Hidden Ambident Reactivity and Electron Transfer Reactions: Solvent and Magnetic Field Effects in the Reaction of *p*-Nitrobenzyl Bromide with Lithium Salt of 2-Nitropropane

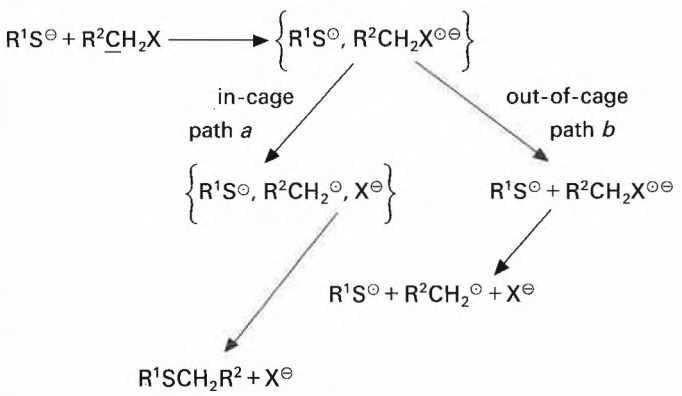
Michel Julliard, Jean-Paul Scagliarini, Michel Rajzmann, and Michel Chanon*

Abstract: Absence of magnetic field effects and variation of solvent viscosity effects on *O*- versus *C*-alkylation of *p*-nitrobenzyl halides with nitronate anions suggest the possibility of hidden electrophilic ambident reactivity. This new concept could provide in some cases an alternative to the in-cage versus out-of-cage scenario. It has applications at the theoretical level and provides a convenient handle to master the selectivity of some processes.

Ambident[1] reactivity is ubiquitous in chemistry; indeed, nucleophilic[2] as well as electrophilic[3] reagents may exhibit this property. The first experimental earmark of an ambident reagent is that isomeric intermediates or products are formed in the reaction studied. In some cases, demonstration of the presence of isomers demands isotopic labeling[4].

Almost as pervasive as ambident reactivity is the notion of selectivity originating from the solvent cage effect[5]. In this concept, it is proposed that product selectivity originates in a common solvent cage: some products would result from an in-cage recombination of intermediates, while some would form after the intermediates had escaped from the cage. *Surzur*'s[6] proposition for benzylic substitution (Scheme 1) illustrates how this concept operates.

Scheme 1



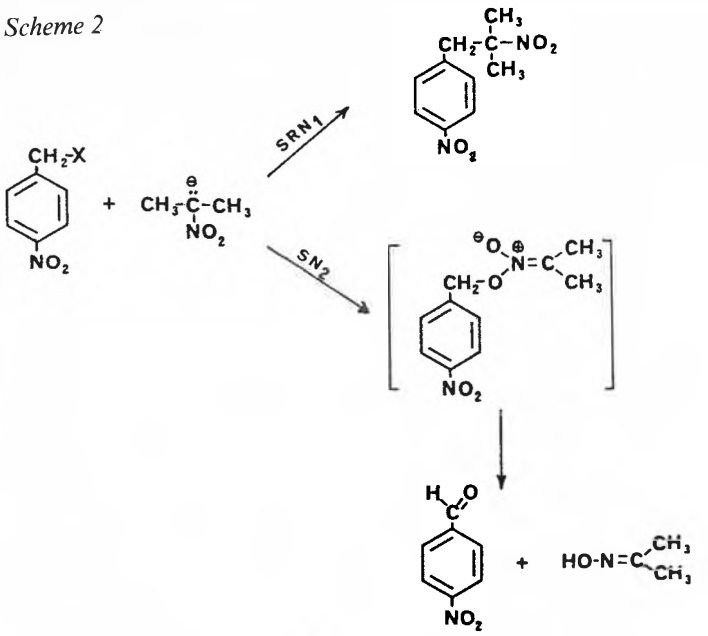
Small amounts of radicals escaping from the solvent cage initiate a polymerization whose products may be measured by simple weighing whereas in-cage recombination leads to the main substitution product. The concept of in-cage versus out-of-cage reactivity is widely used in organic[7], organometallic[8], inorganic[9], and polymer[10] chemistry. Such schemes have probably been most firmly supported using CIDNP[11] and photochemical techniques[12].

