360 J. Org. Chem. 1980, 45, 360-361

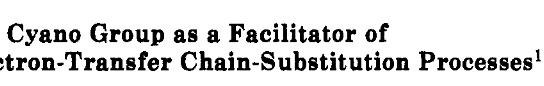
Communications

The Cyano Group as a Facilitator of Electron-Transfer Chain-Substitution Processes[1]

Summary: Electron-transfer chain substitution at a saturated carbon atom has been achieved for the first time in the absence of nitro groups.

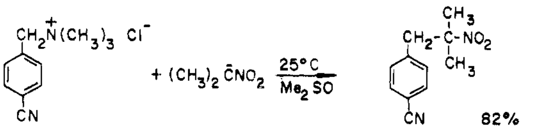
Sir: It is now generally recognized that nucleophilic substitution at a saturated carbon atom may proceed as an electron-transfer chain reaction.[2] But, while there are numerous examples of such processes, it is noteworthy that in every instance a nitro group is present either in the compound undergoing substitution or in the attacking nucleophile. On the basis of the available evidence it might, therefore, appear that a nitro group is necessary for electron-transfer chain substitution at a saturated carbon atom; this paper provides a demonstration that such is not the case.

To begin with, it is not necessary to have a nitro group in the compound undergoing substitution.[3] Thus, when *p*-cyanobenzyl chloride reacts with the lithium salt of 2-nitropropane, the aldehyde, i.e., the oxygen alkylate, is produced (eq 1) and this, it is now generally accepted,



(1)

derives from a simple S_N2 displacement process.[4,2a,3] In contrast, treatment of (*p*-cyanobenzyl)trimethylammonium chloride with the lithium salt of 2-nitropropane gives the carbon alkylate (eq 2).[5] Here, with a difficultly displaced



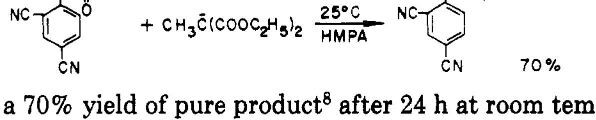
(2)

leaving group the electron-transfer chain reaction has a chance to compete and, as a consequence, carbon alkylation of the nitro paraffin anion is observed. Strong support for this mechanistic assignment is provided by the fact that the reaction of eq 2 is completely inhibited by 20 mol % of *m*-dinitrobenzene or di-*tert*-butyl nitroxide.[6] And it does not proceed in the dark.[7] The transformation of eq

(3)

3 again illustrates the point that it is not necessary to have a nitro group in the compound undergoing substitution. With chlorine on a tertiary carbon atom the S_N2 displacement does not compete and the cyano group facilitates electon-transfer chain substitution. In accord with this view, *m*-dinitrobenzene and di-*tert*-butyl nitroxide inhibit the reaction and light accelerates it.[7]

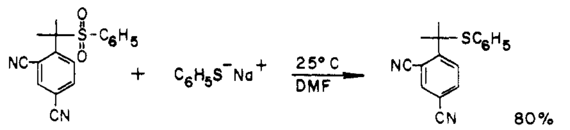
The processes of eq 4 and 5 are of special interest because they demonstrate that electron-transfer chain substitution can occur even when the compound undergoing substitution and the nucleophile are devoid of nitro groups. Thus, treatment of *o*,*p*-dicyano-α-phenylsulfonylcumene with the sodium salt of diethyl methylmalonate (eq 4) gives



(4)

a 70% yield of pure product[8] after 24 h at room temperature.[7] That this is indeed an electron-transfer chain process is clear from the fact that this reaction does not occur in the dark and it is inhibited by 20 mol % of *m*-dinitrobenzene or by 20 mol % of di-*tert*-butyl nitroxide.[6]

The transformation of eq 5 occurs in less than 10 min at 25 °C and the pure sulfide is isolated in 80% yield.[9] This reaction is also inhibited by di-*tert*-butyl nitroxide.



(5)

The experiments of eq 6 and 7 provide yet another demonstration of the ability of cyano groups to foster electron-transfer chain substitution. For, whereas the

---

[1] From the Ph.D. thesis of M. J. Fifolt, Purdue University, December 1977. This is paper 23 in the series "Substitution Reactions Which Proceed via Radical Anion Intermediates". For the preceding paper, see H. Feuer, J. K. Doty, and N. Kornblum, *J. Heterocycl. Chem.*, **15**, 1419 (1978).

[2] (a) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975); (b) N. Kornblum, S. C. Carlson, and R. G. Smith, *J. Am. Chem. Soc.*, **101**, 647 (1979). The replacement of SCH_3 by hydrogen in cumylic systems presumably is another example of an electron-transfer chain process in which nitro groups are not involved. This matter is being investigated. (c) Electron-transfer substitution by a nonchain process in the absence of nitro groups is well recognized. For example, P. J. Krusic, P. J. Fagan, and J. San Filippo, *J. Am. Chem. Soc.*, **99**, 250 (1977); B. W. Bangerter, R. P. Beatty, J. K. Kouba, and S. S. Wreford, *J. Org. Chem.*, **42**, 3247 (1977); J. San Filippo, J. Silbermann, and P. J. Fagan, *J. Am. Chem. Soc.*, **100**, 4834 (1978).

