J. Org. Chem. 1988, *53*, 6065–6067

Photostimulated Reaction of Carbanions from α,β-Unsaturated Nitriles with Aryl Halides by the $S_{RN}1$ Mechanism

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Received March 17, 1988

The photostimulated reaction of *p*-bromoanisole, *p*-iodoanisole, and 1-iodonaphthalene with the carbanion **2** of the cyclohexylideneacetonitrile **1** gave good yields of the isomeric substitution products 2-(*p*-anisyl)-1-cyclohexenylacetonitrile (**3a**), 2-(*p*-anisyl)cyclohexylideneacetonitrile (**3b**), 2-(1-naphthyl)-1-cyclohexenylacetonitrile (**8a**), and 2-(1-naphthyl)cyclohexylideneacetonitrile (**8b**). The substitution occurred exclusively in the C_γ. These reactions do not occur in the dark, and the photostimulated reactions are inhibited by 1,4-dinitrobenzene. Thus it is proposed that these reactions occur by the $S_{RN}1$ mechanism of nucleophilic substitution.

Nitrile α-hydrogens such as the cyanomethyl anion are acidic enough to form carbanions in liquid ammonia, and they react with halobenzenes stimulated by solvated electrons or light to give the substitution product phenylacetonitrile together with benzene, toluene, 1,2-diphenylethane, and other minor products (eq 1).[1,2]

$$\mathrm{PhX} + {}^{-}\mathrm{CH_2CN} \xrightarrow{h\nu \text{ or } e^-} \mathrm{PhCH_2CN} + \mathrm{PhH} + \mathrm{PhCH_3} + (\mathrm{PhCH_2})_2 \quad (1)$$

The amount of the products depends on the halobenzene used, the method to initiate the reaction, and the experimental conditions.[1,2] These reactions occur by the $S_{RN}1$ mechanism of nucleophilic substitution,[3] being the main reaction pathways sketched in Scheme I.

The radical anion of the substrate fragments giving phenyl radicals and halide ions (eq 2). Phenyl radicals can react with solvated electrons or other species, giving ultimately benzene (eq 3), or they can couple with the nucleophile producing a new radical anion (eq 4). This radical anion intermediate can either fragment to give a benzyl radical and a cyanide ion (eq 5) or the substitution product and the radical anion of the substrate by electron transfer to the substrate (eq 6). Benzyl radicals are reduced to toluene (eq 7) or dimerize to 1,2-diphenylethane (eq 8).[1,2]

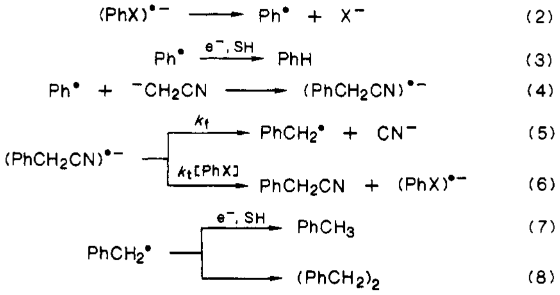
The fact that phenylacetonitrile radical anion fragments (eq 5) suggests that the π^* molecular orbital and the σ^* molecular orbital of the C–CN bond have similar energy and that it fragments from the σ^* state.[4] When aryl halides with a low-lying π^* molecular orbital, such as 1-halonaphthalenes, were used as substrates, no fragmentation of the radical anion intermediates was observed.[4,5]

We have studied the photostimulated reaction of carbanions derived from α,β-unsaturated nitriles with aryl halides in liquid ammonia to determine if they were suitable nucleophiles in the $S_{RN}1$ mechanism, and then in which position of these conjugated system they react, and if they fragment as in the reaction of the carbanion of phenylacetonitrile in the sense of eq 5.