Support for both schemes (ambident reactivity and in-cage versus out-of-cage reactivity) relies heavily on the nature of the products formed. The *purpose of this report is to suggest that in some cases the two schemes overlap strongly and that experiments which are usually explained in the framework of the scheme may, in fact, be the result of the other provided that one accepts the concept of «hidden ambident reactivity»*. The word *hidden* stands to indicate that the nature of the final products (even if one uses isotopic labeling) does not give an hint for the intervention of ambident reactivity at a given step of the overall mechanism. For example in the case of *p*-nitrobenzyl bromide that we are going to study in this report the formed products suggest that all the molecular events starting from the reagents going to products involve the underlined (scheme 1) electrophilic carbon atom. Nevertheless, in addition to this obvious electrophilic center, the *p*-nitrobenzyl substrate possesses another electrophilic center which must be recognized to rationalize the overall pattern of reactivity displayed by this substrate. This second, «hidden» electrophilic center, is delocalized on the nitro group and the aromatic ring. It accepts one electron from the nucleophile in an outer-sphere or inner-sphere without atom transfer process[20]. This first electron transfer is then followed by a rapid intramolecular electron transfer from this hidden electrophilic center to the apparent electrophilic center which is strongly activated by this transfer.

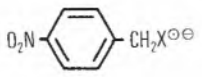
The reaction of the lithium salt of 2-nitropropane with 4-nitrobenzyl bromide (Scheme 2) has been rationalized by proposing that «oxygen alkylation is the consequence of a simple S_N2 displacement by the nitro paraffin anion on the alkyl halide and – in 1964 – that carbon alkylation derives from an electron transfer process in which radical anions and free radicals are intermediates»[13]. Several views have been expressed concerning the molecular crossroad at which the selectivity is determined in this reaction and in nucleophilic displacement reactions in general. One view generalizes *Walling*'s earlier proposition[14] of mesomeric representations of transition states including both paramagnetic and diamagnetic canonical wavefunctions; it has been proposed for the C electrophilic center by *Bilevitch* et al.[15] and then by *Bank* and *Noyd*[16] and later thoroughly discussed by *Pross* and *Shaik*[17] within the valence bond formalism. Another view results from stereochemical studies of the alkylation of the anthracene radical anion by optically active 2-octyl halides (I, Br, Cl, F). The authors of this work[18] propose that «the properly oriented reactant pairs will undergo an energetically facile reaction leading to bond formation with inversion of the configuration inside the solvent cage whereas the reactant pairs that do not possess this privileged orientation but have a sufficiently higher energy will exchange one electron». This view cannot be directly related to the *p*-nitrobenzyl halide case because in the same paper the authors estimate the variation of the electron transfer rate constant with the halogen in the C–I, C–Br, C–Cl series, and observed a large variation: 10^3 M^{-1} s^{-1} for RBr, 0.3 $M^{-1}s^{-1}$ for RCl. This variation is in the opposite direction to the observed selectivities in the *p*-nitrobenzyl halide series; it is clear that for this series the proportion of the electron transfer component is higher when X = Cl than when X = Br[13].

* *Correspondence:* Prof. Dr. M. Chanon
Laboratoire de Chimie Inorganique Moléculaire, U.A. 126
Faculté des Sciences et Techniques de Saint Jérôme
Rue Henri Poincaré, F-13397 Marseille Cedex 13 (France)

Scheme 2



We wish to *verify experimentally whether the point in the molecular crossroad at which selectivity is determined originates in a common solvent cage or elsewhere:* Here the *C*-alkylation would result through escape from the solvent cage and the development of a chain reaction (path *b* in Scheme 1), and the *O*-alkylation product would result from an in-cage recombination (path *a* in Scheme 1). In 1980, *Neta* et al.[19] reported pulse radiolysis experiments which appear to assign meaning to the foregoing experiments. *Neta*'s results show that when a pulse of electron is directed to *p*-nitrobenzyl halides, the first transient observed is the radical anion



which then is cleaved at a measurable rate to form the *p*-nitrobenzyl radical and halide ion. These results suggest that one could propose an alternative to the foregoing (Scheme 1) in-cage versus out-of-cage molecular description when an oxidizable nucleophile attacks *p*-nitrobenzyl halide. This description would be that of electrophilic ambident reactivity in which one electrophilic center is the sp^3-C carbon atom (underlined in Scheme 1) and the other one (hidden) is the molecular orbital centered mainly on NO_2 and Aryl (Table 3). On the first center, reactivity would involve a transition state with high inner-sphere character (i.e. S_N2) whereas the second one would involve a transition state more of an outer-sphere type[20]. In such a picture, the crossroad of selectivity *would be earlier in the succession of events* than as is suggested by the in-cage versus out-of-cage scenario.

