Experimental Section

sym-Dibenzcyclooctatetraene, synthesized as described in the literature, was purified by sublimation and melted at 107–108° (lit.[5c] m.p. 109°).

E.s.r. Measurements. Samples were prepared using techniques described by Bolton and Fraenkel.[22] However, in order to examine both the e.s.r. and n.m.r. spectra of the reaction mixtures as the hydrocarbon in THF reacted with the alkali metals, a different technique was used. An n.m.r. sample tube (5-mm. o.d.) with a slight constriction near the top was connected to a joint for attachment to a vacuum manifold. The hydrocarbon (10 mg.), dry THF (0.5 ml.), and a large piece of alkali metal were placed in the tube so that the metal remained above the constriction. The tube was degassed and sealed. Reaction was effected by inverting the tube and shaking, and spectra were determined at various times by reverting the tube.

The e.s.r. spectrometer was the X-band superheterodyne instrument with 1000-c.p.s. field modulation and a Varian Model V4012-3B 12-in. magnet and power supply, described by Bolton and Fraenkel.[22] The magnetic field was controlled by a Varian V3506 magnetic flux stabilizer that can scan a wide range of magnetic fields. Field measurements were made directly from calibrated strip-chart recordings.

Polarographic Measurements. High purity dioxane (Burdick and Jackson) was passed through alumina, refluxed with Na–K alloy, and distilled. A solution of 0.175 *M* tetra-*n*-butylammonium iodide in 96% dioxane–4% water was polarographically pure. The polarograms were determined against an s.c.e. electrode using a 1 m*M* solution of the hydrocarbon in this solvent. The instrument was an electronic one previously used.[2d]

N.m.r. Measurements. N.m.r. measurements were made using samples described in the e.s.r. section above and using samples in which the hydrocarbon concentration was initially greater. A 0.5 *M* solution of the hydrocarbon (0.48 mg.) in dry THF (0.5 ml.) and excess lithium metal were combined in an n.m.r. tube, similar to the one described above, the solution was degassed, and the tube was sealed. The n.m.r. spectrum, determined before the solution and metal could react, showed the spectra of THF and the hydrocarbon, but, after reacting for 1, 2, and 4 days and 1 year,[23] the solution produced the spectra of THF and the hydrocarbon dianion. Spectra were determined using a Varian A-60 instrument.

Hydrolysis of Dilithium sym-Dibenzcyclooctatetraenide. *sym*-Dibenzcyclooctatetraene (48.0 mg.), 0.5 ml. of dry THF, and a clean piece of lithium metal were combined in an n.m.r. tube that was then degassed and sealed. The reaction was monitored by periodically examining the n.m.r. spectrum. After formation of dilithium *sym*-dibenzcyclooctratetraenide was complete, the tube was opened in a nitrogen atmosphere and the solution poured into 10 ml. of 0.1 *N* hydrochloric acid. White crystals (m.p. 53–56.5°) separated and were purified by vacuum sublimation. The yield of 5,6-dihydro-*sym*-dibenzcyclooctatetraene, m.p. 58°, was 21.3 mg.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.30; H, 6.89.

The n.m.r. spectrum in CCl_4 relative to tetramethylsilane (TMS) consists of three singlets, at τ 3.02, 3.34, and 6.88, of relative intensity 8.3:2.0:3.7.

Acknowledgments. We are grateful to Professor George K. Fraenkel for the generous use of his e.s.r. equipment and for his advice, to Professor William Reinmuth for the use of his polarographic equipment, and to Messrs. R. Gibson and D. Noonan for polarograms. We are grateful to the National Science Foundation (NSFGP748), the National Institutes of Health (MH08912-01), and the Air Force (AF-AFOSR-285-63) for their support.

(22) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, 40, 3307 (1964).

(23) We thank William Okamura for this spectrum.

Radical Anions as Intermediates in Substitution Reactions. The Mechanism of Carbon Alkylation of Nitroparaffin Salts[1,2]

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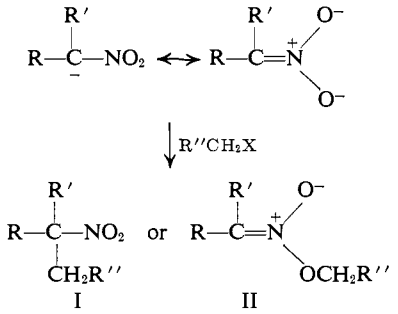
Oxygen alkylation of the nitroparaffin anion derives simply from an SN2 displacement by the oxygen of this ambident anion. In contrast, the carbon alkylation observed on treating nitroparaffin salts with o- and p-nitrobenzyl halides is viewed as a radical-anion process (eq. a–c). Evidence in support of the radical-anion mechanism is presented; particularly striking is the ability of a powerful electron acceptor such as p-dinitrobenzene to inhibit carbon alkylation. It is suggested that other substitution reactions may proceed via radical-anion intermediates.

(1) This research was supported, in part, by a grant from the Explosives Department of E. I. du Pont de Nemours and Co. and, in part, by the National Science Foundation.

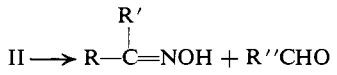
(2) Paper VII in the series, "The Chemistry of Ambident Anions." A preliminary account of this work appeared in R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, **86**, 3904 (1964). For the preceding paper in this series see N. Kornblum, R. Seltzer, and P. Haberfield, *ibid.*, **85**, 1148 (1963). This paper is also taken to be number XXIII in the series, "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

(3) National Science Foundation Cooperative Graduate Fellow, Purdue University, 1962–1964.

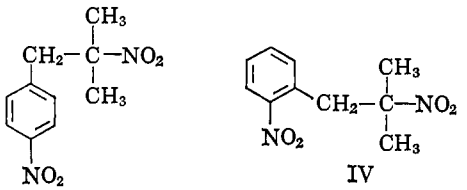
The anion derived from an aliphatic nitro compound is capable of covalency formation at either carbon or oxygen, *i.e.*, it is an ambident anion. Whereas the



carbon alkylation product I is stable, the nitronic ester II is never isolated; instead the carbonyl compound and oxime are obtained, and it is generally assumed that they arise from the nitronic ester.[4]



Reactions of the salts of nitro compounds with aliphatic, allylic, and benzylic halides usually produce carbonyl compounds and, in fact, serve as a useful means of preparing aldehydes and ketones.[4,5] However, instances are known in which the result is carbon alkylation. Thus, when *p*-nitrobenzyl chloride is treated with a salt of 2-nitropropane an 83–95% yield of III is obtained[4a,b,5b,6]; and from the reaction employing *o*-nitrobenzyl chloride a 46% yield of the carbon alkylate IV is isolated.[4b] Alkylation of nitroparaffin



salts with 2,4-dinitrobenzyl chloride also results in carbon alkylation.[4a,b] On the other hand, *m*-nitrobenzyl chloride gives no carbon alkylate,[4b] a result, as we shall see, of considerable significance.[7]

In 1949 a study of the reaction of a series of *para*-substituted benzyl halides with the sodium salt of 2-nitropropane revealed that only *p*-nitrobenzyl chloride gives carbon alkylation; benzyl halides substituted in the *para* position by CN, CF_3, $^+N(CH_3)_3$, $CH_3C{=}O$, $CH_3OC{=}O$, Br, and CH_3 give only oxygen alkylation.[4b] More recently it has been found that the uniqueness of the *p*-nitrobenzyl system depends not only on the *p*-nitro group but also on the leaving group.[6] Thus, whereas *p*-nitrobenzyl chloride gives 95% carbon alkylation, *p*-nitrobenzyl iodide gives 81% oxygen alkylation. From Table I it is clear that carbon alkylation predominates in the *p*-nitrobenzyl system only when the leaving group is one which is difficultly displaced. It is also noteworthy that the unsubstituted benzyl system shows no leaving group effect; the reactions of benzyl chloride, bromide, iodide, or tosylate with the lithium salt of 2-nitropropane all give 82–84% yields of benzaldehyde.

