^{13}C NMR spectra were recorded on either a Varian Associates Model XL-100 spectrometer equipped with a variable-temperature probe or on a Varian Associates Model FT-80 spectrometer equipped with a broad-band variable-temperature probe. The chemical shifts in parts per million are referenced from capillary tetramethylsilane.

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Registry No. 2a, 29728-48-1; **2b**, 5857-67-0; **2c**, 40544-10-3; **3a**, 38256-01-8; **3b**, 54821-21-5; **3c**, 54781-14-5; **3d**, 80514-81-4; **3e**, 75782-41-1; **3f**, 80514-82-5; **3g**, 80514-83-6; **3h**, 80514-84-7; **3i**, 80514-85-8; **3j**, 80514-86-9; **7a**, 80514-87-0; **7b**, 80514-88-1; **7c**, 80514-89-2; **7e**, 80514-90-5; **7f**, 80514-91-6; **8**, 80514-92-7; 2,2,4,4-tetramethylpentane, 1070-87-7; di-*tert*-butylmethylium, 80514-93-8; 2,2,3,4,4-pentamethylpentane, 16747-45-8; 1,1-di-*tert*-butylethylium, 80514-94-9; 1,1′-methylenebistricyclo[3.3.1.1^{3,7}]decane, 54781-15-6; bis(tricyclo[3.3.1.1^{3,7}]decan-1-yl)-1,1-ethylidene, 75782-42-2; 1-adamantyl cyanide, 23074-42-2.

Regiochemistry of the Association Step in $S_{RN}1$ Reactions: Kinetically Controlled Coupling of *aci*-Nitronate Ions and *p*-Nitrobenzylic Radicals[1]

Robert K. Norris* and David Randles

Department of Organic Chemistry, The University of Sydney, NSW, 2006 Australia

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The regiochemistry of the coupling between *p*-nitrobenzylic radicals and *aci*-nitronate ions in the association step of $S_{RN}1$ reactions is shown to be dependent on steric factors. Branching at the carbon which is α to the reaction site causes a shift in product distribution toward O-alkylation (C–O bond formation) and away from C-alkylation (C–C bond formation). The association step is believed to be a kinetically controlled irreversible process. Evidence for lack of rearrangement of *aci*-nitronate esters to C-alkylates is presented.

Nucleophilic substitution at a saturated carbon by a reaction which involves a chain process having radical anions and free radicals as intermediates has been ably exploited by Kornblum and co-workers.[2] These reactions belong to a general class of substitutions which have been conveniently termed $S_{RN}1$.[3] The steps in this reaction for a *p*-nitrobenzylic substrate are presented in Scheme I.[4]

Our interest in these reactions was aroused by their apparent insensitivity to steric hindrance as amply demonstrated in the tertiary *p*-nitrocumyl system (Scheme I, $R^1 = R^2 = Me$).[2] In particular, we wished to prepare compounds such as **1** and **2** whose analogue **3**[5] and other related compounds[6] had been prepared by other workers in our department. The compound **3** and its analogues display dynamic NMR (DNMR) phenomena.[5-7] We wished to determine the effect on rotational barriers and conformational preferences of replacing the *tert*-butyl groups by the CMe_2NO_2 moiety. Our approach involved reaction of the substrates **4**, **5**, and **6** with lithium 2-nitro-2-propanide (**7**). These attempts were frustrated by the occurrence of an ionic chain substitution process with

Scheme I

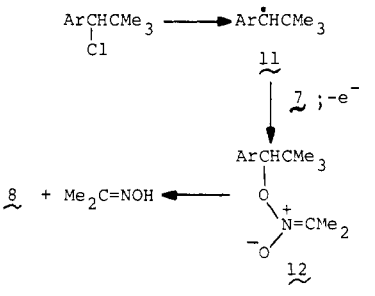
$$ArCR^1R^2X + A^- \longrightarrow [ArCR^1R^2X]^{\cdot -} + A^{\cdot} \quad (1)$$

$$[ArCR^1R^2X]^{\cdot -} \longrightarrow Ar\dot{C}R^1R^2 + X^- \quad (2)$$

$$Ar\dot{C}R^1R^2 + A^- \longrightarrow [ArCR^1R^2A]^{\cdot -} \quad (3)$$

$$[ArCR^1R^2A]^{\cdot -} + ArCR^1R^2X \longrightarrow ArCR^1R^2A + [ArCR^1R^2X]^{\cdot -} \quad (4)$$