In an attempt to discriminate between the model suggested by *Neta*'s experiments and the in-cage versus out-of-cage depiction, we have used the methodology devised by photochemists[12] to study the fate of paramagnetic species formed in a cage. This methodology rests on the study of the reaction in the presence of magnetic fields and without magnetic fields and on the effect of viscosity on the selectivity of products formed. The results listed in Tables 1 and 2 show that neither the magnetic field effect (Table 1) nor viscosity effects (Table 2) are in the direction expected for a representation involving in-cage versus out-of-cage reactivity. Within such a scenario, magnetic fields should influence selectivity provided that the lifetime of the in-cage radicals is long enough to allow spin polarization[11]. In another electron transfer induced reaction, *Holm* et al.[21] have reported the same kind of selectivity independence with respect to magnetic field modifications. On the other hand, no magnetic field effects on selectivity are expected in the «hidden ambident reactivity» scenario. Viscosity effects argue even more clearly against the in-cage versus out-of-cage scenario because the decrease in *O*-alkylation when the viscosity of the solvent increases (Table 2) is exactly the opposite of what would be expected within such a scenario. The foregoing results therefore draw one's attention to the point that for some substrates, the in-cage versus out-of-cage scenario does present an alternative which should be considered in discussions. MNDO (*m*odified *n*eglect of *d*iatomic *o*verlap) calculations on the *p*-nitrobenzyl chloride system allow to quantify this alternative. The values of the coefficients associated with the atomic orbitals in the frontier molecular orbitals given in Table 3 show that the LUMO (i.e. the place where the in-coming electron should go) is mainly localized in the C^5NO_2 part of the molecule. This localization is, however, not complete and thus should allow a facile intramolecular electron transfer to C^6, where a good overlap with the σ^* C–Cl bond (molecular orbital no. 33) allows an efficient bond activation. Consideration of the coefficients in the HOMO shows that the notion of hidden ambident reactivity could be even more prevalent in the photochemically stimulated reaction. It is indeed clear that the HOMO is strongly localized on the NO_2 part of *p*-nitrobenzyl chloride. After excitation, the «hole» created by the electron transfering from the HOMO to the LUMO should, therefore, be strongly localized on the NO_2, thereby attracting attack at this part of the molecule. Table 3 also points out the possible importance of conformers in the act of electron transfer activation. When the C–Cl bond is oriented perpendicular to the plane defined by the carbon atoms of the benzene ring, it overlaps far better with the LUMO (MO no. 30) than it does when it is parallel to this plane. In the perpendicular conformation the intramolecular electron transfer from the π^* type LUMO to the σ^* C–X bond orbital should be much more probable.

The substrates for which the possibility of hidden ambident reactivity should be examined are those in which a good *captor* (electron acceptor, i.e. NO_2, $C^{\oplus}$, C=O, CN, $M(CO)_n$ where M = transition metal)[22] is present in the structure in a position, relative to the electrophilic center, such that (either through conjugation

Table 1. Magnetic field effect on the rates of the $S_{RN}1$ and S_N2 channels for the nucleophilic substitution reaction of 4-nitrobenzyl bromide with the 2-nitropropan-2-id ion ($Li^{\oplus}$ counterion).

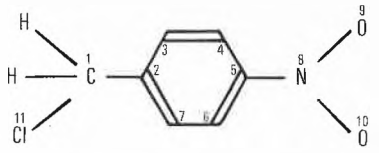
Magnetic field intensity B^* [G]	Ethanol		Diethylene glycol	
	C-Alkylation [%]	*O*-Alkylation [%]	*C*-Alkylation [%]	*O*-Alkylation [%]
0.5	38	29	36	32
21 000	34	28	40	34

Table 2. Irradiation and solvent effect on the $S_{RN}1$ and S_N2 channels for the nucleophilic substitution reaction of 4-nitrobenzyl bromide with the 2-nitropropan-2-id ion ($Li^{\oplus}$ counterion). Concentrations: $NO_2C_6H_4CH_2Br$ 5×10^{-3} M, $(CH_3)_2CNO_2^{\ominus}$ 15×10^{-2} M.