Table I. Nature of Reaction of p-$O_2NC_6H_4CH_2X$ with the Lithium Salt of 2-Nitropropane in DMF as a Function of X[a]

X	C, %	O, %
$^+NMe_3$	93	0
C_6Cl_5COO	93	0
Cl	95	1
OTos	40	32
Br	17	65
I	7	81

[a] *Cf.* ref. 5b for details.

To all these facts yet one more must be added. Whenever carbon alkylation in the *p*-nitrobenzyl system occurs to the essential exclusion of oxygen alkylation (*i.e.*, when the leaving group is NMe_3, pentachlorobenzoate, or chloride), the reaction rate is much faster than for the corresponding unsubstituted benzyl compound. But when the *p*-nitro group is unable to effect carbon alkylation of the 2-nitropropane anion, it simultaneously fails to produce a large increase in rate relative to the corresponding benzyl compounds (Table II).

Table II

X	Reaction rates $\frac{p\text{-}O_2NC_6H_4CH_2X}{C_6H_5CH_2X}$
$^+NMe_3$	>100
C_6Cl_5COO	>100
Cl	>100
OTos	8
Br	6
I	3

On the basis of these findings it was proposed that oxygen alkylation, the usual mode of reaction of a nitroparaffin anion, derives simply from nucleophilic displacement by the oxygen of the anion on the benzylic carbon but that in the *p*-nitrobenzyl series, when the leaving group is one which is difficultly displaced, a second mode of attack by the nitroparaffin anion has a chance to compete and it is this second process which is productive of carbon alkylation.[6] The nature of the carbon alkylation process is the subject of this paper and, as will be seen from the sequel, the studies herein described provide strong support for the view that carbon alkylation is a radical-anion process. Three lines of evidence, the last of which we regard as particularly compelling, form the basis for our view: (a) rate studies, (b) e.p.r. studies, and (c) inhibition of carbon alkylation.

Rate Studies. The proposal that oxygen alkylation derives simply from a nucleophilic displacement by the oxygen of the nitroparaffin anion and that, in con-

(4) (a) L. Weisler and R. W. Helmkamp, *J. Am. Chem. Soc.*, **67**, 1167 (1945); (b) H. B. Hass and M. L. Bender, *ibid.*, **71**, 1767, 3482 (1949); (c) N. Kornblum and R. A. Brown, *ibid.*, **86**, 2684 (1964).

(5) (a) H. B. Hass and M. L. Bender, *Org. Syn.*, **30**, 99 (1950); (b) for a summary, *cf.* N. Kornblum and P. Pink, *Tetrahedron*, **19**, Suppl. 1, 17 (1963).

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

(7) 5-Nitrofurfuryl chloride, in which the nitro and chloromethyl groups stand in relation to one another as they do in *p*-nitrobenzyl chloride, also gives a substantial amount of carbon alkylate: N. Chessin, M. S. Thesis, Ohio State University, 1951.

trast, carbon alkylation is an indirect process[6,8] suggested that separation of the over-all rates at which the lithium salt of 2-nitropropane reacts with nitrobenzyl halides into the carbon and the oxygen components might be illuminating. If carbon alkylation is indirect, then its rate might be expected to be less dependent on leaving group than that of oxygen alkylation.

For such a kinetic analysis reliable data concerning the yields of products were required. Although it is relatively easy to isolate the carbon alkylates III and IV, precise determination of *o*- and *p*-nitrobenzaldehydes, the products of oxygen alkylation, is not so easy; eventually, a simple and effective procedure was devised, (*cf.* Experimental) and the data obtained are given in Table III.

Table III. Products of Alkylation of the Lithium Salt of 2-Nitropropane by *o*- and *p*-Nitrobenzyl Halides[a]

X	*o*-$O_2NC_6H_5CH_2X$ % C[b]	*o*-$O_2NC_6H_5CH_2X$ % O[c]	*p*-$O_2NC_6H_5CH_2X$ % C[d]	*p*-$O_2NC_6H_5CH_2X$ % O[c]
Cl	31	52	92	6
Br	1	98	20	60
I	..	..	8	86

[a] At 0° in DMF. [b] By v.p.c. [c] By oxidation to the nitrobenzoic acid (*cf.* Experimental Section). [d] Isolated.

It should be noted that the *o*-nitrobenzyl system, like the *p*-nitrobenzyl system, shows a pronounced leaving group effect. Furthermore, it is clear that the *o*-nitro group is considerably less effective at fostering carbon alkylation than the *p*-nitro group.

In Table IV over-all rate constants for the reaction between *o*-, *m*-, and *p*-nitrobenzyl halides and the lithium salt of 2-nitropropane are recorded. The *m*-nitrobenzyl rates were determined because *m*-nitrobenzyl halides give only oxygen alkylation; this provides a standard of reference for the rate effect in the oxygen alkylation process as the leaving group is changed from chlorine to bromine to iodine.[9]

Table IV. Over-All Rate Constants for Reaction between Nitrobenzyl Halides and the Lithium Salt of 2-Nitropropane[a]

X	*ortho*	*para*	*meta*
Cl	0.0052	0.023	0.0013
Br	0.33	0.34	0.28
I[b]	...	1.9	1.4

[a] In M^{-1} sec.$^{-1}$; at 0° in DMF. [b] Extrapolated from −23°.

When the over-all rates of Table IV are broken down into their carbon and oxygen components by use of the product data of Table III a striking fact emerges. In the *o*-, or the *m*-, or the *p*-nitrobenzyl series, on passing from the chloride to the bromide to the iodide, the rate of oxygen alkylation increases by a factor of 1000; in sharp contrast, the rate of carbon alkylation only increases by a factor of seven (Table V). In other words, the rate of oxygen alkylation is strongly dependent on the leaving group, whereas the rate of carbon alkylation is relatively insensitive to the leaving group.

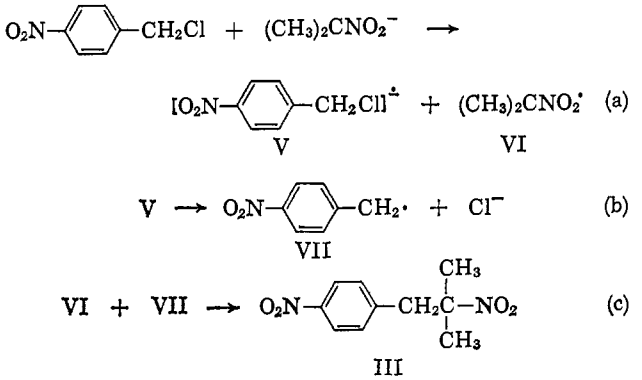
Table V. Rates of Carbon and Oxygen Alkylation of the Lithium Salt of 2-Nitropropane by Nitrobenzyl Halides[a,b]

Halide	k_{oxygen} *ortho*	k_{oxygen} *meta*	k_{oxygen} *para*	k_{carbon} *ortho*	k_{carbon} *para*
Cl	0.0036	0.0013	0.002	0.0016	0.021
Br	0.32	0.28	0.27	0.004	0.068
I[c]	...	1.4	1.8	...	0.15

[a] In DMF at 0°; k in units of M^{-1} sec.$^{-1}$. [b] $k_{carbon} = k_{over\text{-}all}$ (% C-alkylation); $k_{oxygen} = k_{over\text{-}all} - k_{carbon}$. For the *meta*, $k_{oxygen} = k_{over\text{-}all}$. [c] Extrapolated from −23°.

