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A novel borane effect on the C/O alkylation ratio in competing $S_{RN}1$–S_N2 reactions

Ana Shifman, Milon Sprecher and Shmaryahu Hoz*

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

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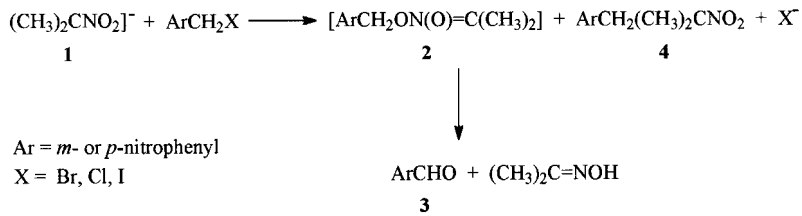
ABSTRACT: The presence of Et_3B in the reaction of 2-nitropropane anion (1) with *p*-nitrobenzyl bromide (5b) in *tert*-butyl alcohol results in an approximately three-fold increase in C-alkylation [yielding 1-(2-methyl-2-nitropropyl)-4-nitrobenzene (9) by an $S_{RN}1$ mechanism] versus O-alkylation (by an S_N2 mechanism, and leading thereafter to *p*-nitrobenzaldehyde). Dioxygen completely inhibits C-alkylation in the absence of Et_3B, but is ineffective in its presence. *p*-Dinitrobenzene does not significantly affect the thermal reaction (30 °C) of 1 with 5b, but partially inhibits C-alkylation in reaction under photostimulation. However, *p*-dinitrobenzene *catalyzes* C-alkylation in the thermal reaction in the presence of Et_3B. Rationalizations of these novel results are presented. Qualitatively similar results were obtained for the reaction of phenylnitromethane anion (16) with 5b. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: borane effect; C/O alkylation ratio; $S_{RN}1$–$S_{RN}2$ reactions



Scheme 1

INTRODUCTION

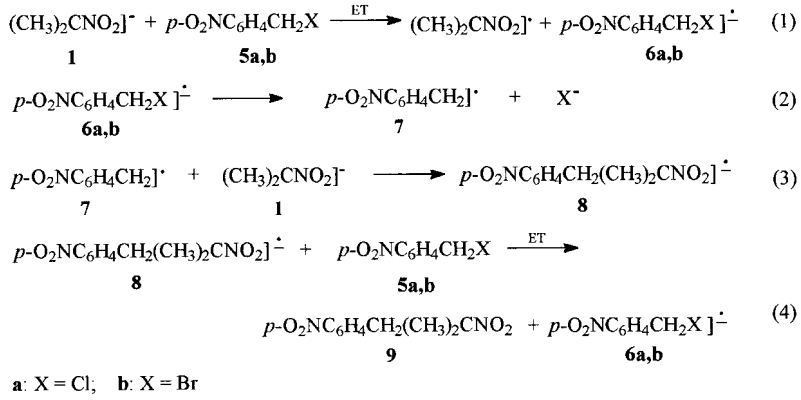
In the course of his classical work on ambident nucleophiles, Kornblum investigated the reaction of the anion **1**, derived from 2-nitropropane (2-NP), with nitrobenzyl halides.[1] Two types of products were isolated: nitrobenzaldehydes (**3**) (plus acetone oxime) and 2-(nitrobenzyl)-2-nitropropanes (**4**). The former are the result of O-alkylation of the nitronate ion followed by fragmentation of the first-formed nitronic esters (**2**),[2] while the latter are the expected product of C-alkylation (Scheme 1).