Scheme II



4,[8] the incursion of a radical anion, radical chain elimination process (the $E_{RC}1$ reaction) with **5**,[9] and the exclusive formation of the ketone, **8**, with **6**.[10] The last reaction was clearly demonstrated to be occurring solely by an $S_{RN}1$ mechanism, unlike the lower homologues **9** and **10**, where S_N2 processes intruded.[10] The sole formation of **8** (none of the C-alkylate, **2**, was formed) was interpreted

(1) (a) Supported by Grant C73–15098 from the Australian Research Grants Committee. (b) Abstracted from the Ph.D. thesis of David Randles, The University of Sydney, Oct 1979.
(2) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.
(3) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 7463. Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.
(4) In this scheme and elsewhere in this paper, the abbreviation Ar stands for p-$O_2NC_6H_4$.
(5) Fallick, C. J.; Sternhell, S., unpublished data; Fallick, C. J. Ph.D. Thesis, The University of Sydney, 1979.
(6) Gall, R. E.; Landman, D.; Newsoroff, G. P.; Sternhell, S. *Aust. J. Chem.* **1972**, *25*, 109.
(7) Baas, J. M. A.; van der Toorn, J. M.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 133. Baas, J. M. A. *Ibit.* **1972**, *91*, 1287.
(8) Girdler, D. J.; Norris, R. K. *Tetrahedron Lett.* **1975**, 431. Freeman, D. J.; Newcombe, P. J.; Norris, R. K. *Aust. J. Chem.* **1976**, *29*, 327.
(9) Freeman, D. J.; Norris, R. K. *Aust. J. Chem.* **1976**, *29*, 2631.
(10) Norris, R. K.; Randles, D. *Aust. J. Chem.* **1976**, *29*, 2621.

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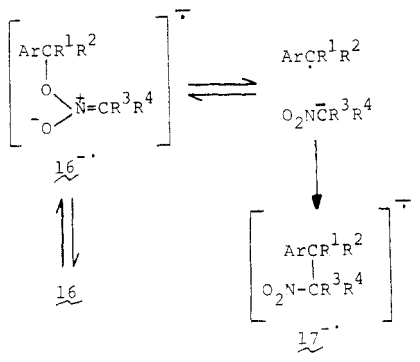
Scheme III



as arising from exclusive O-alkylation of the intermediate benzylic radical **11** under kinetic control, followed by eliminative loss of acetone oxime from the intermediate nitronate ester **12** (Scheme II).

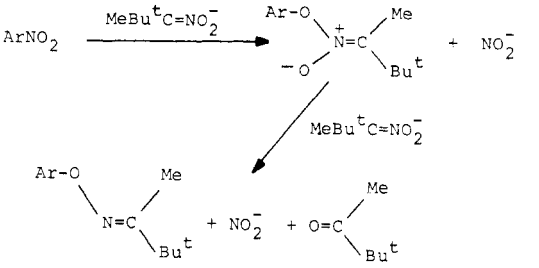
ArCHXY

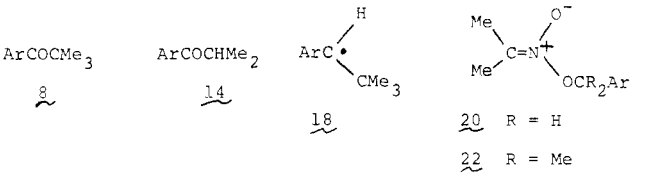
	X	Y		X	Y
1	CMe_2NO_2	CMe_2NO_2	9	Me	Cl
2	CMe_2NO_2	CMe_3	10	Et	Cl
3	CMe_3	CMe_3	13	$CHMe_2$	Cl
4	OAc	OAc	15	$CHMe_2$	$CHMe_2NO_2$
5	Cl	Cl	19	H	Cl
6	CMe_3	Cl			

A similar result was obtained with the α-isopropyl chloride **13** wherein the major product was the ketone **14**, together with small amounts ($\leq$7%) of the C-alkylate **15**.[11]