The large spread in the rate of oxygen alkylation on going from a chloride to a bromide to an iodide is to be expected for an SN2 displacement in a dipolar aprotic solvent such as DMF[10] and provides support for the proposed[6] SN2 mechanism for oxygen alkylation. By the same token, the lack of sensitivity of the rate of carbon alkylation to the leaving group strongly suggests that here we do not deal with a single-stage SN2 displacement but, rather, with an indirect process.[6,8] In addition, the rate data provide an insight as to the nature of the indirect process which leads to carbon alkylation. It will be seen from Table V that the rate of carbon alkylation in the *ortho* series is less than one-tenth that in the *para* series. This presumably reflects the steric inhibition to resonance to which the *o*-nitro group is subject. Even more dramatic, with the nitro group in the *meta* position, the rate of carbon alkylation becomes immeasureably slow. Clearly, conjugative electron acceptance by the nitro group is an important aspect of the indirect process.

We propose that carbon alkylation proceeds by a radical-anion mechanism; on this basis a simple rationale is provided for the facts which have been described and for those which follow.[11]



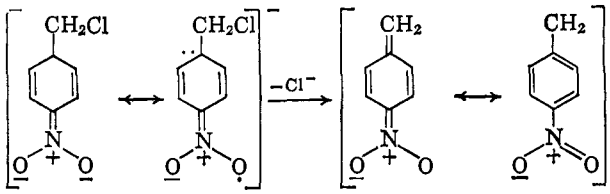
Loss of chloride from the radical anion V to give the *p*-nitrobenzyl radical VII (step b) seems somewhat contrived until the structures are written out in more detail; it then becomes apparent that ejection of the chloride ion from V is, in essence, nothing more than

(8) Paul C. Pink, Ph.D. Thesis, Purdue University, Aug. 1961, pp. 28–33.

(9) The *m*-nitrobenzyl halides provide a better standard than the unsubstituted benzyl halides because they react in SN2 reactions at nearly the same rates as the *p*-nitrobenzyl halides and, accordingly, allow more accurate determination of relative rates: *cf.* J. B. Conant, W. R. Kirner, and R. E. Hussey, *J. Am. Chem. Soc.*, 47, 488 (1925); R. Fuchs and D. M. Carlton, *J. Org. Chem.*, 27, 1520 (1962).

(10) A. J. Parker, *J. Chem. Soc.*, 1332 (1961).

(11) Actually, this mechanism was first proposed by us in 1960: Status Report No. 1 to the Office of Ordnance Research (Durham) under Contract No. DA-33-008-ORD-1951, pp. 5, 6; also see ref. 8 of the present paper.



V VII

an elimination reaction producing an olefin; this olefin happens to have the special property that it is also a free radical, a property which is utilized in step c.

E.p.r. Studies. In step a it is postulated that the anion derived from 2-nitropropane transfers one electron to a nitroaromatic system. Actually, direct evidence for this view has been obtained.

A solution initially 0.01 *M* in *p*-nitrobenzyl chloride and 0.02 *M* in the lithium salt of 2-nitropropane (prepared in a nitrogen atmosphere with deoxygenated DMF) at −30° showed a weak signal when investigated by e.p.r. However, when the concentrations were increased to 0.2 *M* chloride and 0.4 *M* lithium salt, an appreciably stronger signal was observed. The resonance was unresolved but had an over-all width of about 30 gauss at −50°. Obviously, observation of resonances in a reacting solution such as this is complicated by several factors. At room temperature the reaction is so fast that there is insufficient time to tune the e.p.r. spectrometer properly before the reaction is complete. At low temperatures, on the other hand, the reaction is slowed down, but the concentrations of radical intermediates are necessarily reduced. At the low concentrations involved no resolution of the e.p.r. spectra into fine structure is possible, and consequently the identification of the radicals is impossible. Moreover, the occurrence of three radical species (V, VI, and VII) in the reaction solution provides a further possible complication.

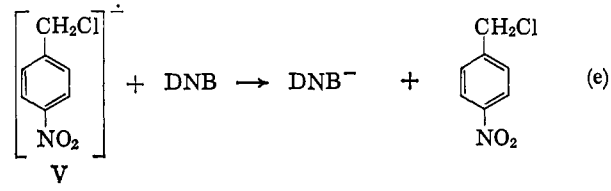
These difficulties were surmounted by the use of nitroaromatics which can form relatively stable radical anions on reduction. Thus a DMF solution 0.4 *M* in the lithium salt of 2-nitropropane and 0.2 *M* in nitrobenzene gave a resonance of about 35-gauss width. This could be resolved into a 10-line spectrum at room temperature, but cooling to −50° in an attempt to improve the resolution destroyed the spectrum entirely. Evidently the reduction of nitrobenzene by the nitroparaffin salt is reversible and endothermic (eq. d). The 10-line spectrum observed at room temperature is

$$C_6H_5NO_2 + (CH_3)_2CNO_2^- \rightleftharpoons C_6H_5NO_2^{\cdot-} + (CH_3)_2CNO_2^{\cdot} \quad (d)$$

fully consistent with the nitrobenzene radical anion, having A_N about 10.5 gauss, and A_H about 3.5 gauss for the *o*- and *p*-hydrogens. Distinction between *ortho* and *para* protons, and further splittings due to the *meta* protons could not be observed because of the line widths of nearly 2 gauss, presumably caused by exchange broadening in the relatively concentrated solutions.[12] Nonetheless, the observed spectrum is in substantial agreement with published coupling constants for the nitrobenzene radical anion in aprotic solvents.[12,13] In the same way, we have observed e.p.r. spectra on treating *m*- and *p*-dinitrobenzene (DNB) and *p*-nitrobenzyl methyl ether with the lithium salt of 2-nitropropane in DMF at room temperature. These results are in agreement with those of Russell, Janzen, and Strom[14] who earlier found that the nitrobenzene radical anion was produced (in 80% DMSO–20% *t*-butyl alcohol) on treating nitrobenzene with nitroparaffin salts.

The e.p.r. results show that electron transfer from the lithium salt of 2-nitropropane to nitroaromatics does occur under the reaction conditions and, thereby, they provide important support for the view that carbon alkylation of nitroparaffin salts goes *via* an electron-transfer mechanism. However, the e.p.r. findings do not constitute a demonstration of the radical-anion mechanism; for reaction a, like reaction d, must be reversible and, conceivably, reaction a is but a blind alley rather than a portion of the road which terminates in carbon alkylation.