Mechanistic investigations[3–5] convincingly demonstrated that in addition to the then well known S_N1–S_N2 type of reactions for nucleophilic displacement at a benzylic carbon, there existed, in appropriate cases, an alternative chain process involving radical anions and electron transfer (ET) that effected such displacement (cf. Scheme 2). This type of process, dubbed an $S_{RN}1$ reaction,[6] was also uncovered in certain aliphatic[1,7] and aromatic systems.[6,8]

In Kornblum and co-workers studies,[3a,9] the reaction in DMF of 2-NP anion (2-NPA; **1**), as its lithium salt, with *p*-nitrobenzyl chloride (**5a**), proceeded entirely, or almost entirely, via the $S_{RN}1$ mechanism, yielding the product of C-alkylation, 1-(2-methyl-2-nitropropyl)-4-nitrobenzene (**9**), while in the reaction with *p*-nitrobenzyl bromide (*p*-NBB; **5b**), which bears a better leaving group, this path and product were secondary (17–20%), and O-alkylation by the S_N2 mechanism followed by decomposition to *p*-nitrobenzaldehyde predominated (60–65%). C-Alkylation (but not O-alkylation) was found to be subject to photostimulation,[4b] and in $S_{RN}1$ reactions of the type under discussion the phenomenon generally involves facilitation of the production of radical anions by ET from the nucleophile (e.g. 2-NPA) to the substrate (e.g. the nitrobenzyl compound), sometimes within a charge-transfer complex and/or to an excited state.[1,10–12] Other possibilities are, however, not precluded (for an imaginative early suggestion, see Ref. 4b).

Following a prior serendipitous finding of a surprising

**Correspondence to:* S. Hoz, Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel.

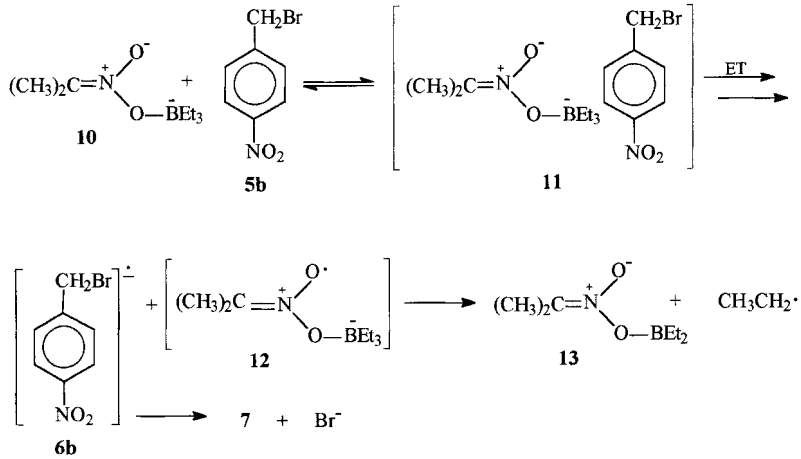


Scheme 2

effect of triethylborane (Et_3B) in a case in which reactants yielded different products by different competing mechanistic pathways, it seemed that the reaction of 2-NPA with *p*-NBB described above might be appropriate for the further investigation of unexpected effects of Et_3B.

RESULTS AND DISCUSSION

Unless specified otherwise, the reaction of *p*-NBB (**5b**) with 2-NPA (**1**) (prepared *in situ* by the reaction of 2-NP with an equivalent of potassium *tert*-butoxide) was conducted in *tert*-butyl alcohol solution under the standard conditions detailed in the Experimental section and for 20 min only, so as to obtain ratios of initial rates. A product isolation run (24 h) confirmed that in *t*-BuOH, as in DMF,[3a] both O-alkylation and C-alkylation occur, leading eventually to *p*-nitrobenzaldehyde and to **9**, respectively. In 20 kinetic runs (20 min) under standard conditions, the average total conversion was 13.6 ± 3.4%, of which 6.1 ± 1.3% was O-alkylation and 7.5 ± 3.3% was C-alkylation. The latter, but not the former, was completely inhibited under an atmosphere containing 0.5 mol equiv. of dioxygen, or in the presence of 0.01 mol equiv. of galvinoxyl, both known free radical scavengers.[13] Contrariwise, it increased to 79.6 ± 7.3% under irradiation by sunlamp (total conversion 83.3 ± 7.6%; O-alkylation 3.7 ± 0.3%). This is in keeping with expectations for an $S_{RN}1$ reaction pathway and parallels the reports of Kornblum and co-workers[1,3a,14] and in particular of Russell and Danen[4] for the analogous reaction with **5a**. To be noted is the occurrence of C-alkylation by an $S_{RN}1$ mechanism even in the absence of light stimulation, although to a much smaller extent.[15] Thus the initiation step of electron transfer from 2-NPA to *p*-NBB is not inhibited by the *t*-BuOH solvent as it is by the better solvating and hydrogen-bonding EtOH.[4b] Recently presented data indicate that in thermal $S_{RN}1$ reactions such as that under discussion ET from 2-NPA may be concerted with bond cleavage. In that case **6** would not be a distinct intermediate, rather **7** would be produced directly with release of halide anion (Schemes 2 and 3).[15b] In contrast to C-alkylation, the extent of O-alkylation was not affected by the presence of dioxygen or galvinoxyl, and decreased slightly in those experi-