These results, which caused us to believe that steric effects do have significant consequences on the regiochemistry of $S_{RN}1$ reactions, have been discussed in a recent publication and have been described as being derived from "a system (which) has built-in ambiguities which effectively preclude the obtaining of meaningful results".[12] The basis of the objection to our interpretation rests on the possibility of kinetically formed O-alkylates, **16**, isomerizing into the usually more thermodynamically stable *C*-alkylates, **17**, under $S_{RN}1$ conditions, as shown in Scheme III. This possibility was proposed[12] by analogy with the demonstrated conversion of *p*-nitrobenzylic sulfinate esters into the isomeric sulfones.[13] If this proposed transformation of O-alkylates (**16**) into C-alkylates (**17**) were indeed to take place (evidence presented below does make this possibility appear unlikely), the effect on product distribution would be a decrease in the proportion of O-alkylates (with corresponding increase in proportion of C-alkylates) in the actual products in a given reaction, over that initially formed kinetically. Hence, in the reaction of the *tert*-butyl derivative **6**, the proportion of O-alkylate actually isolated (i.e., ketone **8**) would be less than (or equal to) the amount of the nitronate ester intermediate which is kinetically formed from coupling salt **7** with the radical **18**. Since the amount of ketone **8** actually isolated approaches 100%, the overwhelming kinetic process in this case is O-alkylation. Similarly in the reaction of the isopropyl derivative **13**, O-alkylation is the major kinetic process. Comparison of these results with those from *p*-nitrobenzyl chloride itself, **19**, should now be made. The reaction of **19** with **7** under $S_{RN}1$ conditions gives overwhelming proportions of C-alkylation (e.g., 92%).[16] It can be readily argued that the C-alkylate must be the kinetic product in this simple, unhindered system. If the O-alkylate (**20**) were formed, it would very rapidly and hence nearly exclusively give *p*-nitrobenzaldehyde. This O-alkylate, when formed from *p*-nitrobenzyl iodide and the salt **7**, does so behave, and at a rate which is substantially greater than the rate of the $S_{RN}1$ process involving **19** and the salt **7**.[16] Clearly, replacement of an α-hydrogen in **19** by a *tert*-butyl or isopropyl group shifts the regiochemistry of the association step from predominant C-alkylation to predominate O-alkylation, a steric effect which is neither ambiguous nor devoid of meaning.

Scheme IV





Reactions of *aci*-Nitronates with Tertiary Benzylic Substrates

It has been proposed[12] that the reaction of tertiary benzylic substrates, e.g., *p*-nitrocumyl chloride, **21**, with *aci*-nitronates, e.g., **7**, also proceeds via initial formation of an O-alkylate, e.g., **22**, which subsequently isomerizes to the observed product, a C-alkylate, e.g., **23**. Although the acyclic nitronic esters of tertiary (including aromatic) substrates cannot be isolated, there is strong evidence for their intermediacy in several different substitution processes.[17] A very rapid, characteristic reaction of these compounds is a formal oxygen transfer process to give the corresponding oxime ethers as shown in Scheme IV. Hence it is a distinct possibility that the nitronate ester **22** would give rise to the oxime ether **24** rather than rearrange to the C-alkylate **23**. This type of reaction has in fact been reported by us in the reaction of chloride **21** with

(11) Norris, R. K.; Randles, D. *Aust. J. Chem.* **1979**, *32*, 1487.
(12) Kornblum, N.; Ackermann, P.; Swiger, R. T. *J. Org. Chem.* **1980**, *45*, 5294.
(13) Two comments on these experiments[12] need to be made. First, the demonstration that sulfinate esters do isomerize to sulfones under $S_{RN}1$ conditions neither proves nor even infers that sulfinate esters are initially formed, kinetically, in the conversion of *p*-nitrobenzylic derivatives into *p*-nitrobenzylic sulfones. Secondly, the radical anions of *both* sulfinate esters and sulfones have been demonstrated to dissociate into sulfinate ions and *p*-nitrobenzylic radicals,[2,12] whereas in the case of the radical ions of the *C*-alkylates formed from benzylic radicals and *aci*-nitronate ions (e.g., **17**), dissociation to the original components has never been observed or demonstrated.[14]
(14) Nitrite ion and not *aci*-nitronate ion appears to result from dissociation of radical ions such as $17^{\cdot-}$ under forcing conditions.[15]
(15) Kornblum, N.; Erickson, A. S. *J. Org. Chem.* **1981**, *46*, 1039.
(16) Kornblum, N.; Pink, P.; Yorka, K. V. *J. Am. Chem. Soc.* **1961**, *83*, 2779.
(17) Norris, R. K.; Randles, D. *Aust. J. Chem.* **1979**, *32*, 2413.