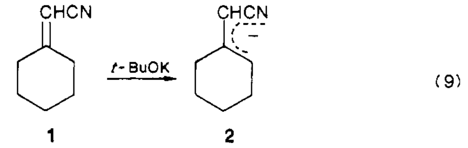
Results and Discussion

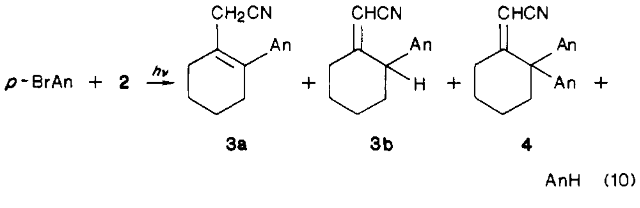
The reaction of potassium *tert*-butoxide (*t*-BuOK) with 1-cyano-2-methyl-1-propene in liquid ammonia gave a dark red solution, and in the photostimulated reaction with *p*-iodoanisole (*p*-IAn) it gave a 96% yield of iodide ion and a mixture of products, probably from oligomerization and polymerization of the nucleophile and/or the substitution product.[6,7] In the dark there is no reaction with *p*-IAn. No further studies of this reaction were carried out.

Scheme I



The carbanion **2** of the cyclohexenylideneacetonitrile (**1**) was formed in liquid ammonia with *t*-BuOK (eq 9). The photostimulated reaction of **2** with *p*-bromoanisole (*p*-BrAn) gave anisole (AnH), a mixture of the two isomers of the monosubstitution product **3a** and **3b**, and small amount of a product, which by mass spectrum suggests the formation of the disubstitution product **4** (Table I) (eq 10).





An = *p*-anisyl

The amount of each isomer (**3a** and **3b**) depends on the method used to neutralize the reaction, through both isomers were always formed (quenching the reaction with ammonium nitrate, **3a**:**3b** ca. 65:35; with water, **3a**:**3b** ca. 80:20). We tried to separate both by using different techniques (column chromatography, acid–base treatment of the isomeric mixture of **3a** and **3b** in acetonitrile or DMSO, etc.), but the complete separation of both isomers

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0022-3263/88/1953-6065$01.50/0

Table I. Reaction of the Nucleophile 2 with Halobenzenes

expt	ArX,[a] M	2, M	$h\nu$, min	X⁻	products (yield, %)[b]
1	p-BrAn, 0.052	0.048	180	52	c
2	p-BrAn, 0.052	0.048	300	97	**3** (69), **4** (5), AnH (20)
3	p-BrAn, 0.052	0.050	180[d]	4	c
4	p-BrAn, 0.052	0.052[e]	300	45	c
5[f]	p-BrAn, 0.050	0.048	300	2	
6	p-IAn, 0.029	0.023	15	27	c
7	p-IAn, 0.029	0.023	120	95	**3** (65), **4** (7), AnH (25)
8	p-IAn, 0.032	0.030	120[d]	2	c
9[g]	p-IAn, 0.030	0.030	120	13	c
10	1-INaph, 0.031	0.078	60	100	**8** (57), **9**,[h] NaphH (40)
11	1-INaph, 0.032	0.080	240	100	**8** (60), **9**,[h] NaphH (35)
12	1-INaph, 0.030	0.080	60[d]	15	c

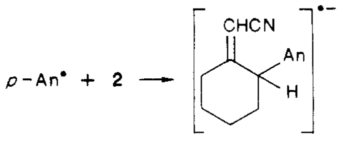
[a] An = anisyl; Naph = naphthyl. [b] Determined by GLC. [c] Not quantified. [d] Dark conditions. [e] KNH_2 was used as a base. [f] 1,4-Dinitrobenzene was added (20 mol %). [g] The solvent was DMSO. [h] Detected but not quantified.

was not possible. Only **3a** was obtained in pure form by column chromatography (see the Experimental Section).

In the dark there was no reaction (bromide ions 4% yield), and the photostimulated reaction was inhibited by 1,4-dinitrobenzene, a well-known inhibitor of $S_{RN}1$ reactions.[3] From these results we suggest that **2** reacts with p-bromoanisole by the $S_{RN}1$ mechanism of nucleophilic substitution.

With p-IAn, the yield was similar but less irradiation time was required for the reaction to proceed to completion (Table I). We also used potassium amide as a base, but the yield was not as high as with t-BuOK. In the photostimulated reaction of **2** with p-IAn in DMSO as solvent, we observed only 13% yield of iodide ion in 120 min of irradiation.