Scheme 3

Table 1. ^{11}B chemical shifts in *t*-BuOH solution

Solute[a]	δ[b]
Et_3B	87.1 (180)[c]
Et_3B + *p*-NBB	87.1 (180)[c]
Et_3B + 2-NP	87.2 (180)[c]
Et_3B + *t*-BuOK	2.9 (800)[c]
Et_3B + 2-NPA (= 2-NP + *t*-BuOK)	66.5 (800)[c]

[a] All solutes 0.1 M in *t*-BuOH as solvent.
[b] In ppm downfield from $Et_2O \cdot BF_3$; $Me_2S \cdot BH_3$ in $CDCl_3$ was used as an external secondary standard, δ −20.1.
[c] Width at half-height, in Hz; ^{11}B, with $I = 3/2$, has short T_1 and broad absorption lines which precluded the determination of B–H coupling at a distance beyond one bond.

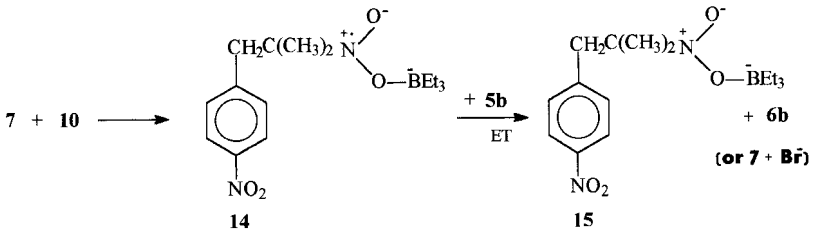
ments in which conditions were modified so as to enhance the competing C-alkylation significantly, the decrease being commensurate with the exhaustion of reactants by the latter. These findings indicate that O-alkylation in *t*-BuOH, as in DMF,[3a] is the result of an S_N2 type process.

Proceeding with our prospecting for novel effects of Et_3B, we indeed found that the addition of 1 mol equiv. of Et_3B to the reaction of *p*-NBB with 2-NPA resulted in an approximate threefold increase in C-alkylation (to $24.0 \pm 5.7\%$) with a concurrent increase of total conversion ($28.2 \pm 5.9\%$) and a barely significant decrease in O-alkylation (to $4.2 \pm 0.8\%$). Doubling the amount of Et_3B to 2 mol equiv. had no clear effect on the yield or on the product distribution. The effect of sunlamp irradiation, inducing a dramatic dominance of C-alkylation, was preserved in the presence of 1 equiv. of Et_3B. The value found ($85.3 \pm 4.9\%$) was marginally higher, and the extent of O-alkylation ($1.3 \pm 0.1\%$) somewhat lower than found in the absence of Et_3B.

The addition of galvinoxyl (0.01 equiv.) in the presence of Et_3B (1 equiv.) reduced the total conversion to only $8.6 \pm 0.4\%$, C-alkylation declining to $4.4 \pm 0.4\%$, but O-alkylation holding steadfast at $4.2 \pm 0.2\%$. Increasing the amount of galvinoxyl to 0.5 mol equiv. had no further significant effect. The residual C-alkylation persisting under these conditions is in contrast to its complete inhibition by galvinoxyl in the absence of Et_3B. Although dioxygen also completely inhibited C-alkylation in the absence of the borane, we found only an insignificant variation in the yields of C- and O-alkylation in a series of experiments in the presence of Et_3B and of dioxygen increasing from 0 to 1 mol equiv.