Solvent	*T* [°C]	*hv*	*C*-alkylation [%]	*O*-alkylation [%]	*O*-alkylation / *C*-alkylation
Ethanol	60	no	35	55	1.58
	20	no	5	65	13
	− 18	yes	78	2	0.025
	− 18	no	no reaction after 2 days		
Diethylene glycol	20	no	63	5	0.079
	20	yes	55	0	0
	− 18	yes	80	0	0
Diethylene glycol + TCNQ	− 18	yes	no reaction after 2 days		

TCNQ = 7,7,8,8-Tetracyanoquinodimethane.

Table 3. Localization of frontier orbitals (MNDO) in *p*-nitrobenzyl chloride: with A) C–Cl in the plane defined by the σ-skeleton of C_6H_4, B) C–Cl perpendicular to this plane[a].



	MO number[b]	Energy[c]	Atomic orbital coefficients on main atoms[d]										
			1	2	3	4	5	6	7	8	9	10	11
A)	27	− 11.46	0	0	0	0	0	0	0	0	0.71	− 0.71	0
	28	− 10.68	0.14	− 0.54	− 0.34	0.17	0.55	0.24	− 0.27	0	− 0.13	− 0.13	0
	29 (HOMO)	− 10.57	0	0	− 0.48	− 0.51	0	0.49	0.52	0	0	0	0
	30 (LUMO)	− 1.54	0	− 0.49	0.21	0.33	− 0.44	0.35	0.20	− 0.29	0.27	0.27	0
	31	− 0.64	0	0	0.51	− 0.51	0	0.49	− 0.49	0	0	0	0
	32	0.13	0	− 0.34	0.24	0	− 0.25	0	0.28	0.58	− 0.40	− 0.40	0
	33	0.66	− 0.24	0	0	0	0	0	0	0	0	0	0.1
			0.21										0.21
			0.68										0.59
B)	28	− 10.74	0	− 0.55	− 0.31	0.21	0.56	0.21	− 0.30	0	− 0.13	− 0.13	− 0.15
	[e] 30 (LUMO)	− 1.64	− 0.12	− 0.48	0.22	0.33	− 0.44	0.33	0.22	− 0.28	0.26	0.26	− 0.16
	32	0.00	− 0.23	− 0.28	0.26	0	− 0.18	0	0.26	0.56	− 0.39	− 0.39	− 0.22
	33	0.92	− 0.21	0.12	0	− 0.23[f]	− 0.32[f]	− 0.23[f]	0	− 0.25[f]	0.15[f]	0.15[f]	0
			0.19										0.16
			0										− 0.47[f]
			− 0.55[f]										− 0.47[f]

[a] Calculations have been performed on Cl rather than on Br for saving computing time: this should not affect the conclusions that we extract from these data. [b] The atomic orbital basis is made of 50 orbitals and we have therefore 50 molecular orbitals. [c] In e.t. [d] When π-type MO the figure stands for the coefficient of p_z; when σ-type MO the coefficients are given in the order s, p_z, p_y. [e] Only the MO where the conformation of C–Cl plays a role are indicated; the other ones remain unchanged in their localization. [f] p_z.

or favourable orbital overlap) the captor can activate the center by intramolecular electron transfer. Examples may be found in the literature[23]. One particular situation is provided when only the product from a hidden remote attack is formed[24,]. In such a case the term «ambident» must be discarded but the basic principle remains the same. From what is known concerning the relative rates of inner-sphere and outer-sphere electron transfer processes, one expects the foregoing type of competition to preferentially occur when the electrophilic center involving the inner-sphere process is deactivated (for example, by a poor leaving group, or by steric hindrance). The foregoing proposition may also be extended to the hidden ambident reactivity of nucleophilic[25] substrates by replacing the term «good captor» in the preceding discussion with «good electron donor» and «electron» with «hole». If the activation induced by electron transfer is very strong the lifetime of the intermediate involved in the «hidden» mechanistic pathway may be short enough to make difficult any direct chemical observation (possible examples in[7]).

Hidden ambident reactivity has consequences in theoretical approaches to reactivity. In the only theoretical treatment of reactivity performed on *p*-nitrobenzyl halide substrates, the implicit assumption was made that the nucleophile must approach on the sp^3-C side, thus giving rise to an incomplete potential energy surface[26]. If the hidden ambident reactivity hypothesis is sound, one should examine a broader potential energy surface and we would expect at least two saddle points on this surface: one corresponding to a spatial conformation in which the nucleophile is near the benzylic carbon atom and the other corresponding to a spatial conformation in which the nucleophile is near the NO_2 substituent. Computations in this direction are in progress.

