53-0; **6a** ($Z^- = I^-$), 10478-75-8; **6a** (Z^- = picrate), 10478-76-9; **6a** ($Z^- = ClO_4^-$), 10478-77-0; **6b** ($Z^- = I^-$), 10478-78-1; **6b** (Z^- = picrate), 10482-27-6; **6b** ($Z^- = ClO_4^-$), 10478-79-2; **7a** ($Z^- = I^-$), 10478-80-5; **7a** (Z^- = picrate), 10478-81-6; **7a** ($Z^- = ClO_4^-$), 10478-82-7; **7b** ($Z^- = I^-$), 10501-30-1; **7b** (Z^- = picrate), 10478-83-8; 1-aza-6-benzylbicyclo[4.4.0]decane, 10498-54-1; 1-aza-6-benzylbicyclo[4.4.0]decane picrate, 10482-28-7; 1-aza-6-benzylbicyclo[4.4.0]decane methiodide, 10478-84-9; N-methyl-1-aza-6-benzylidenecyclodecane, 10478-85-0; N-methyl-1-aza-6-benzylidenecyclodecane picrate, 10478-86-1.

The Nitration of 2-Nitro-1,4-dialkylbenzenes

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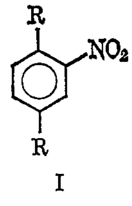
Previous workers[1] have shown that 2-nitro-1,4-dimethylbenzene nitrates predominantly in the 3 position. This somewhat surprising conclusion was based entirely on the orientation assignments of Lellman,[2] which appeared equivocal. It was therefore decided to reinvestigate this nitration, using nmr techniques for analysis, and to extend the results to the 2-nitrodiethyl-, -diisopropyl-, and -di-*t*-butylbenzenes. 2-Nitrodi-*t*-butylbenzene had previously been reported to nitrate in the 5 position,[3] but in these experiments the yields were low.

The mononitrodialkylbenzenes (I) were prepared by the methods given by Franck and Williamson;[4] final purification was found to be best effected by preparative vpc on an Apiezon L-Chromosorb P column at 180°. The nmr spectra of these compounds were measured, and our results matched those of Franck and Williamson,[4] whose work appeared while ours was in progress. We measured the ultraviolet spectra of these compounds, together with that of nitrobenzene in cyclohexane solution and calculated the apparent angle of twist (φ) by the method of Wepster[5] (I).



I

$R = CH_3, \varphi = 35°$
$R = CH_2CH_3, \varphi = 42°$
$R = CH(CH_3)_2, \varphi = 48°$
$R = C(CH_3)_3, \varphi = 65°$

The second nitration of these compounds was carried out in sulfuric acid, and the crude material, obtained by pouring onto ice, was examined directly by nmr. The results are given in Table I, and nmr data are given in Table II.

Table I

Isomer Proportions Obtained by Nitration of 2-Nitro-1,4-dialkylbenzenes

Compd I, R	Over-all yield (calcd as dinitro product)	II, %	III, %	IV, %	*ortho/para* ratio
H[a]		6.12	2.06	91.8	1.5 ($^1/_2$ *o/p*)
Me	97	48	12	40	4.0
Et	80	52	19	29	2.7
i-Pr	60	Complex aromatic region in nmr spectrum			
t-Bu	70	Predominantly III			

[a] A. D. Mesuré and J. G. Tillet, *J. Chem. Soc., B*, 669 (1966).

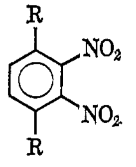
Table II

Nmr Spectra of the Dinitro-1,4-dialkylbenzenes

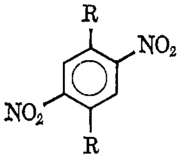
R	II, τ	III, τ	IV, τ
(A) Aromatic Proton Resonances[a,b]			
Me	2.62, 2.17[c]	2.12, 1.93[c]	2.22, 2.02[c]
Et	2.46, 2.58[d]	2.10, 2.23[d]	2.17, 2.30[d]
t-Bu		2.47, 2.31[c]	
(B) Alkyl Proton Resonances[a,b]			
Me	7.56, 7.39[c]	7.37, 7.18[c]	7.48, 7.12, 7.46[c]
Et			
CH_3CH_2 (C*H*₃)	8.70, 8.72[d] (triplet)	8.67, 8.67[d] (triplet)	8.67, 8.68[d] (triplet)
CH_3CH_2 (C*H*₂)	7.24, 7.03[d] (quartet)	7.09[d,e] (quartet)	7.14, 7.20[d,e] (quartet)
t-Bu		8.56, 8.46[c]	8.52, 8.26, 8.36[c]