To aid in the rationalization of the previously undocumented effect of Et_3B reported above, the extent of its coordination, as a Lewis acid, with the solutes in the present reaction was determined with the aid of ^{11}B NMR. Results are presented in Table 1. It is clear that there is no discernible extent of coordination to either of the neutral molecules, *p*-NBB or 2-NP, in the face of the presumed coordination to the *t*-BuOH solvent, even at solute concentrations five times those used in the reaction runs. On the other hand Et_3B clearly coordinates with *tert*-butoxide ion and with 2-NPA. The very much larger ^{11}B upfield shift in the former case than in the latter is to be attributed to the greater basicity and charge localization in *tert*-butoxide than in 2-NPA. ^1H NMR determinations on *t*-BuOH solutions containing Et_3B, *t*-BuOK and 2-NP showed that when these reactants were added in equimolar quantities (concentration 0.1 M), $10 \pm 3\%$ of the 2-NP remained non-ionized, indicating that at equilibrium that portion of the Et_3B is bound to *tert*-butoxide. The value of δ reported for ^{11}B on the last line of Table 1 is therefore a weighted average of values for the fraction of Et_3B bound to *tert*-butoxide and that bound to 2-NPA.

Whereas the Et_3B-bound 2-NPA, **10**, (Scheme 3) would be expected to be a poorer electron donor than 'free' 2-NPA, yet it could still be viable in that role, either photostimulated or not, especially within a complex with the acceptor *p*-NBB (**11**). An ET would yield **6b** accompanied by the radical **12**. Release of an ethyl radical from the latter by B—C homolysis would produce the neutral and stable **13**. Such an ET would be energetically more favorable were it concomitant with B—C homolysis without **12** as a distinct intermediate on the projected path.[15b,16] Another possible initiation process to be considered has its basis in the much studied[17] and extremely rapid reaction[18] of trialkylboranes with dioxygen, which releases alkyl radicals. As adventitious traces of dioxygen impurity have been found to suffice for this phenomenon,[17b,19] the increase in C-alkylation in the presence of Et_3B may be ascribable to the release of ethyl radicals and their reaction with *p*-NBB, abstracting bromine [17b] and yielding ethyl bromide and the more stable, and chain-propagating, *p*-nitrobenzyl radicals (**7;** Scheme 2). The inhibition by galvinoxyl supports the presumption of the free radical nature of the reaction also in the presence of Et_3B. The failure of dioxygen to inhibit C-alkylation in the presence of Et_3B stems from its dual reactivity, both trapping radicals and inducing their production. In the experiments conducted under sunlamp irradiation they may have been produced by photolysis of **10**. On the basis of recently reported calculation results, one would expect the tetracoordination of the boron atom in such a structure to lead to very substantial weakening of the B—C bonds,[20] since the boron radical formed upon homolysis could delocalize spin density on to the nitronate ligand. Whatever the nature of the chain-initiating steps in the presence of Et_3B, with or without photostimulation, the very low concentration of 'free' 2-NPA at equilibrium makes it highly unlikely that it is the target of *p*-nitrobenzyl radical addition in the C-alkylation step. This conclusion is supported by the finding that doubling the Et_3B concentration, which would further depress the 'free' 2-NPA concentration, had no significant effect on yield or product distribution. It therefore appears likely that **10** is the substrate of *p*-nitrobenzyl radical addition, resulting



Scheme 4

in the radical anion **14**. The latter presumably transfers an electron to *p*-NBB (**5b**) and thus continues the chain (Scheme 4).

Compared with the complexity which governs C-alkylation, the factors which influence the S_N2 reaction of O-alkylation appear simple. Triethylborane reduces the nucleophilicity of 2-NPA by binding to an oxygen of the nitro group, and in part, by binding to solvent, indirectly causes protonation of a limited amount of 2-NPA to 2-NP. Consequently, the already small yield of O-alkyl product is further reduced. An additional reduction occurs under light irradiation because most of the reactants are siphoned off by the successfully competing C-alkylation.