Another theoretical consequence is that if one wishes to apply the Marcus theory[22] to substrates presenting the possibility of hidden ambident reactivity, the structural modifications to be taken into account in the reorganization energy term must be those of the captor and not those of the apparently reactive center[27]. Hidden ambident reactivity and hidden remote attack provide another[22] example of a molecular concept well accepted in inorganic chemistry[28] but little used in organic chemistry.

A practical consequence of hidden ambident reactivity follows from the fact that one electrophilic center displays an inner-sphere type of transition state whereas the other one is more outer-sphere in character[20]. The former one usually cannot be photostimulated whereas the second can. Therefore to increase the selectivity of the reaction involving the outer-sphere process (here *C*-alkylation) one may lower the temperature to suppress the inner-sphere component of the overall transformation and irradiate with light to favour predominantly C–C bond formation (Table 2, third entry).

Experimental Section

General methods: ^{1}H-NMR spectra were recorded on a Varian EM 360 spectrometer in $CDCl_3$ or $(CD_3)_2SO$ with tetramethylsilane as an internal standard. Magnetic field effects and CIDNP experiments were performed on a Perkin Elmer R32 (21 000 gauss) spectrometer at 35 °C in methanol and at 60 °C in diethylene glycol. – The mass spectra were obtained by using a high resolution mass spectrometer. Gas chromatographic analyses were performed on a Intersmat IGC 121 FL instrument fitted with a flame ionization detector. A 2m × 1/8 in stainless steel column packed with 10% silicon SE 30 on chromosorb WAW DMCS, 80–100 mesh was used. The chromatograph was coupled with an ENICA 10, DELSI integrator.

Preparation of the lithium salt of 2-nitropropane: 1.74 g (0.25 mol) of Li metal cleaned with CCl_4 were dissolved in 250 mL of dried ethanol. 23 g (0.25 mol) of freshly distilled 2-nitropropane were added. The solution was kept at 20 °C under stirring for 3 h. The solvent was then removed under vacuum and the residual lithium salt of 2-nitropropane (white solid, *m.p.* 250 °C) was kept into a closed flask in the dark.

Reaction of 4-nitrobenzyl halide with the anion of 2-nitropropane: 6×10^{-4} mol of 4-nitrobenzyl bromide were dissolved into 50 mL of dried ethanol. The flask was thermostated so that the temperature of the medium had a value of 70 °C during the reaction time (70 min). 8.5×10^{-4} mol of sodium or lithium salt of 2-nitropropane were added and the mixture was stirred until complete consumption of 4-nitrobenzyl halide (GLC test). The solution was acidified and concentrated under vacuum. The white precipitate of lithium or sodium halide was removed by filtration. The filtrate was diluted with ether, concentrated by distillation, the precipitate was filtered, and the residual solution was kept for GLC analysis.

Identification of the 2-nitro-2-methyl-1-(4-nitrophenyl)propane (C-alkylation product): The solution for CPV analysis was washed with a saturated $NaHSO_3$ solution, the 4-nitrobenzaldehyde (*O*-alkylation product)–$NaHSO_3$ complex was filtered, and the residual solution was evaporated. The yellow residue was recristallized in a 1:1 water–ethanol mixture, and dried under vacuum (80% yield for the reaction of 4-nitrobenzyl chloride with 2-nitropropane); *m.p.* 65 °C. ^{1}H-NMR ($CDCl_3$); δ = 1.52 (s, 6H, CH_3), 3.30 (s, 2 H, benzylic CH_2), 7.60–7.75 (d, 2 H, H arom.), 8.13–8.28 (d, 2 H, H arom.). Elemental analysis correct for $C_{10}H_{12}N_2O_4$ (224.22).

Identification of the 4-nitrobenzaldehyde (O-alkylation product): It was performed by identification of the GLC signal with a commercial sample.

Magnetic field effect on the $S_{RN}1/S_N2$ ratio: Two reactions were performed at the same time: one in a R32 Perkin Elmer spectrometer (21 000 gauss), the other in a thermostated bath in the magnetic field of the earth and without light. The temperatures were 35 °C in ethanol and 60 °C in diethylene glycol. In a typical run 81 mg (8.5×10^{-4} mol) of sodium salt of 2-nitropropane were added to 130 mg (6×10^{-4} mol) of 4-nitrobenzyl bromide dissolved in 10 mL of solvent. The reaction time was 80 min. – Solvent ethanol: When the reaction was complete, the solution was worked up as in the general procedure. – Solvent diethylene glycol: After reaction, the solution was washed with an equivalent amount of acetic acid–water (1:1 mixture). The reaction products were extracted with several portions of ether–chloroform (1:1). The extract was concentrated and dried over sodium sulfate. – In the two cases,

the ratio *C*-alkylation product/*O*-alkylation product was determined by GLC analysis.