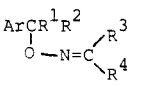
$ArCR^1R^2CR^3R^4NO_2$

	R^1	R^2	R^3	R^4
23	Me	Me	Me	Me
28	Me	Me	H	$CHMe_2$
38	Me	Et	Me	Me
39	Me	Me_3CCH_2	Me	Me
40	Me	$CHMe_2$	Me	Me
43	Me	Me	Et	Me
44	Me	Me	$CHMe_2$	Me
46	Me	Et	Et	Me

the salt **25**, wherein the oxime ether **26** was produced.[17]

$M^+ {}^-CR^1R^2NO_2$

	M	R^1	R^2
7	Li	Me	Me
25	Li	Me	CMe_3
27	NBu_4	H	$CHMe_2$
34	NBu_4	Me	Me
41	Li	Me	Et
42	Li	Me	$CHMe_2$
45	NBu_4	Me	Et
47	Li	H	Me



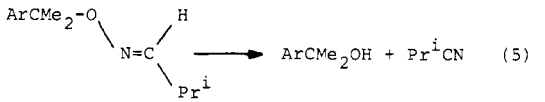
	R^1	R^2	R^3	R^4
24	Me	Me	Me	Me
26	Me	Me	Me	Bu^t
30	Me	Me	H	Pr^i
33	Me	Pr^i	H	Pr^i

We now present several other reactions which support the above contention that nitronate esters derived from tertiary substrates do not rearrange to C-alkylates under $S_{RN}1$ conditions but form the corresponding oxime ethers. The reaction of the chloride **21** with the salt **27** was undertaken in an attempt to prepare the C-alkylate **28**.[18] This reaction proceeded smoothly (Me_2SO, 20 °C, 20 min) and inspection of the crude rection product (^1H NMR) showed that no detectable (ca. <5%) amount of **28** had been formed. In fact, the reaction products consisted of trace amounts *p*-nitrocumyl alcohol **29** and a major component which had NMR and MS parameters consistent with those expected for the oxime ether **30**. Attempted purification of this compound by preparative TLC gave the alcohol **29**, whose formation from **30**, as shown in eq

$ArCR^1R^2X$

	R^1	R^2	X
21	Me	Me	Cl
29	Me	Me	OH
31	Me	$CHMe_2$	NO_2
32	Me	$CHMe_2$	OH
35	Me	Me	NO_2
36	Me	Et	NO_2
37	Me	Me_3CCH_2	NO_2

5 has ample precedent in the analogous reaction of *O*-aryl oxime ethers.[19]



(5)

In similar fashion, reaction of the more hindered benzylic substrate **31** with the salt **27** gave only the alcohol **32** and the oxime ether **33**, which subsequently (preparative TLC) decomposed to **32**.

The formation of the oxime ethers **26**, **30**, and **33** in the above reactions not only strongly supports the contention that nitronate esters from tertiary substrates are converted into the corresponding oxime ethers, rather than rearrange to C-alkylates, but also indicates that certain substitution patterns affect the regiochemistry of the association of benzylic radicals with *aci*-nitronate ions. In an attempt to establish these substitution patterns we inspected the proportions of C-alkylates formed in various reported[20] and new (see Experimental Section)[1b] $S_{RN}1$ reactions. These are summarized in Table I. If one considers the reaction of the unbranched but tertiary anion of 2-nitropropane with tertiary benzylic substrates (Table I, expt 1–4), it is found that the isolated yield of C-alkylates is close to 80%. It is strikingly obvious that a sharp discontinuity occurs in the above sequence (Table I, expt 5) when a carbon adjacent to the reaction site (C_β) bears more than one alkyl group. It is further significant that if there is only one alkyl group on a given C_β, even a *tert*-butyl group, the yield of C-alkylate is unaffected (expt 4). A similar discontinuity occurs in the reactions of the *p*-nitrocumyl system with *aci*-nitronate ions (expt 1, 6, and 7). Once again, when a tertiary radical and a tertiary *aci*-nitronate are involved in the association step, branching at a C_β prevents C-alkylation (expt 7). It appears, however, that C-alkylation still predominates if there are alkyl groups attached to two *different* C_β's (expt 8).

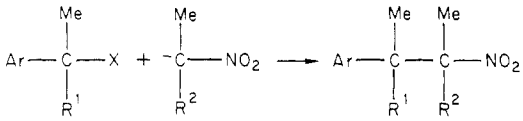
The importance of branching at C_β is also apparent in reactions in which one component in the radical + anion association step is tertiary and the other secondary. A single branch (i.e., one of the C_β's with two geminal alkyl groups) reduces C-alkylation to less than 10% (e.g., **7** with **13** and **27** with **21**), whereas double branching (e.g., one of the C_β's with three alkyl groups) prevents C-alkylation altogether (e.g., **6** with **7**).