Inhibition of Carbon Alkylation. Radical anions derived from nitroaromatics are relatively long-lived species.[13,15] Furthermore, electron transfer from nitroaromatic radical anions to nitroaromatics is often very rapid.[16] Consequently, it appeared possible that an easily reduced nitroaromatic such as a dinitrobenzene (DNB) might be able to take an electron away from the radical anion V before loss of chloride occurred (eq. b) and, thereby, prevent carbon alkylation. The net effect of such interception would be to retard



V (e)

carbon alkylation without affecting oxygen alkylation, and, hence, the proportion of oxygen alkylate should rise even as that of carbon alkylate falls.[17] As can be seen from Table VI, when the lithium salt of 2-nitro-

Table VI. The Influence of Nitroaromatics on the Reaction of *p*-Nitrobenzyl Chloride with the Lithium Salt of 2-Nitropropane[a]

Added nitroaromatic (mmoles)	% yield C-Alkylate	% yield O-Alkylate
None	92	6
$PhNO_2$ (40)	84	7
m-DNB (10)	61	29
m-DNB (20)	40	48
p-DNB (2)	6	88
p-DNB (10)	2	72

[a] In DMF at 0° using 10 mmoles of chloride and 21 mmoles of lithium salt.

(12) See, for instance, R. L. Ward, *J. Am. Chem. Soc.*, **83**, 1296 (1961); *J. Chem. Phys.*, 30, 852 (1959).

(13) (a) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960); (b) T. Kitagawa, T. P. Layloff, and R. N. Adams, *Anal. Chem.*, **35**, 1086 (1963); (c) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963); (d) T. Fujinaga, Y. Deguchi, and K. Umemoto, *Bull. Chem. Soc. Japan*, **37**, 822 (1964).

(14) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

(15) L. H. Piette, P. Ludwig, and R. N. Adams, *ibid.*, **84**, 4212 (1962).

(16) See, for example, S. I. Weissman, *Z. Elektrochem.*, **64**, 47 (1960); R. L. Ward, *J. Chem. Phys.*, **32**, 410 (1960); M. T. Jones and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4269 (1962).

(17) Direct interaction of the electron acceptor with the 2-nitropropane anion may also occur but this should not in itself affect the relative amounts of C- and O-alkylation since both processes are apparently second order and should, therefore, be equally affected by the lowered concentration of the free nitroparaffin anion.

propane is alkylated with *p*-nitrobenzyl chloride in the presence of aromatic nitro compounds, carbon alkylation is, indeed, suppressed. It will be noted that the effectiveness of the nitroaromatics in suppressing carbon alkylation decreases in the order *p*-DNB > *m*-DNB > $PhNO_2$ and this coincides with their ease of reduction: *p*-DNB > *m*-DNB > $PhNO_2$.[18,19]

The view that *p*-DNB increases the proportion of oxygen alkylate by retarding carbon alkylation, rather than by increasing the rate of oxygen alkylation, is fully supported by rate studies. Whereas the reaction of *p*-nitrobenzyl chloride (0.01 *M*) with the lithium salt of 2-nitropropane (0.02 *M*) has a second-order rate constant $k_2 = 23 \times 10^{-3}\ M^{-1}$ sec.$^{-1}$, in the presence of *p*-DNB (0.01 *M*), the over-all rate is reduced by a factor of ten ($k_2 = 2.0 \times 10^{-3}\ M^{-1}$ sec.$^{-1}$). In contrast, the rate for alkylations employing *m*-nitrobenzyl chloride is but slightly reduced on adding *p*-DNB; k_2 goes from 1.3×10^{-3} to $0.90 \times 10^{-3}\ M^{-1}$ sec.$^{-1}$.

The results of the run using only 2 mmoles of *p*-DNB are especially interesting in that the yield of carbon alkylate III is reduced from 92 to 6%, *i.e.*, from 9.2 mmoles to 0.6 mmole; in other words, the presence of 2.0 mmoles of *p*-DNB decreases the yield of C-alkylate by 8.2 mmoles. Clearly each *p*-DNB molecule is capable of repeatedly interrupting the carbon-alkylation process. This can be rationalized by assuming that the *p*-DNB radical anion gives an electron to the 2-nitropropyl radical (eq. f)[20]; the

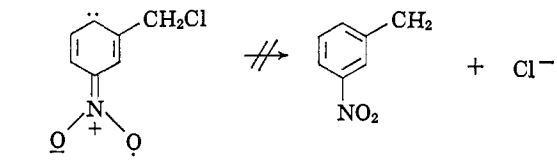
$$p\text{-DNB}^{\cdot-} + \underset{\text{VI}}{(CH_3)_2\dot{C}NO_2} \rightleftharpoons p\text{-DNB} + (CH_3)_2CNO_2^- \quad \text{(f)}$$

process described by eq. f should be an efficient one because, in our view, the 2-nitropropyl radical VI and the radical anion V (produced in the reaction of eq. a) remain together for a significant period (*vide infra*) and, as a consequence, *p*-DNB$^{\cdot-}$ and VI should be in the same solvent cage. The over-all result of reactions e and f, then, is that all substances revert to their initial oxidation states. Furthermore, on this basis the absence of 2,3-dimethyl-2,3-dinitrobutane, the dimer of the 2-nitropropyl radical VI, in reaction mixtures containing *p*-DNB or other nitroaromatics is easily understood.

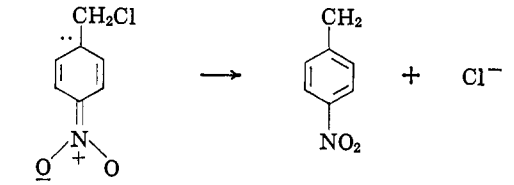
Alkylation of the lithium salt of 2-nitropropane with *p*-nitrobenzyl chloride in ethanol[4] must proceed by the same mechanism as in DMF. In the absence of nitroaromatics a 90% yield of carbon alkylate III is obtained, but the presence of 2 mmoles of *p*-DNB (per 10 mmoles of *p*-nitrobenzyl chloride) cuts the yield of carbon alkylate III to 31% and produces an unmistakable rise in the amount of oxygen alkylate. Furthermore, oxygen has an inhibitory effect on carbon alkylation, as might be expected for a radical process.

The absence of symmetrical coupling products, 2,3-dimethyl-2,3-dinitrobutane (from the 2-nitropropyl radical VI) and *p,p'*-dinitrobibenzyl (from the *p*-nitrobenzyl radical VII), and the high yields of carbon alkylate III, can only mean that the radicals VI and VII are formed in the immediate vicinity of each other and couple cleanly as in eq. c. This, in turn, requires that the 2-nitropropyl radical VI must remain in the vicinity of the radical anion V until the latter eliminates halide ion to give the *p*-nitrobenzyl radical VII with which the 2-nitropropyl radical couples. The preference of the radical anion V and the 2-nitropropyl radical VI for remaining together may derive from weak bonding between them, perhaps due to a π-complex in which the radical anion V acts as a donor toward the 2-nitropropyl radical.[21] The postulated weak interaction between the radical anion V and the 2-nitropropyl radical is also consonant with the explanation proposed for the suppression of carbon alkylation by *p*-DNB; for by increasing the lifetime of the radical anion V, interception by *p*-DNB, as shown in eq. e, is facilitated.