Photochemical techniques: The photostimulated reactions were performed in pyrex tubes irradiated by a medium pressure Hg lamp (HANAU Q 81) cooled by a pyrex water-jacket. For the low temperature (−18 °C) reactions water was removed from the jacket, the lamp and the tubes were immerged in a methanol bath whose temperature was kept low by a thermostated cooling machine. In a typical run 57 mg (6×10^{-4} mol) of lithium salt of 2-nitropropane dissolved in 3 mL dimethylformamide (DMF) at −18 °C were added to 42.6 mg (2×10^{-4} mol) of 4-nitrobenzyl bromide dissolved in 1 mL DMF at −18 °C. The mixture was irradiated until the reaction was complete and worked up as in the general procedure.

Received: November 25, 1985 [FC 47]

[1] N. Kornblum, A.P. Lurie, *J. Am. Chem. Soc. 81* (1959) 2705.
[2] J. March: *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure,* 2nd Ed., McGraw Hill, London (1977), p. 338; S.A., Shevelev, *Russ. Chem. Rev. 39* (1970) 844; R. Gompper, *Angew. Chem. 76* (1964) 412; *Angew. Chem. Int. Ed. Engl. 3* (1964) 560; N. Kornblum, R.R. Smiley, R.K. Blackwood, D.C. Iffland, *J. Am. Chem. Soc. 77* (1955) 6269; A.L. Kurts, I.P. Beletskaya, *Bull. Acad. Sci. USSR Div. Chem. Sci.* (1970) 781; A.H., Norbury, A.I.P. Sinha, *Q. Rev. Chem. Soc. 24* (1970) 69; P.A.S. Smith, G.L. De Wall, *J. Am. Chem. Soc. 99* (1977) 5751; M. Ono, *Yuki Gosei Kagaku Kyokai Shi 38* (1980) 836.
[3] R.A., Wohl, *Chimia 28* (1974) 1; D.N. Kirk, *Chem. Ind. London* (1973) 109; J.G. Buchanan, H.Z. Sable, *Sel. Org. Transform. 2* (1972) 1; A.A. Akhrem, A.M. Moiseenkov, V.N. Dobrynin, *Russ. Chem. Rev. 37* (1968) 448; R.J. Gritter, in S. Pataï (Ed.): *The Chemistry of the Ether Linkage,* Wiley-Interscience, New York (1967), p. 390; R.E. Parker, N.S. Isaacs, *Chem. Rev. 59* (1959) 737; M. Ono, *Yuki Gosei Kagaku Kyokai Shi 38* (1980) 923.
[4] J.D. Roberts, H.E. Simmons, L.A. Carlsmith, C.W. Vaughan, *J. Am. Chem. Soc. 75* (1953) 3290; M. Polanyi, A.L. Szabo, *Trans. Faraday Soc. 30* (1934) 508; H.C. Van der Plas, *Acc. Chem. Res. 11* (1978) 462.
[5] E.S. Amis: *Solvent Effects on Reaction Rates and Mechanisms,* Academic Press, New York (1966), p. 192–199; E.M. Kosower: *Physical Organic Chemistry,* Wiley, New York (1968), p. 352.
[6] E. Flesia, M.P. Crozet, J.M. Surzur, M. Jauffred, C. Ghiglione, *Tetrahedron 34* (1978) 1699.
[7] L. Horner, E. Schwenk, *Angew. Chem. 61* (1949) 411; L. Horner, *J. Polym. Sci. 18* (1955) 438; J.J. Zupancic, K.A. Horn, G.B. Schuster, *J. Am. Chem. Soc. 102* (1980) 5279; G.A. Olah, V.V. Krishnamurthy, *ibid. 104* (1982) 3987; D.S. Grierson, H.P. Husson, *J. Chem. Soc. Chem. Commun.* (1983) 891; W.A. Pryor, W.H. Hendrikson, *J. Am. Chem. Soc. 105* (1983) 7114; W.H. Hendrikson, W.D. McDonald, S.T. Howard, E.J. Cologado, *Tetrahedron Lett. 26* (1985) 2939.