The above empirical rules have been demonstrated to hold in other substrates.[1b,11] Furthermore, substrates in which the branching at one C_β is maintained while the actual number of C_β's is reduced (e.g., in the reaction of secondary substrate **6** with the secondary *aci*-nitronate **47**) give yields of C-alkylates which fall between the above

(18) In a somewhat preemptive list of potential substrates for the investigation of steric effects in $S_{RN}1$ reactions of *p*-nitrobenzylic substrates, it has been suggested[12] that a point will be reached where steric interactions will be overriding and the C-alkylates will no longer be "thermodynamically stable". This criticism cannot be leveled at this C-alkylate (i.e., **28**) since inspection of space-filling molecular models reveals no serious steric problems, and indeed the isomeric compound **15**, which has similar steric interactions to those which would be present in **28**, is a perfectly stable, normal compound.

(19) Knudson, R. D.; Snyder, H. R. *J. Org. Chem.* **1974**, *39*, 3343.
(20) Kornblum, N.; Carlson, S. C.; Widmer, J.; Fifolt, M. J.; Newton, B. N.; Smith, R. G. *J. Org. Chem.* **1978**, *43*, 1394.

Table I. Yield of C-Alkylates from the Reaction of *aci*-Nitronate Salts with *p*-Nitrobenzylic Derivatives



expt	substrate	salt	R^1	R^2	time, h	C-alkylate (% yield)
1	35	7	Me	Me	2[a]	23 (84)[20]
2	36	7	Et	Me	3[a]	38 (76)[20]
3	36	34	Et	Me	0.5[b]	38 (78)
4	37	34	Me_3CCH_2	Me	0.5[c]	39 (76)
5	31	34	Me_2CH	Me	5[c]	40 (0)
6	35	41	Me	Et	6[a]	43 (74)[20]
7	21	42	Me	Me_2CH	18[c]	44 (0)
8	36	45	Et	Et	0.25[c]	46 (77)

[a] In HMPA at 25 °C. [b] In Me_2SO at 25 °C. [c] In Me_2SO at 50 °C.

extremes. Hence the demonstrated $S_{RN}1$ reaction between **6** and **47** gives a C- to O-alkylation ratio of 52:17.[11]

Conclusions

The above and other results[1b,11] show that there is a regular predictable relationship between substrate structure (in particular branching at C_β) and product distribution (namely, amount of C-alkylation) in the $S_{RN}1$ reaction between *p*-nitrobenzylic substrates and *aci*-nitronate ions. This product distribution can be attributed to kinetic selection between C- and O-alkylation pathways at the radical + anion association step. Inspection of molecular models reveals that in the association step, in which a near planar radical and a planar *aci*-nitronate combine, a single alkyl substituent on a C_β can rotate to the opposite face of the appropriate component, leaving the way clear for C–C bond formation (i.e., C-alkylation), but when two or more alkyl substituents are present on the *same* C_β, this circumstance is not possible and the alternative, sterically unrestricted C–O bond formation (i.e., O-alkylation) may occur.

In absence of steric restraints C-alkylation is the predominant process. Rather than resorting to arguments based on reversibility of the association step and relative thermodynamic stabilities of the C- and O-alkylates, we believe that there is sufficient theoretical grounds for believing that the C-alkylate is the expected product (in absence of steric restraints) from the association step. Hence the C–C coupling of *p*-nitrobenzyl radical with the anion of 2-nitropropane is consistent with perturbational molecular orbital theory.[21] Furthermore it has been proposed recently that reactions between radicals and anions are kinetically controlled. On the basis of energy and molecular orbital considerations, the basicity of a given site in an ambident anion (in the case of *aci*-nitronates, the carbon site is more basic) may influence the radical-anion formation step to a greater extent than the stability of the resulting radical ion.[22]

Experimental Section

Melting points were determined on a Kofler melting-point apparatus and are uncorrected. ^1H NMR spectra were determined on a Varian Associates HA 100 or a JEOL FX 60Q NMR spectrometer with Me_4Si as internal standard on 10% w/v solutions in $CDCl_3$ (unless otherwise stated). IR spectra were recorded on a Perkin-Elmer 221 spectrophotometer and UV spectra on a Perkin-Elmer 402 spectrophotometer. Mass spectra were recorded on an AEI MS902 spectrometer at 70 eV. Dimethyl sulfoxide (Me_2SO) was dried according to the procedures recommended by Burfield and Smithers.[23] Light petroleum refers to the fraction of bp 60–65 °C. Analyses were carried out at the Australian Microanalytical Service, Melbourne. Thin-layer chromatography (TLC) and preparative thin-layer chromatography (PLC) were performed with Merck silica gel grades $HF_{254+366}$ (Type 60) and $60PF_{254+366}$, respectively and with benzene/light petroleum mixtures as eluent.