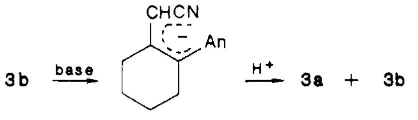
The fact that only reduction and substitution products **3** and **4** were formed suggests that the radical anion $\mathbf{3b}^{\bullet-}$ in the coupling of p-anisyl radical with the nucleophile **2**, is formed. It does not fragment in the sense of eq 5 since only electron transfer to the substrate is observed to give **3b** (eq 11 and 12). In the basic reaction conditions, **3b** is deprotonated to give the anion $\mathbf{3}^-$, and in the neutralization of the reaction, isomers **3a** and **3b** are both produced (eq 13).[8]



(11)

$\mathbf{3b}^{\bullet-}$

$$\mathbf{3b}^{\bullet-} + p\text{-BrAn} \longrightarrow \mathbf{3b} + (p\text{-BrAn})^{\bullet-} \quad (12)$$

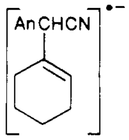


(13)

$\mathbf{3}^-$

The carbanion **2** has two carbon atoms that are nucleophilic (C_α and C_γ), but only arylation in the C_γ to give radical anion $\mathbf{3b}^{\bullet-}$ was observed. Coupling of radical in the γ position gave the most stable radical anion $\mathbf{3b}^{\bullet-}$ in which the double bond and the nitrile group are conjugated, the odd electron being now located in the π^* molecular orbital of this system.[9] The energy gap between the σ^* molecular orbital of the C–CN bond and the π^* molecular orbital is larger than in the phenylacetonitrile radical anion **6**. Consequently, no fragmentation of the radical anion was observed.

If there had been coupling of the p-anisyl radicals in the C_α, radical anion **5** would have formed, so there is not conjugation between the C≡N group and the double bond, and therefore the radical anion **5** is not expected to be more stable than **6**. This means that arylation in C_α would give fragmentation of the radical anion intermediate **5**.



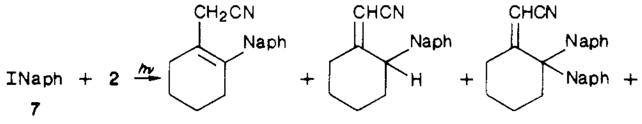
5

$(PhCH_2CN)^{\bullet-}$

6

These results are similar to those of the arylation of a related carbanion, such as that derived from 1,3-pentadiene, where only the radical coupling at C_1, which gives the most stable radical anion intermediate, was observed and not at C_3.[10,11]

The photostimulated reaction of **2** with 1-iodonaphthalene (INaph) **7** in liquid ammonia gave the isomeric substitution products **8a** and **8b**, together with the reduction product, naphthalene, and a small amount of a product, which by mass spectrum suggests the formation of the disubstitution product **9** (eq 14). This reaction did not occur in the dark (Table I).



7 **8a** **8b** **9**

NaphH (14)

Naph = 1-naphthyl

We can conclude that carbanions derived from *alicyclic* α,β-unsaturated nitriles can be formed in liquid ammonia, but their condensation and oligomerization make this carbanion not suitable for $S_{RN}1$ reactions. However, carbanions derived from α,β-unsaturated *cyclic* nitriles, such as **2**, are good nucleophiles to react with aryl halides by the $S_{RN}1$ mechanism. The fact that this reaction only gave arylation in the C_γ with no fragmentation of the radical anion intermediate opens an interesting route to C-arylation of aliphatic rings.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrophotometer, and ^1H NMR and ^{13}C NMR spectra in a Bruker FT 80 MHz nuclear magnetic

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(8) See, for example: d'Angelo, J. *Tetrahedron* **1976**, *24*, 2979 and references cited therein.

(9) At Huckel level, the π^* molecular orbital of $H_2C{=}CHC{\equiv}N$ ($\alpha - 0.49\beta$) is lower in energy than the π^* molecular orbitals of anisole ($\alpha - 1.00\beta$) and of the C≡N group ($\alpha - 0.82\beta$), see ref 5.