Entirely unforeseen were our further findings upon adding *m*- or *p*-dinitrobenzene (*m*-, *p*-DNB) to this system. In Kornblum's work which established the formation of radical anions on the path of C-alkylation in these reactions, he utilized dinitrobenzenes as single electron acceptors to compete with **5a** [cf. Scheme 2, Eqns (1) and (4)] and thus inhibit the reaction sequence. Specifically, when reacting lithium 2-NPA (0.42 M) with **5a** (0.2 M) in DMF solution for 48 h, the presence of *m*-DNB (0.4 M) reduced C-alkylation from 92 to 40% while allowing a rise in O-alkylation from 6 to 48%. The more readily reduced *p*-DNB[21] proved much more effective even at 0.04 M concentration, reducing the C-alkylation yield to 6%, and permitting 88% O-alkylation. With reactants at half these concentrations in EtOH solution for 96 h, *p*-DNB (0.02 M) was less effective, reducing C-alkylation from 90 to 31%.[3a] Similar findings were reported by Russell.[4b]

In contrast, we found that under our conditions in the absence of Et_3B, a 50% molar equivalent of *m*-DNB had no significant effect (when compared with control runs) on either the total conversion or the product distribution in reaction times of 45 min. The same was found to be the case for *p*-DNB in a more extensive series of experiments using various molar equivalents, from 5 to 80%, and reaction times of up to 150 min. However, in reactions (20 min) under sunlamp irradiation the presence of a 0.05 molar equiv. of *p*-DNB did reduce the extent of C-alkylation from $82.6 \pm 4.9\%$ (O-alkylation, $3.8 \pm 0.3\%$) to $49.1 \pm 8.6\%$ (O-alkylation, $7.6 \pm 1.6\%$). Raising the amount of *p*-DNB to 0.5 molar equiv. further reduced the C-alkylation to 33.1% (O-alkylation, 9.7%). Our reaction conditions differ from those Kornblum and of Russell in the concentrations of the reactants (0.02 vs 0.075–0.4 M) and the dentities of the solvent (*t*-BuOH vs DMF or EtOH), the cation (K^+ vs Li^+) and the *p*-nitrobenzyl halide (bromide vs chloride). Although it is possible, in the absence of evidence to the contrary, to speculate on plausible rationalizations for the contribution of all of these differences to the differing DNB effect, it is most probably the transition from **5a** to **5b** and the concomitant weaker C–X bond which are to be held mainly responsible. The radical anion of **5b** has been found to dissociate unimolecularly to **7** and halide anion [Scheme 2, Eqn. (2)] with a rate constant about two orders of magnitude larger than that of **5a** ($\sim 10^5$ vs 10^3 s^{-1}, in aqueous *t*-BuOH).[22] At the concentrations of the present runs this unimolecular chain-propagating dissociation of any **6b** formed would be able to compete effectively with the inhibitory bimolecular ET to DNB ($k < 10^{7\pm1}$ l mol^{-1} s^{-1}).[22]

Table 2. 2-NPA + *p*-NBB: effect of *m*-dinitrobenzene in presence of triethylborane[a]

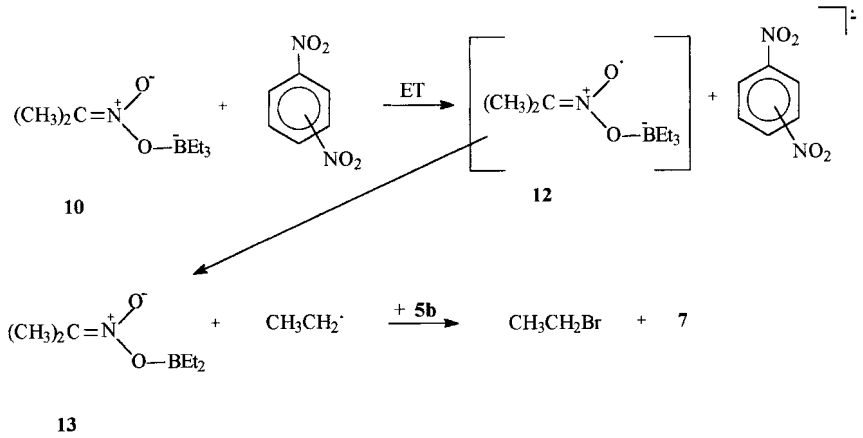
	m-DNB (mol equiv.)				
	0	0.05	0.25	0.50	1.0
C-alkylation[b] (%)	56	62	72	77	93
O-alkylation[b] (%)	7.5	5	5	4.5	3

[a] Standard reaction conditions; see Experimental section; 1 mol equiv. of Et_3B; reaction time, 60 min.
[b] HPLC analysis after reaction quench.