2-Methyl-1-nitropropane,[24] 2-nitrobutane,[25] 2-methyl-3-nitrobutane,[17] *p*-(1-chloro-1-methylethyl)nitrobenzene (**21**),[26] *p*-(1-nitro-1-methylethyl)nitrobenzene (**35**),[27] *p*-(1-methyl-1-nitropropyl)nitrobenzene (**36**),[27] *p*-(1,2-dimethyl-1-nitropropyl)nitrobenzene (**31**),[17] and *p*-nitro(1,3,3-trimethyl-1-nitrobutyl)benzene (**37**)[7] were prepared by the indicated literature procedures. The lithium and tetrabutylammonium *aci*-nitronates were prepared from the appropriate nitroalkane by the usual procedures.[17,28]

Reactions of *p*-Nitrobenzylic Substrates with Lithium and Tetrabutylammonium *aci*-Nitronates. General Procedure. A solution of the appropriate *p*-nitrobenzylic derivative in Me_2SO was deoxygenated by passage of dry nitrogen through the solution for 15–20 min. The appropriate *aci*-nitronate salt was then added and the solution was stirred under nitrogen with irradiation by a 500-W G.E. sunlamp until reaction was complete by TLC. All reactions were performed in a water or oil bath kept at constant temperature. The reactions were worked up by dilution with water followed by threefold extraction with ether. The ether layers were washed 3 times with water (to remove Me_2SO) and then with brine. The dried ($MgSO_4$) extract was then evaporated under reduced pressure. Products were isolated by PLC with benzene and light petroleum mixtures as eluent and are listed in order of increasing polarity.

Reaction of *p*-Nitrocumyl Chloride 21 with Tetrabutylammonium 2-Methyl-1-nitro-1-propanide (27). The chloride **21** (499 mg, 2.5 mmol) was allowed to react with the salt **27** (1.72 g, 5.0 mmol) in Me_2SO (10 mL) at 20 °C for 20 min. The reaction mixture was acidified with hydroxylamine hydrochloride, and then worked up in the usual manner. The ^1H NMR spectrum of the crude reaction product revealed that there was one major component, whose ^1H NMR and mass spectral parameters were consistent with the oxime ether **30**: ^1H NMR δ 1.04 (d, 6 H, $CHMe_2$, J = 6.7 Hz), 1.74 (s, 6 H, CMe_2), 2.65 (m, 1 H, $CHMe_2$, J = 6.7, 7.3 Hz), 6.09 (d, 1 H, N=CH, J = 7.3 Hz), AA'XX' pattern 7.63 (m, 2 H), 8.18 (m, 2 H), $J_{AX} + J_{AX'}$ = 9.0 Hz, aromatic protons; mass spectrum, m/e 250 (M^+, 2%), 164 (100). Only trace amounts (ca. 5%) of the alcohol **29** (methyl singlet at δ 1.64) were detectable. Attempted purification of the crude reaction mixture by PLC lead only to isolation of the alcohol **29**[12,17] (190 mg, 42%). None of

(21) Hudson, R. F. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 36.
(22) Tolbert, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 3531.
(23) Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966.
(24) Bachman, G. B.; Maleski, R. J. *J. Org. Chem.* **1972**, *37*, 2810.
(25) Kornblum, N.; Larson, H. O.; Blackwood, R. K.; Mooberry, D. D.; Oliveto, E. P.; Graham, G. E. *J. Am. Chem. Soc.* **1956**, *78*, 1497.
(26) Okamoto, Y.; Brown, H. C. *J. Am. Chem. Soc.* **1957**, *79*, 1909.
(27) Kornblum, N.; Cheng, L.; Kerber, R. C.; Kestner, M. M.; Newton, B. N.; Pinnick, H. W.; Smith, R. G.; Wade, P. A. *J. Org. Chem.* **1976**, *41*, 1560.
(28) Kerber, R. C.; Urry, G. W.; Kornblum, N. *J. Am. Chem. Soc.* **1965**, *87*, 4520.

the several minor bands from the PLC plates amounted to more than 5% of the reaction product.