[3] Subsequent to the completion of this work[1] an interesting and useful example of such a process was reported in which the mercury of organomercury halides is displaced by nitro paraffin anions: G. A. Russell, J. Hershberger, and K. Owens, *J. Am. Chem. Soc.*, **101**, 1312 (1979).

[4] N. Kornblum, P. Pink, and K. V. Yorka, *J. Am. Chem. Soc.*, **83**, 2779 (1961).

[5] About 3% of the product suffers loss of HNO_2 to give the olefin.

[6] These are, respectively, diagnostics for radical anions and free radicals.[2]

[7] The reaction flask was held under two 20-W ordinary fluorescent lights.

[8] Satisfactory elemental analyses and NMR spectra were obtained for all new compounds.

[9] The following is a typical example. Under N_2 0.528 g (4 mmol) of sodium thiophenoxide[10] was dissolved in 10 mL of DMF and, then, 0.310 g (1 mmol) of *o*,*p*-dicyano-α-phenylsulfonylcumene was added without opening the system.[11] The resulting orange solution was stirred for 10 min[7] and then was poured into water containing NaCl. After repeated extraction with ethyl ether and then with benzene the extracts were combined, back-washed with water, and dried ($MgSO_4$). Removal of the solvents gave 0.329 g of crude product which was dissolved in ethyl acetate–hexane (1:4) and chromatographed on silica gel. The resulting 0.285 g on recrystallization from hexane gave 0.222 g of white needles (80% yield), mp 85–86 °C.[12]

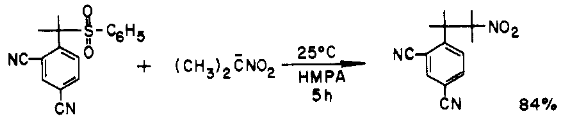
[10] Prepared as described for *p*-chlorothiophenol [N. Kornblum, S. D. Boyd, and N. Ono, *J. Am. Chem. Soc.*, **96**, 2587 (1974)].

[11] N. Kornblum, S. C. Carlson, J. Widmer, M. Fifolt, B. N. Newton, and R. G. Smith, *J. Org. Chem.*, **43**, 1397 (1978).

[12] In a separate experiment a dimorph was obtained: diamond-shaped plates, mp 89–90 °C.

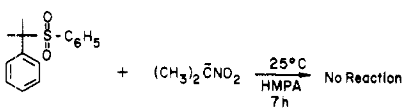
0022-3263/80/1945-0360$01.00/0

dicyano sulfone of eq 6 reacts rapidly with the lithium salt



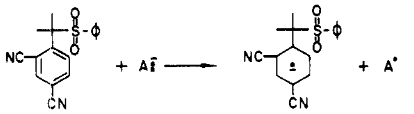
(6)

of 2-nitropropane and gives an 84% yield of the pure product,[13] there is no reaction when the unsubstituted sulfone of eq 7[14] is treated with the lithium salt of 2-nitropropane.

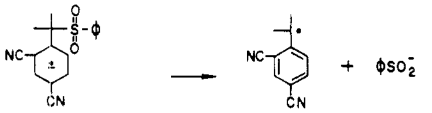


(7)

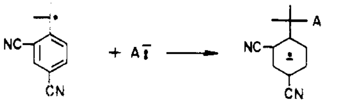
The reactions of eq 4 and 5 presumably proceed via the mechanistic sequence of eq 8–11. It is also apparent from



(8)



(9)



(10)

(11)

the transformations of eq 2 and 3 that monocyano compounds readily accept one electron from nitro paraffin salts to give radical anions and that these readily lose trimethylamine, or chloride ion, thereby giving rise to the corresponding radicals; i.e., the monocyano compounds exhibit characteristics analogous to those described by eq 8 and 9.[15]

Facilitation by the cyano group of electron-transfer chain substitution must involve the cyano group's ability to delocalize an electron. That a cyano group is converted to a cyano radical anion on exposure to a "high-pressure" source of electrons such as metallic sodium or lithium anthracene is well-known.[16] But the present studies do not involve potent one-electron donors and yet a chain reaction involving radical anions and free radicals is set up under very mild conditions. That this is so could not have been predicted since, electrochemically, cyano groups undergo one-electron reduction much more difficultly than nitro groups. That the capability of a single cyano group for fostering electron-transfer substitution may well be marginal is suggested by preliminary experiments in the *p*-cyanocumyl system using NaCN and NaN_3; in these two instances substitution has not been observed.[17]

Most important of all, it has now been demonstrated for the first time that electron-transfer chain substitution can occur at a saturated carbon atom in the complete absence of nitro groups and that these reactions are synthetically valuable. Aside from their intrinsic interest, the results herein presented lead one to anticipate that electron-attracting groups other than nitro and cyano, singly or in combination, will also be able to facilitate electron-transfer substitution at a saturated carbon—both chain and nonchain.