The fact that *o*-nitrobenzyl chloride gives carbon alkylation at a rate one-tenth that of *p*-nitrobenzyl chloride is readily understood in view of Geske's report that *o*-nitrotoluene is significantly more difficult to reduce than *p*-nitrotoluene.[22] This is reasonably assumed to be due to steric hindrance to coplanarity in the *ortho* isomer, which lowers the reducibility of the system by tending electronically to isolate the nitro group from the ring. In contrast, *m*-nitrotoluene is as easily reduced polarographically as *p*-nitrotoluene,[22] yet *m*-nitrobenzyl chloride fails to give any carbon alkylation. This reflects the inability of the *m*-nitrobenzyl chloride radical anion to lose chloride ion by an internal elimination analogous to that available to the *p*-nitrobenzyl chloride radical anion.[23] Thus, the *p*-nitrobenzyl chloride radical anion



whereas



V has the special property that by loss of a stable anion it is readily transformed into the corresponding free radical VII, and this is what sets it apart

(18) Polarographic reduction potentials *vs.* the saturated aqueous calomel electrode, in acetonitrile at 25°: *p*-DNB, −0.69 v.; *m*-DNB, −0.90 v.; $PhNO_2$, −1.15 v.: A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

(19) A small, but probably real, effect is also observed with *p*-$C_6H_4(CN)_2$; the presence of 10 mmoles results in 86% C- and 10% O-alkylation. With $CuCl_2$ (10 mmoles) 82% C- and 8% O-alkylate is obtained.

(20) It will be noted that the reactions of eq. a, d, and f are all of the form: Aryl-NO_2 + $(CH_3)_2$C-NO_2^- ⇌ Aryl-$NO_2^{\cdot-}$ + $(CH_3)_2CNO_2^{\cdot}$ but in the case of reaction a, the radical anion V has an additional avenue of reaction open to it (eq. b).

(21) We are not attracted to the view that this is simply a solvent cage effect [J. Franck and E. Rabinowitz, *Trans. Faraday Soc.*, **30**, 120 (1934); R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950)] because almost identical yields (92 and 90%) of carbon alkylate III are obtained with *p*-nitrobenzyl chloride in DMF and in ethanol. Also, to argue that the absence of symmetrical coupling products is due to the inability of V or VI to leak out of the solvent cage while insisting that *p*-DNB can leak into the solvent cage and intercept the radical anion V seems a bit contrived.

(22) D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.*, **86**, 987 (1964).

(23) This difference not only derives from the quite disparate stabilities of the *m*- and *p*-nitrobenzyl radicals but is also consistent with the e.p.r. results of nitrobenzene and derivatives, which invariably show appreciable electron densities in the positions *ortho* and *para* to the

from other radical anions which have, hitherto, been described.[24]

The failure of such alkylating agents as *p*-cyanobenzyl or *p*-acetylbenzyl chloride to bring about carbon alkylation of the 2-nitropropane anion[4b] must reflect their lower reducibility relative to the nitrobenzyl chlorides.[25] There is, however, no reason why the *o*- and *p*-nitrobenzyl systems should be unique. Thus, we anticipate that 2,4,6-tricyanobenzyl chloride (and probably 2,4-dicyanobenzyl chloride) will alkylate nitroparaffin anions on carbon; *i.e.*, they, too, will be capable of reacting by the radical-anion mechanism.

That carbon alkylation is not a light-induced process was shown by an experiment in which *p*-nitrobenzyl chloride and the lithium salt of 2-nitropropane were allowed to react in DMF solution, at 0°, in total darkness. A 94% yield of carbon alkylate III and a 6% yield of oxygen alkylate resulted. Thus the reaction follows the same course in the presence and in the absence of light (*cf.* Table III).

Recognition of radical anions as intermediates in the carbon alkylation of nitroparaffin salts raises an important question: How widely do radical anions occur as intermediates in substitution reactions? Furthermore, the finding that the 2-nitropropane anion alkylates on oxygen while the 2-nitropropyl radical alkylates on carbon suggests that with other ambident systems there may also be substantial differences in the way the anion and the radical react. It is hoped that studies in progress of a wide variety of substitution processes, employing both ambident and nonambident nucleophiles, will provide answers to these questions.[26]

Experimental Section[27]

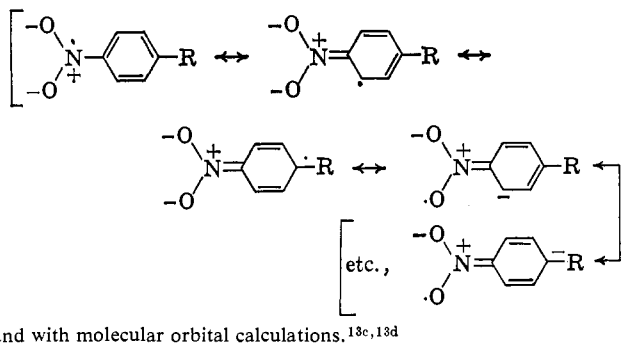
Dimethylformamide (DMF) was dried by mixing with about 10% (volume) of benzene and distilling off the benzene at atmospheric pressure. The DMF was then stirred overnight at room temperature with phosphorus pentoxide, siphoned off, and stirred over potassium hydroxide for 3 hr.; it was then siphoned off again and distilled at reduced pressure, b.p. 47–49° (15 mm.). A highly purified sample of 2-nitropropane (99.9+%) was supplied by Commercial Solvents Corp.[28] *p*-Nitrobenzyl chloride and bromide and *m*-nitrobenzyl chloride were Eastman White Label products; *o*-nitrobenzyl chloride was from Columbia Organic Chemicals. The *ortho* bromide and the nitrobenzyl iodides were prepared by treating the appropriate chloride with sodium iodide or sodium bromide in acetone. The *meta* bromide was prepared by treating *m*-nitrobenzyl alcohol with concentrated aqueous HBr.[29] All halides were recrystallized from hexane–benzene, and had melting points in agreement with literature values.

Lithium Salt of 2-Nitropropane. A lithium ethoxide solution was prepared by careful addition of lithium hydride (Lithium Co. of America, 0.78 g., 0.098 mole) to 100 ml. of absolute ethanol. After the solution had become clear, 9.00 g. of 2-nitropropane (0.101 mole) was added, and the solution was transferred to a 1-l. round-bottom flask and stripped down at room temperature on a rotatory evaporator. When the solution became viscous, but before precipitation of the salt began, about 700 ml. of absolute ether (Mallinckrodt) was added to cause precipitation. The resulting slurry was filtered in a nitrogen-filled glove box, and the precipitate was washed with ether and transferred to a 200-ml. round-bottom flask. It was subjected to vacuum overnight, crushed, and kept under oil-pump vacuum for another 24 hr. Potentiometric titration of weighed samples with ethanolic picric acid showed a neut. equiv. of 95.5 (theoretical neut. equiv. 95.0).

Alkylation of the Lithium Salt of 2-Nitropropane with p-Nitrobenzyl Chloride. The lithium salt (2.00 g., 21.0 mmoles) was dissolved in 40 ml. of DMF and cooled to 0°. Then 1.72 g. of *p*-nitrobenzyl chloride (10.0 mmoles) was added and washed in with 10.0 ml. of DMF. The flask was flushed with nitrogen, sealed with Parafilm, and kept at 0°. After 48 hr., the solution was added to 100 ml. of water, acidified with 2 ml. of concentrated nitric acid, and extracted with three 50-ml. portions of benzene and one of ether. Titration of the aqueous phase for chloride ion showed the reaction to be 95% complete. The combined organic layers were dried over magnesium sulfate and evaporated, and the residue was made up to 50.0 ml. with benzene, yielding solution A.

A 20.0-ml. aliquot of solution A was evaporated, the residue was dissolved in a mixture of 40 ml. of dioxane and 100 ml. of water, and to this was added 10 ml. of 5% aqueous sodium hydroxide solution and 6.00 g. of potassium permanganate. The mixture was stirred without heating for 4.5 hr., after which it was acidified with concentrated hydrochloric acid and treated with enough sodium bisulfite to produce a clear solution. The resulting acidic solution was repeatedly extracted with ether and the extracts were washed repeatedly with 1% aqueous sodium hydroxide; the alkaline washings were acidified with hydrochloric acid and extracted with ether. Evaporation of the

nitro group, and only small values in the *meta* positions, in agreement with resonance structures such as



and with molecular orbital calculations.[13c,13d]

(24) Obviously, the *o*-nitrobenzyl chloride radical anion also possesses this characteristic.

