DMSO.

Results and Discussion

The photostimulated reaction of **1** (a mixture *ca.* 1:1 of the two isomers *exo:endo*) with acetone enolate ion in DMSO at 60°C gave 100% of iodide ions, and a low yield of a complex mixture of products (*ca.* 20%), while in dark conditions it gave *ca.* 25% of iodide ions. The product mixture could not be resolved due to its volatility, although the high iodide ion release in the photostimulated reaction may suggest an ET reaction. There are precedents that reduction of alkyl radicals competes with the coupling reaction with acetone or pinacolone enolate ions[10,11] so we left aside these reactions for more reactive carbanions in $S_{RN}1$ reactions with alkyl halides.

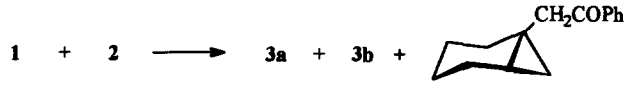
The photostimulated reaction of **1** with acetophenone enolate ion **2** in DMSO (with an **2/1** ratio of *ca.* 10) gave 87% yield of the substitution products *exo*- **3a** and *endo*- **3b**, with an **3a\3b** ratio of 16 (eq. 4) (Expt. 1, Table I).

(4)

1 **2** **3a** **3b**

Spectroscopic data have been reported on compounds related to substitution products **3a** and **3b**, whose *exo* and *endo* configurations have been previously determined by chemical correlation and X rays structural analysis.[13] These studies allowed to establish the *exo* and *endo* isomers of (bicycloalkyl)acetic acid derivatives. From comparison of the ^{1}H-NMR chemical shifts of these analog compounds, the configuration of the substituted bicycloheptyl compounds obtained could be established. A low field shift is observed in the methylenic hydrogen signals neighbor to carbon 7 for the *endo* isomer with respect to the *exo* isomer. This fact results from a deshielding due to the currents of the bicyclo rings. This effect is also assumed to apply for the products synthesized in view of the similarity of their structures, which allows the determination of the stereochemistry of isomers.

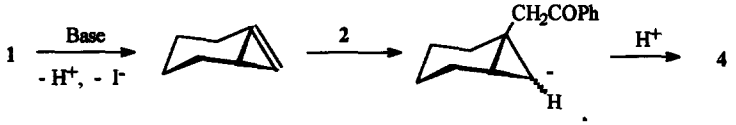
Neither products derived from opening of the cyclopropane ring, nor *cine* substitution products were found, whereas a selective formation of the *exo* isomer **3a** was obtained. In dark conditions, besides the substitution products **3a** and **3b** (51% with an **3a/3b** ratio of 22), there was 20% yield of the *cine* substitution product **4** (eq. 5) (Expt. 2, Table I).



(5)

4

The fact that in dark conditions were formed **3a**, **3b** and **4** suggests that there is a competition between spontaneous ET to give **3a** and **3b**, and the elimination reaction[5] of **1** in this basic reaction conditions to give **5**, which reacts with **2** to give the anion **6**, which is protonated finally to give **4** (eq. 6).



(6)

5 **6**

In the photostimulated reaction in presence of *p*-DNB, there was a decrease of products **3a** and **3b** (22% yield with an **3a/3b** ratio of 23); however, the yield of **4** was 18%, quite similar to the dark reaction (Expt. 3, Table I). When the photostimulated reaction was carried out at room temperature (30°C), there was a decrease of products **3a** and **3b**, but **4** was not formed (Expt. 4, Table I). All these results indicate that there is a thermal as well as a photostimulated ET to initiate the $S_{RN}1$ reactions.

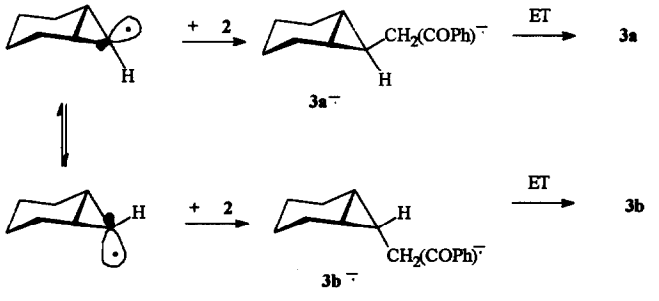
When the dark reaction was carried out in presence of *p*-DNB, the yield of **3a** and **3b** was only 18%, and **4** increased to 24% (Expt. 5, Table I), and in the dark conditions at room temperature there was no substitution product (Expt. 6, Table I). In these conditions there is neither ET nor elimination-addition reactions, the latter occurring only at 60°C.