Table 3. 2-NPA + *p*-NBB: effect of *p*-dinitrobenzene in presence of triethylborane[a]

	p-DNB (mol equiv.)				
	0	0.05	0.10	0.25	0.50
C-alkylation[b] (%)	25	71[c,d]	68[d]	62	59[e]
O-alkylation[b] (%)	5	0.5[c,d]	0.4[d]	0.2	0.2[e]

[a] Standard reaction conditions; see Experimental section; 1 mol equiv. of Et_3B; reaction time, 20 min.
[b] HPLC analysis after reaction quench.
[c] After 3 min C- and O-alkylation were 13 and 0.2%, respectively.
[d] Substantially the same results were obtained in experiments in which 2 mol equiv. of Et_3B were used.
[e] Although the addition of 0.1 mol equiv. of dioxygen had no significant effect, that of 0.5 mol equiv. of galvinoxyl decreased C-alkylation to 44% (O-alkylation, 0.5%).



Scheme 5

Most surprisingly, in reaction mixtures containing Et_3B the DNBs acted as *catalysts*, rather than inhibitors, significantly enhancing C-alkylation. Table 2 shows the results of a series of experiments (60 min) using increasing amounts of *m*-DNB. Although the catalytic effect of *m*-DNB is very moderate, it increases with concentration. More effective catalysis was noted when *p*-DNB was added in the presence of Et_3B. Table 3 lists the results of a series of reactions (20 min) using increasing amounts of *p*-DNB. At a relative concentration of only 0.05 equiv. *p*-DNB results in a 2.8-fold enhancement of C-alkylation, but further increases in its relative concentration lead to a slow decline. In a series of light-irradiated reactions containing 1 mol equiv. of Et_3B, the product distribution (C-alkylation, $82.9 \pm 9.4\%$; O-alkylation, $1.3 \pm 0.4\%$) was unaffected by the addition of 0.05 mol equiv. of *p*-DNB (C-alkylation, $82.9 \pm 9.3\%$; O-alkylation, $0.8 \pm 0.4\%$).

The catalytic effect of the DNBs may be the result of their action as oxidants in a manner paralleling that of **5b** in Scheme 3, leading to the release of ethyl radicals. The latter than convert **5b** to chain-propagating **7**, as suggested above (see Scheme 5). At relatively high concentrations of *p*-DNB its interception of radical anions in the chain begins to be felt. The phenomena observed are in qualitative agreement with the order of efficacy *p*-DNB > *m*-DNB >**5b** as electron acceptors.[21]

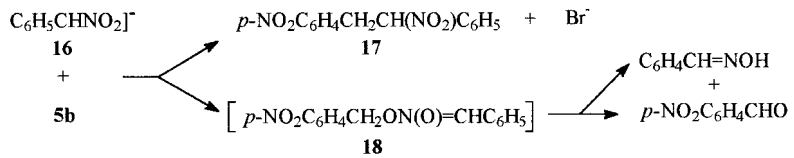
In an extension of the above work we checked the effect of Et_3B and of *p*-DNB on the reaction of phenylnitromethane anion (PNMA; **16**) with *p*-NBB in *t*-BuOH. The product of C-alkylation of PNMA is 1-(2-nitro-2-phenylethyl)-4-nitrobenzene (**17**), while O-alkylation gives the nitronate ester (**18**) which decomposes to *p*-nitrobenzaldehyde and the oxime of benzaldehyde (Scheme 6).

The reaction conditions paralleled those used in the case of 2-NPA except for the reaction time, which was increased to 1.75 h because PNMA is a poorer nucleophile and poorer electron donor. The results are summarized in Table 4. In this case too, Et_3B greatly increases C-alkylation, and a further increase, although modest, obtains when a catalytic amount of *p*-DNB is also added.