[8] J.K. Kochi: *Organometallic Mechanisms and Catalysis,* Academic Press, New York (1978), p. 167, 350, 358, 360, 420, 514, 519, 523; T.T. Tsou, J.K. Kochi, *J. Am. Chem. Soc. 101* (1979) 6319; F.C. Ashby, R. De Priest, *ibid. 104* (1982) 6144; H.G. Kuivila, M.S. Alnajjar, *ibid. 104* (1982) 6146.
[9] A.C. Harkness, J. Halpern, *J. Am. Chem. Soc. 81* (1959) 3526; F.A. Jones, E.S. Amis, *J. Inorg. Nucl. Chem. 26* (1964) 1045.
[10] N.J. Turro, M. Grätzel, A.M. Braun *Angew. Chem. 92* (1980) 712; *Angew. Chem. Int. Ed. Engl. 19* (1980) 675.
[11] L.T. Muus, P.W. Atkins, K.A. McLauchlan, J.B. Pedersen: *Chemically Induced Dynamic Nuclear Polarization,* Reidel, Dordrecht (1977).
[12] I.R. Gould, N.J. Turro, M.B. Zimmt, *Adv. Phys. Org. Chem. 20* (1984) 1; see also S.L. Mattes, S. Farid, *J. Am. Chem. Soc. 105* (1983) 1386.
[13] Kornblum N., in S. Patai (Ed.): *The Chemistry of Functional Groups, Supplement F: The Chemistry of Amino, Nitroso, and Nitro Compounds and their Derivatives,* Wiley-Interscience, New York (1982), p. 361.
[14] C. Walling, Mc Elhill, *J. Am. Chem. Soc. 73* (1951) 2927; G.A. Russell, *Tetrahedron 5* (1959) 101.
[15] K.A. Bilevich, O.Yu. Okhlobystin, *Russ. Chem. Rev. 37* (1968) 12.
[16] D. Noyd, *«Investigation of Possible Electron-Transfer Contributions to Some Bimolecular Displacement Reactions»,* Ph. D. Dissertation, State University of New York at Albany (1972).
[17] S.S. Shaik, *J. Am. Chem. Soc. 103* (1981) 3692; A. Pross, *Acc. Chem. Res. 18* (1985) 212.
[18] E. Hebert, J.P. Mazaleyrat, Z. Welvart, J.M. Saveant, J. Nadjo, *Nouv. J. Chim. 9* (1985) 75.
[19] P. Neta, D. Behar, *J. Am. Chem. Soc. 102* (1980) 4798.
[20] For the distinction inner-sphere/outer-sphere processes as applied to organic substrates see M. Julliard, M. Chanon, *Chem. Rev. 83* (1983) 425. – In the case of *p*-nitrobenzyl halide substrates, another possibility has to be considered too: the observation of CTC could suggest that an inner-sphere electron transfer without atom transfer better describes the molecular event taking place on the «hidden» electrophilic center. This question is under study in our group.
[21] T. Holm, I. Crossland, *Acta Chem. Scand. B33* (1979) 421.
[22] L. Eberson, *Adv. Phys. Org. Chem. 18* (1982) 79. – One should stress that captors seem even more efficient when directly linked to an aromatic or heteroaromatic system.
[23] H. Stamm, P. Assithianakis, B. Buchholz, R. Weiss, *Tetrahedron Lett. 23* (1982) 5021.
[24] H.M. Walborsky, E.J. Powers, *Isr. J. Chem. 21* (1981) 210; T. Sato, T. Wada, Y. Komeichi, M. Kainosho, *Bull. Chem. Soc. Jpn. 58* (1985) 1452.
[25] J. Halpern, *Angew. Chem. 97* (1985) 308; *Angew. Chem. Int. Ed. Engl. 24* (1985) 279.
[26] B. Bigot, D. Roux, L. Salem, *J. Am. Chem. Soc. 103* (1981) 5271.
[27] L. Eberson, *Acta Chem. Scand. B 36* (1982) 533.
[28] M.Z. Hoffman, M. Simic, *J. Chem. Educ. 58* (1981) 109; R.D. Cannon: *Electron Transfer Reactions,* Butterworth, London (1980), p. 155–161, 230–237; E.S. Gould, *Acc. Chem. Res. 18* (1985) 22.