In order to see the effect of temperature, the dark reaction was carried out at 100°C. There was a decrease of products **3** (27%) and **4** (9%) (Expt. 7, Table I, compare with Expt. 2) although there was 100% of iodide ions release (probably at this temperature there is an increase of side reactions, such as condensation products, etc.). At this temperature and in presence of *p*-DNB, the yields are similar to the previous reaction (Expt. 8, Table I).

When the concentration ratio of **2/1** was only 3, the photostimulated reaction gave the substitution products **3** (with a **3a/3b** ratio of 17), and in dark conditions there is an overall decrease of the reactivity, thus products **3** were formed in only 18%, whereas **4** was formed only in 2% yield (compare with Expt. 2, Table I) and in the photostimulated reaction in presence of *p*-DNB, product **4** was not formed (Expts. 9-11, Table I). With this concentration and at room temperature, there was almost no reaction even in 16 h (Expts. 12-13, Table I).

The photostimulated reaction in liquid ammonia (at the boiling point of -33°C) gave almost pure **3a** although in a relatively low yield (37%), and the **3a/3b** ratio was *ca.* 55 (Expt. 13, Table I).

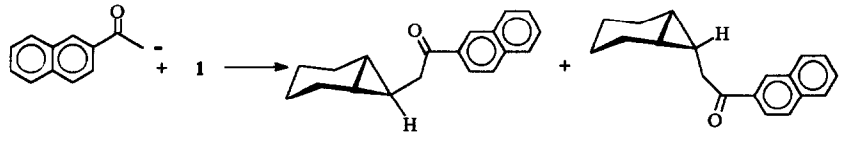
The remarkable stereoselectivity of these reactions may be explained in terms of radical intermediates. The fact that substrate **1** is a mixture of *ca.* 1:1 of the *exo* and *endo* isomers, but the substitution product is mainly the *exo* isomer **3a** (eq. 7a), implies that 7-norcaranyl radicals are intermediates, and these radicals could have two non-equivalent structures, as was reported for substituted cyclopropane radicals, which exist in fast equilibrium between *exo*- and *endo*- radicals,[14] the *exo*-isomer being more reactive.



(7a)

(7b)

The photostimulated reaction of **1** with 2-acetonaphthone enolate ion **7** gave 40% yield of the product *exo*- **8a**, and a small amount of the isomer *endo*- **8b**, with an **8a\8b** ratio of *ca.* 45 (Expt. 15, Table I) (eq. 8).

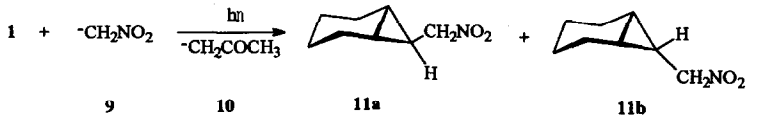


(8)

7 **8a** **8b**

The higher selectivity of this nucleophile **7** may be due to a greater steric requirement compared with **2**. Also a different behavior was observed in the reaction in dark conditions, since it did not react at all with **1** at 60°C (Expt. 16, Table I), showing that **7** reacts with **1** only by photostimulated $S_{RN}1$ reactions.

The anion of nitromethane **9** did not give substitution products under irradiation (Expt. 1, Table II); however, in the presence of acetone enolate ion **10** the photostimulated reaction gave the substitution products *exo*- **11a** and *endo*- **11b**, with an **11a/11b** ratio of ca. 7.3 (eq. 9) (Expt. 2, Table II). The fact that **9** reacts in presence of **10** to give substitution products **11a** and **11b** indicates that **10** is able to initiate the $S_{RN}1$ mechanism donating one electron to **1**, but the radical 7-norcaranyl thus formed reacts faster with **9** than with **10**, giving finally the products observed.