(10) Rossi, R. A.; Bunnett, J. F. *J. Org. Chem.* **1973**, *38*, 3020.

(11) Rossi, R. A. *J. Chem. Ed.* **1982**, *59*, 310.

resonance spectrophotometer through the courtesy of Professor E. Rúveda (Universidad Nacional de Rosario). Infrared spectra were recorded on a 5 SXC Nicolet FTIR spectrophotometer. Mass spectral measurements were obtained with a Finnigan Model 3300 mass spectrometer, and gas chromatographic analyses were performed on a Varian Aerograph series 1400 instrument with a flame ionization detector by using a column packed with 3% SE30 on Chromosorb P (0.5 m × 3 mm) or 5% OV 17 on Chromosorb P (1.5 m × 3 mm). Column chromatography was performed on silica gel (70–230 mesh, ASTM, Merck). Irradiation was conducted in a reactor equipped with four 250-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated). Microanalyses were performed in UMYMFOR (Universidad de Buenos Aires), through the courtesy of Professor E. Gros.

Materials. *p*-Bromoanisole (Baker), *p*-iodoanisole (Fluka), and 1-iodonaphthalene (Fluka) were commercially available and used as received. Cyclohexylideneacetonitrile (1) was prepared according to the literature.[12] It gives a mixture of 1 (85%) and the isomer 1-(cyanomethyl)cyclohexene (15% yield), and this mixture was used in the reactions reported, giving the same carbanion 2 in the basic medium.

Photostimulated Reactions of 2 with *p*-Bromoanisole. The following procedure is representative of these reactions: into a three-necked 500-mL round-bottomed flask, equipped with a cold-finger condenser charged with dry ice–ethanol, a nitrogen inlet, and a magnetic stirrer, were condensed 250 mL of ammonia previously dried with sodium metal under nitrogen. To the ammonia was added *tert*-butyl alcohol (22 mmol), potassium metal (22 mmol), and a small amount of $FeCl_3$ to form potassium *tert*-butoxide.[13] Cyclohexenylideneacetonitrile (12 mmol) was added, and after 5 min *p*-BrAn (13 mmol) was added and the solution was irradiated for 300 min. The reaction was quenched by the addition of excess ammonium nitrate, and the ammonia was then allowed to evaporate. Water (100 mL) was added to the residue, and the mixture was extracted with diethyl ether. In the aqueous solution the bromide ions were determined potentiometrically. The ether was analyzed by GLC, using the internal standard method (standard *p*-chlorobromobenzene) compared with a pure sample of **3a**. In another experiment, removal of the ether by distillation gave a residue from which, after column chromatography on silica gel (elution with petroleum ether–benzene, 70:30), gave pure 2-(*p*-anisyl)-1-cyclohexenylacetonitrile (**3a**): MS, *m*/*e* (relative intensity) 277 (M^+, 33), 187 (21), 159 (67), 146 (40), 121 (49), 108 (44), 91 (49), 81 (9), 41 (100), 27 (60); molecular weight 227.307, found 227.308; IR (cm^{-1}) 3001, 2932, 2245, 1573, 1459, 833, and 785; ^1H NMR (CCl_4) δ 1.28–2.50 (8 H, m), 2.80 (2 H, s), 3.70 (3 H, s), 6.6–7.2 (4 H, m). Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.12. Found: C, 78.98; H, 7.54; N, 5.90. The other isomer 2-(*p*-anisyl)cyclohexylideneacetonitrile (**3b**) (in small amount) could not be obtained in pure form, but the ^1H NMR (50% **3a**, 50% **3b**) (CCl_4) is δ 1.6–2.2 (8 H, m), 3.10 (1 H, t), 3.80 (3 H, s), 4.31 (1 H, s), 6.82–7.35 (4 H, m); 4 was also isolated in a small amount, and its mass spectrum suggests the disubstitution product: MS, *m*/*e* (relative intensity) 334 (4), 308 (100), 277 (6), 201 (17), 121 (24), 91 (10).