Reaction of p-(1,2-Dimethyl-1-nitropropyl)nitrobenzene (31) with the Salt 27. The nitro compound **31** (596 mg, 2.5 mmol) was allowed to react with the salt **27** (1.72 g, 5.0 mmol) in Me_2SO (10 mL) at 50 °C for 30 min. The reaction mixture was acidified with hydroxylamine hydrochloride and then worked up in the usual manner. The ^1H NMR spectrum of the crude reaction product revealed that there was one major component, whose NMR parameters strongly suggested the oxime ether **33**: δ 0.74 (d, 3 H, MeCHMe, J = 6.8 Hz), 1.02 (d, 3 H, MeCHMe, J = 6.8 Hz), 1.07 (d, 6 H, Me_2CH, J = 6.8 Hz), 1.80 (s, 3 H, Me), 2.10 (m, 1 H, MeCHMe), 2.65 (m, 1 H, Me_2CH), 6.06 (d, 1 H, N=CH, J = 7.6 Hz), AA'XX' pattern 7.56 (m, 2 H), 8.18 (m, 2 H), $J_{AX} + J_{AX'}$ = 9.0 Hz. The only other identifiable compound in the crude reaction product (ca. 10%) was the alcohol **32**. Attempted purification of **33** by PLC lead to decomposition and gave 50% (262 mg) **3-methyl-2-(p-nitrophenyl)-2-butanol (32)**: mp 48-49 °C; ^1H NMR δ 0.76 (d, 3 H, MeCHMe, J = 6.7 Hz), 0.94 (d, 3 H, MeCHMe, J = 6.7 Hz), 1.56 (s, 3 H, Me), 1.76 (s, 1 H, OH), 2.04 (sept, 1 H, Me_2CH, J = 6.7 Hz), AA'XX' pattern 7.59 (m, 2 H), 8.18 (m, 2 H), $J_{AX} + J_{AX'}$ = 9.1 Hz; IR ($CHCl_3$) 3605, 1600, 1510, 1350, 1170, 1070, 1010, 850 cm^{-1}; UV (MeOH) 274 nm (ε 1.02×10^4); mass spectrum, m/e 209 (M^+, 0.6%), 194 (1), 167 (19), 166 (100), 150 (9), 120 (13), 105 (12), 77 (15), 43 (100), 41 (13).

Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.13; H, 7.25; N, 7.02.

Reaction of p-(1-Methyl-1-nitropropyl)nitrobenzene (36) with Tetrabutylammonium 2-Nitro-2-propanide (34). Reaction of the nitro compound **36** (560 mg, 2.5 mmol) with the salt **34** (1.65 g, 5.0 mmol) in Me_2SO (10 mL) at 25 °C for 30 min gave, after workup, purification by PLC, and recrystallization from ethanol, p-(1-ethyl-1,2-dimethyl-2-nitropropyl)nitrobenzene (**38**; 518 mg, 78%), mp 96-97 °C (lit.[20] mp 94-95.5 °C). The use of the tetrabutylammonium salt **34** rather than the lithium salt **7** does not affect the yield of **38** but reduces the reaction time from 3 h (in HMPA).[20]

Reaction of p-(1,3,3-Trimethyl-1-nitrobutyl)nitrobenzene (37) with Tetrabutylammonium 2-Nitro-2-propanide (34). Reaction of the nitro compound **37** (532 mg, 2.0 mmol) with salt **34** (1.32 g, 4.0 mmol) in Me_2SO (8 mL) at 50 °C for 30 min gave, after workup, PLC, and recrystallization from light petroleum, **p-[1,3,3-trimethyl-1-(1-methyl-1-nitroethyl)butyl]nitrobenzene (39**; 468 mg, 76%): mp 117-118 °C; ^1H NMR δ 0.77 (s, 9 H, CMe_3), 1.40 (q, 3 H, $MeC(NO_2)Me$, J = 0.7 Hz), 1.57 (q, 3 H, $MeC(NO_2)Me$, J = 0.7 Hz), 1.64 (d, 3 H, Me, J = 1.0 Hz), 1.97 (d, 1 H, HCH, J = 14.9 Hz), 2.34 (dq, 1 H, HCH, J = 14.9, 1.0 Hz), AA'XX' pattern 7.55 (m, 2 H), 8.17 (m, 2 H), $J_{AX} + J_{AX'}$ = 9.1 Hz; IR ($CHCl_3$) 1605, 1595, 1530, 1520, 1370, 860, 855 cm^{-1}; UV (hexane) 264 nm (ε 1.24×10^4); mass spectrum, m/e 262 ($M^+ - NO_2$, 0.03%), 246 (1), 220 (3), 206 (6), 164 (64), 89 (18), 57 (100), 43 (24), 41 (37).

Anal. Calcd for $C_{16}H_{24}N_2O_4$: C, 62.31; H, 7.85; N, 9.09. Found: C, 62.57; H, 7.87; N, 8.91.

Reaction of p-(1,2-Dimethyl-1-nitropropyl)nitrobenzene (31) with Tetrabutylammonium 2-Nitro-2-propanide (34). Reaction of the nitro compound **31** (600 mg, 2.5 mmol) with the salt **34** (1.65 g, 5.0 mmol) in Me_2SO (10 mL) at 50 °C for 5 h gave no detectable amounts of C-alkylation products. The only isolable products after PLC were the reduction product p-(1,2-dimethylpropyl)nitrobenzene (92 mg, 19%), identical by TLC, IR, and ^1H NMR with an authentic sample,[29] and the alcohol **32** (44%, 221 mg), identical with the sample isolated above.