9 **10** **11a** **11b** (9)

Table I: Reactions of **1** and Carbanions **2** and **7** in DMSO.[a]

Expt.	Carbanion (mmole)	Conditions	I^- (%)	Substitution Products, (%)		*Exo-/endo-* Ratio
				3	**4**	
1	**2** (10)	hν, 60°C	100	87	-	16
2	**2** (10)	Dark, 60°C	100	51	20	22
3[b]	**2** (10)	hν, 60°C	73	22	18	23
4	**2** (10)	hν, 30°C	68	63	<1	15
5[b]	**2** (10)	Dark, 60°C	73	18	24	23
6	**2** (10)	Dark, 25°C	19	0	<1	-
7	**2** (10)	Dark, 100°C	100	27	9	11
8[b]	**2** (10)	Dark, 100°C	95	26	20	22
9	**2** (3)	hν,[c] 60°C	100	48	0	17
10	**2** (3)	Dark,[c] 70°C	50	18	2	16
11[b]	**2** (3)	hν,[c] 60°C	35	23	0	16
12	**2** (3)	Dark,[c] 25°C	11	5	0	[d]
13	**2** (3)	Dark,[c] 25°C	19	[d]	0	[d]
14[f]	**2** (10)	hν, -33°C	89	37	[d]	55
15	**7** (10)	hν, 60°C	82	40	[d]	45
16	**7** (10)	Dark, 60°C	3	0	0	-
17	-	hν	<1	-	-	-

[a]Reaction time 1 h, unless otherwise indicated, in 25 mL of DMSO and 1 mmol of **1**. [b]*p*-DNB (24 mole%) added. [c]Reaction time 2 h. [d]Not quantified. [e]Reaction time 16 h. [f]Solvent liquid ammonia (250 mL), reaction time 3 h.

The $S_{RN}1$ mechanism is a chain process with initiation, propagation and termination steps, and the reactivity of the nucleophiles is not necessarily the same for all these steps. Thus carbanion 10 is reactive in the initiation step, but 9 is not, but showed a different reactivity in the coupling reaction of the propagation cycle, 9 being more reactive than 10. These results have precedents in the reactions of 1-iodoadamantane and carbanions.[15] The photostimulated reaction in two hours did not improve the results obtained in one hour.

The dark reaction of 1 with 9 in the presence of 10 gave some dehalogenation reactions, but no substitution products were found in one hour. In two hours less than 1% of product 11a was formed (Expts. 3-4, Table II).

In order to determine the relative reactivity for the nucleophiles 2 and 9 toward 7-norcaranyl radicals, we performed the photostimulated reactions of 1 with nucleophiles 2 and 9 in excess. The relative reactivities were estimated as in previous works.[16] By this procedure and with 2 and 9 in excess, we determined that nucleophile 9 is more reactive than enolate ion 2, with an average value $k_{9/2}$ of 6.4 ± 1.[17] These results are in agreement with previous results, in which nitromethane ion 9 is 3.0 times more reactive than 2 toward 1-adamantyl radicals.[14]

Table II: Reactions of 1 with Nitromethane Anion 9 at 60°C.[a]

Expt.	1 mmole	9 mmole	10 mmole	Conditions	I⁻, %	11, %
1	0.5	5.0	--	hν, 2 h	17	0
2	0.5	5.0	5.0	hν, 1 h	80	41[b]
3	0.5	5.0	5.0	Dark, 1 h	29	0
4	1.0	3.0	10	Dark, 2 h	28	<1
5	1.0	3.0	10	hν, 2 h	85	40

[a]Reaction carried out in 25 mL of DMSO. [b]With an *exo / endo* ratio of 7.3.

Conclusions: Substrate 1 reacts with 2 at 60°C in the dark by two competing mechanisms: an elimination-addition to give the *cine* substitution product 4, or by a thermal ET to follow the $S_{RN}1$ mechanism yielding the *ipso* substitution products 3a and 3b. Under irradiation, 1 reacts with 2 only by the $S_{RN}1$ mechanism. At room temperature, 1 did not react with 2. Under irradiation at room temperature or 60°C the only mechanism is the $S_{RN}1$ reaction. There was no photostimulated reaction of 1 without nucleophile present (blank reaction), showing that 1 does not photolyze in our experimental conditions (Expt. 17, Table I).

It is important the high degree of selectivity found in 7-norcaranyl radicals toward carbanions, such as 2 to give mainly the *exo*- isomer 3a, and the selectivity is increased by lowering the temperature in liquid ammonia, or with the bulkier carbanion 7.[18] With carbanion 9 there was no photostimulated reaction with 1, but it reacts in presence of a good electron donor, such as 10, but 9 reacts faster with the intermediate 7-norcaranyl radical, giving only substitution products derived from 9. From competition experiments, 9 is *ca.* 6.4 times more reactive than 2.