EXPERIMENTAL

Materials. *t*-BuOH, from Merk, was refluxed over CaH_2 and distilled. *t*-BuOK (99%), from Merk, was sublimed (0.2 Torr/170 °C) before use. *p*-Nitrobenzyl bromide (95%), from Merk, was purified by recrystallization from light petroleum (b.p. 60–80 °C); m.p. 99–100 °C. 2-Nitropropane (95%), from Aldrich, was purified to 99% by distillation through a fractionating column; the remaining 1% was 1-nitropropane. *p*-Dinitrobenzene (95%), from Fluka, was purified by sublimation (0.5 Torr/170 °C). *m*-Dinitrobenzene, galvinoxyl and the solution of BEt_3 in THF (1 M, under N_2) were obtained from Aldrich.

Instrumentation. NMR spectra were determined on Bruker AM-200 and AM-300 instruments. Unless specified otherwise, the solvent was $CDCl_3$ and chemical shifts (δ) are reported in ppm downfield from TMS as



Scheme 6

Table 4. 2-PNMA + *p*-NBB: effect of triethylborane and *p*-dinitrobenzene[a]

	Et_3B/*p*-DNB (mol equiv.)			
	0/0	1/0	0/0.05	1/0.05
C-alkylation (%)[b]	12	59	9	71
O-alkylation (%)[b]	6	1	5	0

[a] Standard reaction conditions; see Experimental section; reaction time, 1.75 h.
[b] ^{1}H NMR analysis after reaction quench.

internal standard. Melting-points were determined on a Fisher-Johns apparatus and are uncorrected. High-performance liquid chromatographic (HPLC) analyses were performed on a Waters Model 510 (two-pump) instrument equipped with a Model 490 programmable multi-wavelength detector and operated by Baseline 810 software. Samples (20 μl) were loaded via a Rheodyne model 7125 injection cell on to an Alltech Econosil column (Si, 10 μm; 250 × 4.6 mm i.d.). CH_2Cl_2 and hexane were fed by separate pumps in a volume ratio of 1:1 and a column flow-rate of 1 ml min^{-1}. Simultaneous detection was conducted at 262 and 270 nm. The HPLC instrumentation and analytical protocol were calibrated and response factors were determined for the various compounds. Retention times were *p*-NBB 6.03, **9** 12.57, *p*-nitrobenzaldehyde 16.88, *p*-DNB 8.9 and *m*-DNB 8.9 min.

Reaction of 2-NPA with p-NBB; kinetic runs; general procedure. Unless otherwise specified, results given are averages of 3–10 runs, and the initial concentration of the reactants was 0.02 M each. For each set of simultaneous runs (6–8), separate fresh stock solutions of known molarity of the individual reactants (*t*-BuOK +1 equiv. of 2-NP; *p*-NBB) in *t*-BuOH were prepared in a glove-box under a dry (P_2O_5), inert atmosphere (N_2 or Ar). Aliquots containing 2-NPA (0.05 mmol), *t*-BuOH when necessary to make up final volume to 2.5 ml and *p*-NBB (0.05 mmol) were distributed in that order with micro-pipettes to the septum-sealed, well mixed reaction vessels. The sealed vessels were removed from the glove-box and kept in a bath at 30 °C and, unless otherwise specified, with the exclusion of light. At the end of the stated reaction time (usually 20 min) the reaction was quenched by the injection of 2 ml of 3% aqueous hydrochloric acid and the mixture was extracted with two portions of CH_2Cl_2. The combined extracts were washed with water followed by brine, dried over $MgSO_4$, and the solvent was evaporated. The residue was dissolved in 20 ml of CH_2Cl_2 and aliquots were subjected to quantitative HPLC analysis. No aromatic products other than **9** and *p*-nitrobenzaldehyde were detected. The material balance was better than 96% in all cases. In reactions run in the presence of Et_3B, a 1 M solution of the latter in THF was injected into the reaction vessel in the required amount immediately prior to the addition of the *p*-NBB.

In reactions run in the presence of predetermined quantities of dioxygen, the latter were injected as a component of dry air 1 min after the addition of *p*-NBB. In reactions run in the presence of galvinoxyl, a 0.025 M solution of the latter in *t*-BuOH (dark green) was injected in the required amount immediately after the addition of *p*-NBB. In these reactions, whether in the presence or absence of Et_3B, the color of the solution at the end of the reaction time was purple.