Photostimulated Reactions of 2 with *p*-Bromoanisole in the Presence of 1,4-Dinitrobenzene. The procedure was similar to that for the previous reaction, except that 20 mol % of 1,4-dinitrobenzene was added.

Reactions of 2 with *p*-Bromoanisole in the Dark. The procedure was similar to that for the previous reaction, except that the reaction flask was wrapped with aluminum foil.

Photostimulated Reaction of 2 with 1-Iodonaphthalene. The nucleophiles were prepared as described before. The procedure was similar to those previously described. In the aqueous solution were titrated iodide ions (see Table I). In the ether extract the products were quantified by GLC by the internal standard method (standard anthracene) compared with a pure sample of **8a**. In another experiment, removal of the ether by distillation gave a residue from which column chromatography on silica gel (elution with petroleum ether–benzene, 80:20) gave pure 2-(1-naphthyl)-1-cyclohexenylacetonitrile (**8a**): MS, *m*/*e* (relative intensity) 247 (M^+, 54), 219 (27), 207 (94), 178 (63), 165 (100), 41 (10); IR (cm^{-1}) 3008, 2246, 1510, 1444, 779; ^1H NMR (CCl_4) δ 1.59–2.37 (8 H, m), 2.76 (2 H, s), 7.17–7.94 (7 H, m); ^{13}C NMR (Cl_3CD, 20.15 MHz) δ 139.3 (s, C-1′ Naph), 137.1 (s, C-10′ Naph), 133.6 (s, C-9′ Naph), 130.4 (s, C-1 cyclohexene), 128.3 (d, C-5′ Naph), 127.3 (d, C-8′ Naph), 126.2 (d, C-4′ Naph), 125.8 (d, C-6′ Naph), 125.36 (d, C-3′ Naph), 125.06 (d, C-7′ Naph), 124.4 (d, C-2′ Naph), 124.12 (s, C-2 cyclohexene), 117.6 (s, CN), 32.3 (t, C-6 cyclohexene), 28.1 (t, C-3 cyclohexene), 22.5 (t, double intensity C-4 and C-5 cyclohexene). Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 86.93; H, 6.72; N, 5.52. The other isomer 2-(1-naphthyl)cyclohexylideneacetonitrile (**8b**) (in small amount) could not be obtained in pure form, but the ^1H NMR (26% **8a**, 74% **8b**) (CCl_4) is δ 1.58–2.00 (8 H, m), 5.07 (1 H, s), 5.94 (1 H, d), 7.17–8.02 (7 H, m); ^{13}C NMR (Cl_3CD) δ 133.9 (s, C-1), 131.75 (s, C-1′ Naph), 130.7 (s, C-10′ Naph), 129.6 (s, C-9′ Naph), 128.5 (d, double intensity, Naph), 127.4 (d, C-6′ Naph), 126.5 (d, C-3′ Naph), 125.6 (d, C-4′ Naph), 125.1 (d, C-2′ Naph), 119.4 (s, CN), 41.6 (d, C-2), 26.6 (t, C-3), 25.1 (t, C-6), 22.4 (t, C-4), 21.55 (t, C-4); **9** was also isolated in a small amount, and its mass spectrum suggests the disubstitution product: MS, *m*/*e* (relative intensity) 374 (10), 337 (18), 327 (11), 278 (15), 247 (82), 216 (37), 206 (2), 204 (41), 190 (100), 178 (33), 165 (62), 128 (30), 81 (20).

Acknowledgment. INFIQC is jointly sponsored by the Consejo Nacional de Investigaciones Cientificas y Técnicas and the Universidad Nacional de Córdoba. This work is partially supported by the Consejo de Investigaciones de la Provincia de Córdoba, Argentina.

Registry No. 1, 4435-18-1; **2**, 116998-10-8; **3a**, 116998-11-9; **3b**, 116998-12-0; **4**, 116998-13-1; **7**, 90-14-2; **8a**, 116998-14-2; **8b**, 116998-15-3; *p*-BrAn, 104-92-7; *p*-IAn, 696-62-8; 1,4-dinitrobenzene, 100-25-4.

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