All these results indicate that the photostimulated reaction of 7-iodonorcaranes with stabilized carbanions gave the substitution product with high degree of selectivity rendering the *exo*- isomers.

Experimental Section

General Method. ^1H NMR and ^{13}C NMR were recorded on a Brucker FT-200 nuclear magnetic resonance spectrometer, and all spectra are reported in parts per million relative to Me_4Si (δ), with CCl_3D as the solvent. Infrared spectra were recorded on a Nicolet FTIR 5-SXC spectrometer. Gas chromatographic analyses were performed on a Shimadzu GC-8A or Konik instrument provided with a flame detector and data system Shimadzu CR-3A, using a column packed with 5% OV17 on Chromosorb G (1.5 m x 3 mm) or a Hewlett Packard 5890 series II gas chromatograph equipped with a 0.53 mm x 10 m column packed with HP-5 (cross-linked 5% phenyl silicone gum phase) with a flame detector and HP data system. Column chromatography was performed on silica gel (70-270 mesh ASTM). Quantitative analyses were done by the internal standard method, authentic samples being employed for the determination of the response factors. High-resolution mass spectra were done in a ZAB-SEQ instrument.

Irradiation was conducted in a reactor equipped with two 250-W lamps emitting maximally at 350 nm (Phillips Model HPT, water refrigerated). Potentiometric titration of halide ions was performed in a pHmeter (Seybold Wien) using a Ag/Ag^+ electrode and $AgNO_3$ standard solution. Melting points were obtained with a Büchi 510 apparatus and are not corrected.

Materials. Potassium *tert*-butoxide (Fluka) was sublimed and DMSO (Carlo Erba) distilled under vacuum and stored over molecular sieves (4 Å). Acetone (Merck) was distilled and stored over molecular sieves (4 Å). Nitromethane (Aldrich) was distilled and dried over Na_2SO_4. Acetophenone was distilled under vacuum. Methyl 2-Naphthyl ketone was recrystallized from petroleum ether. 7-Iodonorcarane was synthesized as described.[19]

Photostimulated Reaction of Acetophenone Enolate Ion (2) with 7-Iodo-norcarane (1). The following procedure is representative of these reactions. They were carried out in a 100 mL three necked round bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 25 mL of dry and degassed DMSO under nitrogen were added 11 mmol of potassium *tert*-butoxide, 10 mmol of acetophenone, and 1 mmol of 7-iodonorcarane. After 60 min of irradiation the reaction was quenched by adding ammonium nitrate in excess and water (100 mL), and extracted with diethyl ether (three portions of 50 mL each one). The iodide ions in the aqueous solution were determined potentiometrically. The ether extract was washed twice with water, and quantified by GLC. 4-Bromobiphenyl was used as internal standard. The solvent was removed under reduced pressure. The residue, after column chromatography on silica gel (eluted with petroleum ether:diethyl ether = 90:10) gave the following compounds.

α-(7-Norcaranyl)acetophenone *exo*: m.p. 40-41°C; IR σ/cm^{-1}: 1696 (C=O); ^1H NMR (δ) 0.64-0.95 (3H, m); 1.03-1.39 (4H, m); 1.52-1.98 (4H, m); 2.86 (2H, d, J=7 Hz); 7.31-7.62 (3H, m); 7.82-8.03 (2H, m). ^{13}C NMR (δ) 200.32; 137.04; 132.80; 128.50; 128.10; 43.79; 23.38; 21.43; 19.11; 17.21. High-resolution MS calcd for $C_{15}H_{18}O$: 214.1358. Found: 214.1363.

α-(7-Norcaranyl)acetophenone *endo*: Not isolated but it was identified in the *exo*:*endo* compounds mixture (10:1): ^1H NMR (δ) 0.63-2.02 (11H, m); 2.98 (2H, d, J=7 Hz); 7.31-8.08 (5H, m); ^{13}C NMR (δ) 200.32; 137.04; 132.80; 128.50; 128.10; 34.23, 22.53; 19.05; 14.24; 10.29.

Dark reaction of Acetophenone Enolate Ion (2) with 7-Iodonorcarane (1). The following procedure is representative of these reactions. They were carried out in a 100 mL three necked round bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 25 mL of dry and degassed DMSO under nitrogen were added 11 mmol of potassium *tert*-butoxide and 10 mmol of acetophenone. The system was enclosed in aluminium foil and 1 mmol of 7-iodonorcarane was added. The mixture was stirred and the flask placed in a 60°C temperature bath. After 60 min, the reaction was quenched by adding ammonium nitrate in excess and water (100 mL), and extracted with diethyl ether (three portions of 50 mL each one). The iodide ions in the aqueous solution were determined potentiometrically. The ether extract was washed twice with water, and quantified by GLC. 4-Bromobiphenyl was used as internal standard.