(25) This view is consistent with the report that substantially more negative potentials are necessary to reduce compounds such as benzonitrile and acetophenone than are necessary for nitrobenzene derivatives[13o]: P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 37, 2811 (1962); P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, 85, 683 (1963).

(26) Three other mechanisms for carbon alkylation were considered: a graded SN1–SN2 process, a carbene mechanism, and a mechanism involving initial attack by the nitroparaffin anion on the carbon of the ring holding the CH_2Cl group. The reasons for their rejection are described in the Ph.D. Thesis of R. C. Kerber, Purdue University, Jan. 1965.

(27) Analyses were performed by Dr. C. S. Yeh of Purdue University or Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(28) We wish to thank Commercial Solvents Corp. for a generous gift of this material.

(29) J. F. Norris, M. Watt, and R. Thomas, *J. Am. Chem. Soc.*, 38, 1071 (1916).

ether solution, followed by drying *in vacuo* over potassium hydroxide, gave 0.037 g. of crude *p*-nitrobenzoic acid, m.p. 216–220° (0.037 g. $\times$ $^{50}/_{20}$ $\times$ $^{100}/_{95}$ = 0.097 g. total in solution A = 6% oxygen alkylate). This oxidation method (procedure I) gave quantitative yields of *p*-nitrobenzoic acid from *p*-nitrobenzaldehyde, from the nitro alcohol *p*-$O_2NC_6H_4CHOH$-CMe_2NO_2, m.p. 148.5–149.5°, prepared by condensing 2-nitropropane with *p*-nitrobenzaldehyde, and from *p*-nitrobenzyl alcohol, but left the carbon alkylate III untouched; it also produced only 2–4% *p*-nitrobenzoic acid from *p*-nitrobenzyl iodide, 14% *p*-nitrobenzoic acid from *p*-nitrobenzyl bromide, and 6% *p*-nitrobenzoic acid from *p*-nitrobenzyl chloride.

Another 20-ml. aliquot of solution A was evaporated and the residue chromatographed on Merck basic alumina using benzene–hexane mixtures and then benzene for elution. In this way 0.782 g. of C-alkylate III, 92% yield, m.p. 66–67° (lit.[5] m.p. 67–68°), was obtained. V.p.c. analysis of solution A using a 5-ft. $\times$ 0.25-in. SF-96 on HMDS-treated Chromosorb W column, at 200° and 20 p.s.i. of helium carrier gas, confirmed the 92% yield of III. Analysis of solution A at 115° on the SF-96 column showed no trace of the dimer of the 2-nitropropyl radical, 2,3-dimethyl-2,3-dinitrobutane. A standard solution of the dimer equivalent to a 2% yield gave an easily discernible peak.

Alkylation of the Lithium Salt of 2-Nitropropane with p-Nitrobenzyl Bromide. A solution containing 2.00 g. (21 mmoles) of the lithium salt of 2-nitropropane in 55 ml. of DMF was cooled to 0° and treated with 4.10 g. (19.0 mmoles) of *p*-nitrobenzyl bromide. After 17 hr. at 0°, under nitrogen, the product was worked up as in the preceding experiment. Bromide ion titration revealed that the reaction was 94% complete. Oxidation of two-fifths of the product (procedure I) gave 0.684 g. of *p*-nitrobenzoic acid, m.p. 235–237°, 57% oxygen alkylation. Chromatography of another two-fifths of the product yielded 0.279 g. of C-alkylate III, m.p. 62–64°, 17% yield.

Alkylation by p-Nitrobenzyl Iodide. A solution of 2.00 g. (21 mmoles) of the lithium salt of 2-nitropropane in 55 ml. of DMF was treated with 5.00 g. (19.0 mmoles) of *p*-nitrobenzyl iodide at 0°, under nitrogen, for 13 hr. The work-up was as for the *p*-nitrobenzyl chloride reaction except that, prior to extracting with benzene, sodium bisulfite was added to the acidic solution to reduce free iodine. Iodide ion titration showed that the reaction had gone 66% to completion. Oxidation of two-fifths of the product (procedure I) gave 0.716 g. of *p*-nitrobenzoic acid, m.p. 235–237° (4.29 mmoles $\times$ $^{5}/_{2}$ $\times$ $^{100}/_{66}$ $\times$ $^{100}/_{19}$ = 86% oxygen alkylation). Chromatography of another two-fifths of the product yielded 0.094 g. of C-alkylate III, m.p. 59–62°, 8% yield.

Kinetic Method. DMF (100 ml.) was pipetted into each of two 250-ml. glass-stoppered Erlenmeyer flasks. In one was dissolved about 2 mmoles of the nitrobenzyl halide (and 2 mmoles of *p*-DNB, when used), and in the other about 4 mmoles (0.380 g.) of the lithium salt of 2-nitropropane, both samples being weighed on an analytical balance. The two solutions were equilibrated at 0 (ice bath) or −23° (CCl_4 slurry) for at least 45 min. with frequent agitation. The salt solution was then rapidly poured into the halide solution, a stopwatch was started, and the solutions were thoroughly mixed by swirling. At the desired intervals, 25-ml. aliquots were removed by pipet, the time being measured at half-delivery, and added to 100 ml. of water acidified with nitric acid. The resulting solution was titrated potentiometrically with 0.03 *M* $AgNO_3$ solution. In the case of *m*-nitrobenzyl iodide only, it was necessary to extract the solution with benzene before titrating; the other halides were stable to the titration conditions. The titration data were converted to per cents of reaction and used to calculate second-order rate constants. Reactions were generally followed to 90% completion. The points gave a linear second-order plot, the slope of which, evaluated graphically and by least squares, was the desired rate constant. The two methods of evaluating the slope usually gave values within 2% of one another. At least three runs were made for each nitrobenzyl halide; rate constants reported in Table IV are average values. Deviations between runs were generally less than 10%.

Data and calculations for a typical run, that using *p*-nitrobenzyl bromide at 0°, are shown in Table VII. Plotting the quantity on the right *vs.* *t* gave a good straight line, whose slope was estimated visually to be 0.342; by least squares the slope was 0.341. Duplicate experiments gave values for the slope of 0.332 and 0.347 M^{-1} sec.$^{-1}$.

Table VII

	A_0 = 0.0200 *M* (salt)		B_0 = 0.0100 *M* (bromide)	[2.303/(A_0 − B_0)]
t (sec.)	% reaction	$A_0 - B_0$ (%/100)	A_0 (1 − %/100)	log ($A_0 - B_0$)/A_0
52	40.0	0.0160	0.0120	28.7
115	54.7	0.0145	0.00906	47.1
182	67.2	0.0133	0.00656	70.4
240	73.6	0.0126	0.00528	87.1
305	80.1	0.0120	0.00398	110.1
390	86.7	0.0113	0.00266	144.7
480	90.5	0.0109	0.00190	172.1

The iodides and bromides were run at −23°, and the bromides and chlorides at 0°. The iodide rate data were extrapolated to 0° by assuming a constant bromide-to-iodide rate ratio at both temperatures.