Reaction of p-Nitrocumyl Chloride (21) with Lithium 3-Methyl-2-nitro-2-butanide (42). Reaction of the chloride **21** (500 mg, 2.5 mmol) with the salt **42** (1.8 g, 5.0 mmol) in Me_2SO (10 mL) at 50 °C for 18 h gave after PLC, α,p-dinitrocumene (**35**; 68 mg, 13%) and p-nitrocumyl alcohol (**29**; 81 mg, 18%) as the only identifiable products. No C-alkylate could be detected.

Reaction of p-(1-Methyl-1-nitropropyl)nitrobenzene (36) with Tetrabutylammonium 2-Nitro-2-butanide (45). Reaction of the nitro compound **36** (448 mg, 2.0 mmol) with the salt **45** (1.38 g, 4.0 mmol) in Me_2SO (8 mL) at 50 °C for 15 min followed by workup and PLC gave the two diastereoisomers of **p-(1-ethyl-1,2-dimethyl-2-nitrobutyl)nitrobenzene (46**; 433 mg, 77%), which were formed in almost equal amounts. The diastereoisomers were inseparable and so the following spectroscopic and analytical data were obtained for the oily mixture: ^1H NMR δ 0.69 (t, CH_2CH_3, J = 7.4 Hz), 0.71 (t, CH_2CH_3, J = 7.4 Hz), 0.80 (t, 2 CH_2CH_3, J = 7.4 Hz), 1.40 (d, Me, J = 0.9 Hz), 1.46 (d, Me, J = 0.9 Hz), 1.50 (d, 2 Me, J = 0.9 Hz), 1.3-2.1 (m, CH_2CH_3), 2.1-2.6 (m, CH_2CH_3), AA'XX' systems 7.41 (m, 2 H), 7.44 (m, 2 H), 8.17 (m, 4 H), $J_{AX} + J_{AX'}$ = 9.2 Hz (both diastereoisomers); IR (liquid film) 1610, 1600, 1530, 1365, 860 cm^{-1}; mass spectrum, m/e 280 (M^+, 0.03%), 179 (24), 178 (100), 164 (27), 150 (41), 136 (47), 132 (35), 117 (28), 103 (67), 91 (20), 43 (31).

Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19, N, 9.99. Found: C, 60.04; H, 7.17; N, 9.75.

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Registry No. 7, 3958-63-2; **21**, 14500-58-4; **23**, 14851-03-7; **27**, 80516-30-9; **29**, 22357-57-9; **30**, 80516-31-0; **31**, 65398-92-7; **32**, 80532-34-9; **33**, 80516-32-1; **34**, 65398-95-0; **35**, 3276-35-5; **36**, 58324-83-7; **37**, 74021-66-2; **38**, 65253-46-5; **39**, 80516-33-2; **41**, 35818-95-2; **42**, 65398-99-4; **43**, 65253-43-2; **45**, 65398-98-3; **46** (isomer 1), 80516-34-3; **46** (isomer 2), 80516-35-4; p-(1,2-dimethylpropyl)nitrobenzene, 80516-36-5.

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Photoinduced Skeletal Rearrangement of Alkylindenes[1,2]

Harry Morrison,* David Giacherio, and Frederick J. Palensky

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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The indene phototransposition reaction, a skeletal rearrangement of certain alkylindenes involving an interchange of carbons 1 and 2 (eq 2), is described. The postulated mechanism (Scheme II) involves a [2 + 2] closure followed by a [1,3] sigmatropic shift, opening to an isoindene and 1,5 hydrogen shifts to re-form the indene system. Results of experiments with indenes containing different alkyl groups at C_1 and C_2 and with 1,1-dimethylindene lend support to the proposed scheme. Experiments with (+)-1,2-dimethylindene indicate that the net migration of C_1 to C_3, necessary for transposition, occurs with clean inversion at C_1 (as would be expected for a ground-state, four-electron, electrocyclic reaction). The reaction derives from the excited singlet state, and partial movement along the initial [2 + 2] reaction surface appears to provide an efficient path for S_1 radiationless decay.

Until recently, most photochemical studies of indene and its simple alkyl derivatives have dealt with sensitized cycloadditions and dimerization.[3] This is in contrast with 1,1-diarylindenes where facile, unimolecular, 1,5 aryl shifts

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