α-(1-Norcaranyl)acetophenone: Liquid isolated by column chromatography on silica gel (eluted with petroleum ether:diethyl ether: 9:1); ^1H NMR (δ) 0.30-0.38 (1H, dd, J=5 Hz); 0.42-0.54 (1H, dd, J=5 Hz and 9 Hz); 0.74-0.90 (1H, m); 1.04-2.06 (8H, m); 2.82 (1H, d, J=18Hz); 3.0 (1H, d, J=18 Hz); 7.36-7.62 (3H, m); 7.84-8.02 (2H, m). ^{13}C NMR (δ) 199.78; 137.79; 132.74; 128.48; 127.98; 49.93; 29.22; 23.86; 21.62; 21.00; 17.83; 16.93; 16.15. High-resolution MS calcd for $C_{15}H_{18}O$: 214.1358. Found: 214.1354.

α-(7-Norcaranyl)methyl naphthyl ketone *exo*: White solid isolated by column chromatography on silica gel (eluted with petroleum ether: diethyl ether: 9:1); m.p. 84.5-85.5°C. Analysis: calculated for $C_{19}H_{20}O$: C, 86.36; H, 7.58: found C, 86.29; H: 7.74; IR σ/cm^{-1} 1683 (C=O); ^1H NMR (δ) 0.70-2.05 (11H, m); 3.00 (2H, d, J=6.3 Hz); 7.46-7.68 (2H, m); 7.79-8.14 (4H, m); 8.38-8.52 (1H, m); ^{13}C NMR (δ) 200.24; 135.47; 134.4; 132.5; 129.7; 129.5; 128.34; 128.27; 127.7; 126.6; 124.0; 43.84; 23.39; 21.43; 19.28; 17.27.

α-(7-Norcaranyl)methyl naphthyl ketone *endo*: Not isolated but it was identified in the *exo*:*endo* compounds mixture. ^1H NMR (δ) 0.70-2.05 (11H, m); 3.11 (2H, d, J=6.4 Hz); 7.46-7.68 (2H, m); 7.79-8.14 (4H, m); 8.38-8.52 (1H, m); ^{13}C NMR (δ) 200.24; 135.47; 134.4; 132.5; 129.7; 129.5; 128.34; 128.27; 127.7; 126.6; 124.0; 34.33; 22.55; 19.08; 14.49; 10.38.

α-(7-Norcaranyl)nitromethane *exo*: Liquid isolated by column chromatography on silica gel (eluted with petroleum ether:diethyl ether: 95:5); ^{1}H NMR (δ) 0.88-1.04 (2H, m); 1.06-1.41 (4H, m); 1.54-1.97 (5H, m); 4.18 (2H, d, J=8 Hz); ^{13}C NMR (δ) 80.31; 22.65; 21.00; 20.84; 16.89. Small amounts of the *endo* isomer was isolated. ^{1}H NMR (δ) 0.9-2.0 (11 H, m); 4.5 (2 H, d, J=8Hz).

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16. The equation used in the relative reactivity determination of pairs of nucleophiles vs. a radical is:

$$\frac{k_{Nu1}}{k_{Nu2}} = \frac{\ln [Nu_1]_o / [Nu_1]_t}{\ln [Nu_2]_o / [Nu_2]_t}$$

where $[Nu_1]_o$ and $[Nu_2]_o$ are initial concentrations, and $[Nu_1]_t$ and $[Nu_2]_t$ are concentrations at time *t* of both nucleophiles. This equation is based on a first order reaction of both anions with the 7-norcaranyl radicals, see Bunnett, J. F., *Investigation of Rates and Mechanisms of Reactions*, 3rd ed.; Lewis E. S., Ed.; Wiley-Interscience: New York, **1974**; Part 1, p. 159.
17. When the ratio of 2 \9 is between 1 - 1.4, the relative reactivity $k_{9/2}$ is ca. 3-4, but when the ratio of 2\9 is between 2 - 3.3 the relative reactivity $k_{9/2}$ is ca. 4.3-7.4. We will further study these competing reactions as it still remains to be known the cause of the relative reactivity dependance on the concentration ratio of the nucleophiles.
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