Reaction of o-Nitrobenzyl Chloride with the Lithium Salt of 2-Nitropropane. A solution of 5.35 g. (56.3 mmoles) of the lithium salt in 200 ml. of DMF was cooled to 0° and treated with 4.84 g. (28.2 mmoles) of *o*-nitrobenzyl chloride. The flask was swirled until a clear solution was produced, and the reaction was allowed to proceed, under nitrogen, at 0° for 22 hr. The work-up followed the lines of the *p*-nitrobenzyl chloride procedure. Chloride ion titration showed the reaction was 87% complete. Oxidation of three-tenths of the product (procedure I) yielded 0.614 g. of *o*-nitrobenzoic acid, m.p. 130–135° (52%).

Oxidation of pure *o*-nitrobenzaldehyde by procedure I gave an 88% yield of *o*-nitrobenzoic acid, m.p. 146–147°.

From another portion of the product a sample of the pure C-alkylate IV was isolated by chromatography on basic alumina followed by preparative v.p.c., m.p.

55–55.5°, lit.[4b] m.p. 54–55°. The infrared and n.m.r. spectra were consonant with the assigned structure, 2-(*o*-nitrobenzyl)-2-nitropropane.

Anal. Calcd. for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.40; N, 12.49; mol. wt., 224. Found: C, 53.59; H, 5.50; N, 12.28; mol. wt., 216.

Chromatography on basic alumina of three-tenths of the product mixture gave 0.483 g. of C-alkylate IV, m.p. 52–55° (31%). Repeat runs gave 28 and 29% C-alkylate IV, 44 and 47% O-alkylate.

Reaction of o-Nitrobenzyl Bromide with the Lithium Salt of 2-Nitropropane. Two 100-ml. portions of DMF were cooled to 0°; in one was dissolved 5.00 g. of lithium salt (52.6 mmoles), and in the other 5.68 g. of *o*-nitrobenzyl bromide (26.3 mmoles). After 1 hr. at 0°, the salt solution was rapidly added to the other, and they were stirred at 0° for 4.5 hr. under nitrogen; the product was worked up as usual. Bromide ion titration showed 100% reaction.

V.p.c. analysis (*vide supra*) showed only 1.1% of C-alkylate and chromatography of one-half of the product on Merck basic alumina gave no C-alkylate. Oxidation of one-fifth of the product (procedure I) yielded 0.743 g. (4.45 mmoles) of *o*-nitrobenzoic acid, m.p. 143–145°; m.m.p. (with an authentic sample, m.p. 146–147°) 144–146°. This is an 84% yield of O-alkylate. Since pure *o*-nitrobenzaldehyde gave only 88%, this clearly represents a nearly quantitative yield of the aldehyde. Treatment of another fifth of the product with 2,4-dinitrophenylhydrazine reagent gave 1.72 g. of the 2,4-dinitrophenylhydrazone of *o*-nitrobenzaldehyde, m.p. 226° dec. (98% yield).

Reaction of m-Nitrobenzyl Chloride with the Lithium Salt of 2-Nitropropane. To an ice-cold solution of 2.0 g. (21 mmoles) of the lithium salt in 50 ml. DMF was added 1.72 g. (10.0 mmoles) of *m*-nitrobenzyl chloride. The reaction was conducted at 0° for 48 hr. under nitrogen, 82% reaction. Oxidation of one-tenth of the product with 6.00 g. of potassium permanganate in a solvent mixture of 100 ml. of water, 40 ml. of dioxane, and 30 ml. of 5% aqueous sodium hydroxide for 6 hr. at room temperature, and working up as in procedure I, gave 0.18 g. of *m*-nitrobenzoic acid, m.p. 134–136° (67% yield); m.m.p. (with authentic *m*-nitrobenzoic acid of m.p. 140–141°) 136–138°.[30]

V.p.c. analysis of the product revealed only the presence of *m*-nitrobenzaldehyde and unreacted *m*-nitrobenzyl chloride. About 2% of the *p*-C-alkylate III could be detected under these conditions.

m-Nitrobenzyl bromide and iodide gave 80 and 84% yields, respectively, of O-alkylate by the above procedure.

E.p.r. Studies. Purified DMF (*vide supra*) was deoxygenated by passing highest purity nitrogen through it for 2 hr. in a nitrogen atmosphere glove box. Spectra were obtained in an e.p.r. flask made by sealing a 4-in. length of 4-mm. Pyrex tubing to the bottom of a 100-ml. round-bottom flask. Solutions were prepared in the glove box by dissolving a weighed amount of lithium salt in 10 ml. of DMF, then adding the nitroaromatic. The flask was stoppered and sealed with Parafilm before removing from the glove box. Spectra were obtained using the AL-X-10 100-kc. X-band spectrometer manufactured by the Alpha Scientific Laboratories, Berkeley, Calif. This instrument possesses a sensitivity of 10^{11} spins per gauss.

The Influence of Dinitrobenzenes on the Reaction of p-Nitrobenzyl Chloride with the Lithium Salt of 2-Nitropropane. (*a*) *Ten Millimoles of Dinitrobenzenes.* To each of two 40-ml. portions of DMF was added 2.00 g. (21.0 mmoles) of the lithium salt of 2-nitropropane and the solutions were cooled to 0°. To one was added a mixture of 1.72 g. of *p*-nitrobenzyl chloride and 1.68 g. of *m*-DNB (10.0 mmoles of each), and to the other was added 1.72 g. of the chloride and 1.68 g. of *p*-DNB. Each mixture was washed in with 10.0 ml. of DMF; the flasks were flushed with nitrogen, sealed, and kept at 0°. After 50 hr., the reactions were stopped by the addition of 10 ml. of 10% nitric acid. Each solution was added to 200 ml. of water and extracted with three 50-ml. portions of benzene and one of ether. The organic layers were dried over magnesium sulfate and evaporated; the residues made up to 50.0 ml. with benzene. The product from the reaction containing *p*-DNB was called solution F, and the other solution G. Titration of the aqueous phases for chloride ion showed that the *p*-DNB reaction had gone 95% to completion and the *m*-DNB reaction 97%. A 20-ml. aliquot of solution F was evaporated, and the residue chromatographed on basic alumina (Merck) using benzene–hexane, benzene, and then ethyl ether–benzene for elution. This yielded *ca.* 20 mg. (2% yield) of the C-alkylate III identified by v.p.c. and infrared comparisons with an authentic sample. In addition, unreacted *p*-DNB and α,*p*-dinitrocumene, m.p. 69–70°, were isolated.[31] In the same way, chromatography of the residue from 20 ml. of solution G yielded 0.531 g. of C-alkylate III, m.p. 66–67°, 61% yield.

Aliquots (10 ml.) of solutions F and G were evaporated and the residues oxidized by procedure I. Solution F yielded 0.235 g. of *p*-nitrobenzoic acid, m.p. 235–237° (72%). Solution G yielded 0.095 g., m.p. 222–225° (29%). Repetition of the *p*-DNB experiment gave 2% C and 73% O; of the *m*-DNB, 57% C and 38% O.

(*b*) *Two Millimoles of p-Dinitrobenzene.* The reaction was run as in (a) except that 0.336 g. (2.0 mmoles) of *p*-DNB was employed (96% reaction). The organic products were dissolved in 50.0 ml. of benzene to yield solution H. Chromatography of the residue from 25 ml. of solution H gave 0.062 g. of C-alkylate III (6%), m.p. 59–63°; m.m.p. (with an authentic sample of m.p. 66–67°) was 61–64°. Chromatography also yielded 0.499 g. of material, m.p. 122–180°, which was shown by t.l.c. on 0.25-mm. silica gel plates to be a mixture of *cis*- and *trans*-4,4′-dinitrostilbene oxides. Authentic samples were prepared by basic condensation of *p*-nitrobenzyl chloride and *p*-nitrobenzaldehyde,[32] m.p. 201–202° and 164–165°.