Acknowledgment. We thank the National Science Foundation for supporting this investigation.

Registry No. *o,p*-Dicyano-α-phenylsulfonylcumene, 72214-06-3; diethyl methylmalonate sodium salt, 18424-77-6; diethyl (α,α-dimethyl-*o,p*-dicyanobenzyl)methylmalonate, 72206-82-7; sodium benzenethiolate, 930-69-8; *o,p*-dicyano-α-phenylsulfmercaptocumene, 72206-82-7; 2-nitropropane lithium salt, 3958-63-2; *o,p*-dicyano-α-(2-nitro-2-propyl)cumene, 72206-83-8; *p*-cyanobenzyl chloride, 874-86-2; *p*-cyanobenzaldehyde, 105-07-7; *N,N,N*-trimethyl-*p*-cyanobenzylammonium chloride, 70579-08-7; 2-methyl-2-nitro-*p*-cyanophenylpropane, 72206-84-9; *p*-cyano-α-chlorocumene, 72206-85-0; *p*-cyano-α-(1-nitroethenyl)cumene, 65253-36-3; nitroethane ion, 25590-58-3.

Nathan Kornblum,* Michael J. Fifolt
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Received August 29, 1979

---

[13] The reaction of eq 6 shows all the characteristics of an electron-transfer chain reaction; it is inhibited by *m*-dinitrobenzene and by di-*tert*-butyl nitroxide, and it is speeded up by light.[7]

[14] Unpublished work by Dr. P. Ackermann, Purdue University.

[15] The demonstration that with monocyano compounds processes analogous to those of eq 10 and 11 occur will require the use of a nucleophile other than a nitro paraffin salt.

[16] C. Fabre and Z. Welvart, *C. R. Hebd. Seances Acad. Sci.*, 270, 1887 (1970); H. D. Hartzler, *J. Am. Chem. Soc.*, 93, 4527 (1971); J.-P. Mazaleyrat and Z. Welvart, *C. R. Hebd. Seances Acad. Sci.*, 274, 800 (1972); J. H. Wieringa, H. Wynberg, and J. Strating, *Tetrahedron Lett.*, 2071 (1972).

[17] These and related reactions are being studied with a view to defining the similiarities and differences in behavior of cyano and nitro compounds.

Lanthanide-Induced Chemical Shifts of Sulfonium Salts

Summary: Lanthanide shift reagents may be used in the structural elucidation of trialkyl- and dialkylarylsulfonium salts.

Sir: The use of lanthanide shift reagents (LSR) as tools in the structural elucidation of organosulfur compounds is well documented.[1] These reagents have routinely been used in the analysis of numerous tricoordinate sulfur(IV) species such as sulfoxides and sulfilimines; however, their application to the structural elucidation of sulfonium salts is virtually unknown.[2,3]

Lanthanide-induced shifts (LIS) have not been routinely applied to structural problems involving ionic moieties. The lack of work in this area is a result of the difficulty in obtaining solvents in which the shift reagent and sub-

---

[1] (a) W. H. Pirkle and D. L. Sikkenga, *J. Org. Chem.*, 40, 3430 (1975); (b) R. R. Fraser and Y. Y. Wigfield, *Chem. Commun.*, 1471 (1970); (c) R. M. Wing, J. J. Uebel, and K. K. Andersen, *J. Am. Chem. Soc.*, 95, 6046 (1973); (d) K. K. Andersen and J. J. Uebel, *Tetrahedron Lett.*, 5253 (1970); (e) R. R. Fraser, T. Durst, M. R. McClory, R. Viau, and Y. Y. Wigfield, *Int. J. Sulfur Chem.*, 1, 133 (1971).

[2] K. B. Lipkowitz, Ph.D. Dissertation, Montana State University, 1975 (Xerox University Microfilms No. 76-13,307). A LIS shift study on a sulfonium salt was performed; two modes of complexation were postulated, one involving complexation at the anion (iodide) and the second involving complexation at the electron pair on sulfur.

[3] (a) M. Casey, L. Blattner, and R. L. Caret, Abstracts, 12th Mid-Atlantic Regional Meeting of the American Chemical Society, Hunt Valley, MD, 1978, No. CU 2; (b) R. L. Caret, M. Casey, and A. Vennos, Abstracts, 13th Mid-Atlantic Regional Meeting of the American Chemical Society, West Long Branch, NJ, 1979, No. ORGN 34 and CU 4.