In reactions run in the presence of *m*-DNB or *p*-DNB, these were injected in *t*-BuOH solution in the required amounts either simultaneously with the injection of the *p*-NBB solution or immediately thereafter. In these runs, at the end of the reaction time cloudiness had appeared in the mixtures. In the absence of Et_3B, the solutions remained colorless. In its presence, the solutions containing *m*-DNB turned pink and those containing *p*-DNB turned purple.

In the case of reactions containing both galvinoxyl and *p*-DNB, the latter was added in THF solution. In these cases the color of the reaction turned red.

Irradiation was performed using a 500 W sunlamp and Pyrex reaction vessels. In all these experiments the set of controls were run simultaneously under the same conditions except that the reaction vessels were wrapped in aluminum foil.

^{1}H NMR spectra of such *tert*-butyl alcohol solutions of equivalent amounts of 2-NP and $(CH_3)_3COK$ showed a singlet only, at δ 2.01, attributable to the CH_3 groups of 2-NPA, and no discernible absorption of 2-NP whose CH_3 groups show a doublet at δ 1.55. Experiments with various relative amounts of 2-NP and $(CH_3)_3COK$ showed that the deprotonation is slow on the NMR time-scale, and that separate non-averaging peaks are obtained for 2-NP and 2-NPA.

Reaction of 2-NPA with p-NBB; product identification. Working in a glove-box, 44 mg (0.4 mmol) of freshly sublimed *t*-BuOK were dissolved in 5 ml of *t*-BuOH, and 0.036 ml (0.4 mmol) of 2-NP, 0.4 ml of a 1 M solution of Et_3B in THF and a solution of 88 mg (0.4 mmol) of *p*-NBB in 15 ml of *t*-BuOH were added in that order. The vessel was closed and the contents were stirred for 24 h at room temperature. After dilution with 25 ml of water the reaction mixture was worked up as described above. The two products were isolated, after evaporation of solvent, by chromatography of the residue on silica using CH_2Cl_2–hexane (8:1) as eluent. The 1-(2-methyl-2-nitropropyl)-4-nitrobenzene (**9**) was recrystallized from EtOH–H_2O; m.p. 67–68 °C (lit.[3a] 66–67 °C). ^{1}H NMR ($CDCl_3$), δ 1.60 (s, 6H), 3.31 (s, 2H), 7.28 (d, J = 9.0 Hz, 2H), 8.16 (d, J = 9.0 Hz, 2H). MS (EI), *m/z* 224 (M^+), 178, 136, 132. *p*-Nitrobenzaldehyde; m.p. 105 °C (lit.[24] 106 °C). ^{1}H NMR ($CDCl_3$), δ 8.1 (d, J = 9.0 Hz, 2H), 8.4 (d, J = 9.0 Hz, 2H), 10.2 (s, 1H).[25]

Phenylnitromethane. This was prepared by the method of Kornblum *et al.*,[26] and final purification was performed by chromatography on silica with CH_2Cl_2 as eluent. ^{1}H NMR ($CDCl_3$), δ 5.42 (s, 2H), 7.43 (s, 5H).[27] ^{13}C NMR ($CDCl_3$), δ 80, 129.1, 129.8, 129.9.[27]

Reaction of PNMA with p-NBB. Sample preparation, reaction conditions and work-up paralleled those described for the kinetic runs with 2-NPA, except for reaction times, which were extended to 1.75 h, and identification and analysis of products, which were done by ^{1}H NMR.

1-(2-Nitro-2-phenylethyl)-4-nitrobenzene (**17**): ^{1}H NMR ($CDCl_3$), δ 3.45 (dd, 1H), 3.92 (dd, 1H), 5.7 (dd, 1H), 7.5 (m, 4H), 7.32 (d, J = 9.0 Hz, 2H), 8.12 (d, J = 9.0 Hz, 2H). Quantitative analysis for **17** was based on integration of the area under the peak at δ = 5.7 and that for *p*-nitrobenzaldehyde on the area under the peak at δ = 10.2 (see above).

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