Anal. Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.74; H, 3.52; N, 9.79. Found (m.p. 201–202°): C, 58.57; H,

(30) This modification of oxidation by procedure I converts *m*-nitrobenzaldehyde to *m*-nitrobenzoic acid in 89% yield; *m*-nitrobenzyl alcohol in 87% yield; the nitro alcohol *m*-O_2N-$C_6H_5CHOHCMe_2NO_2$ (m.p. 157–158°) in 97% yield; *m*-nitrobenzyl chloride in 8% yield; and does not oxidize the *p*-C-alkylate III.

(31) We shall discuss the genesis of α,*p*-dinitrocumene in a subsequent paper.

(32) E. Bergmann and J. Hervey, *Ber.*, **62**, 893 (1929).

3.51; N, 9.69. Found (m.p. 164–165°): C, 58.56; H, 3.82; N, 9.65.

Oxidation of the residue from 5 ml. of solution H by procedure I yielded 0.186 g. of *p*-nitrobenzoic acid, m.p. 235–236°; m.m.p. 236–238° (56%). 4,4′-Dinitrostilbene oxide was not oxidized by procedure I; therefore, the total yield of O-alkylates is 88%, assuming the oxide to be produced from one molecule each of *p*-nitrobenzaldehyde and *p*-nitrobenzyl chloride.

Solutions F, G, and H were analyzed by v.p.c. for traces of the dimer, 2,3-dimethyl-2,3-dinitrobutane. A solution of 19.5 mg. of authentic dimer in 10 ml. of benzene (equivalent to a 5% yield) showed a distinct peak at 1.9 min. on a 5-ft. × 0.25-in. SF-96 on Fluoropak column at 160°, 20 p.s.i. helium carrier gas. The same quantity of solutions G and F showed no trace of a peak at 1.9 min.; solution H showed a trace. In all cases, the amount of dimer must have been less than 1%.

All other reactions in the presence of acceptors in DMF were run and worked up in the same manner as the above examples.

p-Nitrobenzaldehyde Diethyl Acetal. *p*-Nitrobenzaldehyde (5.00 g., 0.033 mole) was dissolved in 50 ml. of absolute ethanol and treated with 5.00 g. of ethyl orthoformate (0.034 mole) and a few crystals of *p*-toluenesulfonic acid. The mixture was refluxed overnight, then cooled to room temperature. The solution was made basic by adding 5 ml. of 5% aqueous sodium hydroxide, then poured into 100 ml. of water, and ether extracted. After drying, the extracts were evaporated and the residual oil was chromatographed on Florisil, eluting with hexane. Short-path distillation gave 6.30 g. (82% yield) of pure acetal; a light yellow oil, $n^{22}D$ 1.5100, b.p. 124° (3 mm.).

Anal. Calcd. for $C_{11}H_{15}NO_4$: C, 58.65; H, 6.71; N, 6.22; mol. wt., 225. Found: C, 58.68; H, 6.42; N, 6.45; mol. wt., 226.

Alkylation of the Lithium Salt of 2-Nitropropane in Ethanol with and without p-DNB. An oven-dried flask was flushed with nitrogen, and 220 ml. of absolute ethanol (distilled from sodium and diethyl phthalate, then deoxygenated with nitrogen) was added. Lithium hydride (0.35 g., 44 mmoles) was dissolved, then 3.92 g. of 2-nitropropane (44.0 mmoles). The solution was stirred under a slow stream of nitrogen for 2 hr., then two 100-ml. aliquots were transferred to dry flasks. To one solution was added 1.72 g. of *p*-nitrobenzyl chloride (10.0 mmoles) and to the other the same amount plus 0.336 g. of *p*-DNB (2.0 mmoles). The flasks were flushed with nitrogen, sealed, and stirred at room temperature. After 4 days, the reactions were stopped by addition of 10 ml. of 10% nitric acid. Each mixture was poured into 200 ml. of water and extracted with three 50-ml. portions of benzene and one of ether. The combined organic layers were then dried over magnesium sulfate and evaporated; the residues were dissolved in benzene to a total volume of 50.0 ml. These solutions were called solution J (no *p*-DNB) and solution K (with *p*-DNB). Titration for chloride ion showed 99% reaction (without *p*-DNB) and 95% reaction (with *p*-DNB).

Aliquots (10 ml.) of solutions J and K were evaporated and the residues oxidized by procedure I; this yielded 0.0227 g. of *p*-nitrobenzoic acid (7%), m.p. 221–223° from solution J, and 0.0892 g., m.p. 227–229° (29%), from solution K.

Chromatography of the residue from 20 ml. of solution J gave 0.809 g. of C-alkylate III, 90% yield, m.p. 65–67°. Similarly, solution K gave 0.264 g. of C-alkylate III, m.p. 65–67°, 31% yield. In addition, solution K yielded an appreciable quantity of *p*-nitrobenzaldehyde diethyl acetal, identified by infrared, n.m.r., and v.p.c. comparison with an authentic sample (*vide supra*). Since this acetal is not oxidized by procedure I, the 29% yield of O-alkylate determined by that method is low.

V.p.c. analysis of solutions J and K for the dimer of the 2-nitropropyl radical showed no trace. By direct test it was shown that a *ca.* 1% yield of 2,3-dimethyl-2,3-dinitrobutane could have been detected.

The Influence of Oxygen on the Alkylation of the Lithium Salt of 2-Nitropropane by p-Nitrobenzyl Chloride. A freshly prepared 0.2 *M* solution of the lithium salt of 2-nitropropane in ethanol was oxygenated by bubbling Drierite-dried air through it for 10 min.; 100 ml. of this solution was added to 1.72 g. of *p*-nitrobenzyl chloride (10.0 mmoles). The flask was sealed and stirred at room temperature for 65 hr., after which the reaction mixture was poured into 250 ml. of water containing 2 ml. of concentrated nitric acid. The mixture was extracted with three 50-ml. portions of benzene and one of ether, and the combined organic layers were dried over magnesium sulfate and evaporated. The residue was made to 50 ml. with benzene (solution L). Titration of the aqueous phase for chloride showed the reaction to be 96% complete.

The residue from evaporating 20 ml. of solution L was oxidized by procedure I; this yielded 0.074 g. of *p*-nitrobenzoic acid, m.p. 225–227°, 12% O-alkylate. The residue from another 20-ml. aliquot of solution L was chromatographed on Merck basic alumina using benzene–hexane and then benzene for elution. This gave 0.410 g. of C-alkylate III, 48% yield, m.p. 65–67°. Further elution with ethyl ether gave 60 mg. of material, m.p. 178–192°; 57 mg., m.p. 136–172°, and, finally, 0.149 g. of an oily solid. These three fractions were combined and digested with acetone, which left white crystals, m.p. 179–194°. The infrared spectrum of this material was virtually identical with that of 4,4′-dinitrostilbene oxide, m.p. 201–202°. The acetone solution after the digestion showed v.p.c. peaks due to *p*-nitrobenzaldehyde, *p*-nitrobenzyl alcohol, and other unidentified products. Thus, oxygen definitely interferes with the reaction in ethanol.

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