[a] Taking tetramethylsilane as standard. [b] Solvent $CDCl_3$ unless otherwise indicated. [c] Solvent pentafluoropyridine. [d] Solvent CCl_4. [e] Unresolved peaks in $CDCl_3$.

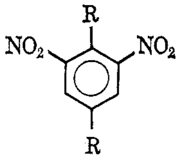
For all three possible dinitro isomers (II, III, and IV), the two remaining aromatic protons are equivalent: of these the protons in II would be expected to resonate at higher field than those of III or IV.[6] The protons of the alkyl groups are equivalent in II and III, but not in IV.



II



III



IV

Considerable difficulty was encountered in resolving the two methyl peaks expected for the 2,6-dinitro-1,4-dimethylbenzene, which was obtained in pure form from the reaction product. It yielded only a single peak for the alkyl region in $CDCl_3$, CF_3COOH, and CCl_4, but the expected, well-separated peaks in 1,3-dichlorobenzene and pentafluoropyridine.

An isomer of dinitro-*p*-diethylbenzene (mp 84°) was obtained from the reaction product. This was assigned the 2,5-dinitro configuration, from the fact that the aromatic protons resonated at lowest field, and only a single quartet was produced in the alkyl region. Accidental coincidence of the chemical shift positions of the two quartets in the 2,6-dinitro isomer does not occur in this case; two methylene peaks of equal intensity, due to the 2,6-dinitro isomer, can be detected

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[1] K. A. Kobe and T. B. Hudson, *Ind. Eng. Chem.*, **42**, 356, 19 (1950).

[2] E. Lellman, *Ann.*, **228**, 250 (1885).

[3] F. Bell and K. R. Buck, *J. Chem. Soc.*, 1890 (1956).

[4] R. W. Franck and M. A. Williamson, *J. Org. Chem.*, **31**, 2420 (1966).

[5] B. M. Wepster, "Progress in Stereochemistry," W. Klyne and P. B. D. de la Mare, Ed., Academic Press Inc., New York, N. Y., 1958, p 110.

[6] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., (1959) p 63.

in the high-resolution nmr spectrum of the nitration product.

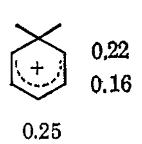
The nmr spectrum of the product from 2-nitro-1,4-diisopropylbenzene was very complicated, containing many peaks in the aromatic region. The position and coupling of these peaks suggested extensive nitro dealkylation, which could not be eliminated or reduced by alteration in nitration conditions. Presumably, even in the deactivated mononitro compound, the isopropyl group is sufficiently small for attack of NO_2^+ or H_3O^+ at the carbon atom of the benzene ring to which it is attached, with formation of a carbonium ion stable enough to make dealkylation a successful competitor to normal nitration.

Small amounts of dealkylation also appeared to occur in the nitration of 2-nitro-1,4-di-*t*-butylbenzene. However, comparison of the spectrum of the mixture with that of pure 2,5-dinitro-1,4-di-*t*-butylbenzene confirmed this isomer as the predominant product.

Considerable attention has been given to the proportion of isomers produced on electrophilic substitution of nitrobenzene and other benzenes substituted with groups of −I, −M type.

The predominant *meta* substitution is readily explicable, but the $^1/_2$ *ortho* to *para* ratios of greater than 1 are surprising. (Thus Mesuré and Tillet[7] have shown recently that nitration of nitrobenzene gives $^1/_2\ o/p = 1.5$). Specific *ortho* activation by dipole[8] interaction has been discounted.[9] Specific *para* deactivation[10] by more efficient resonance of the nitro group with the *para* than the *ortho* position seems unlikely. In our systems such resonance is considerably reduced owing to rotation of the nitro group from the plane of the ring. Moreover, there is ample evidence that the resonance effect of the nitro group with the benzene ring in nitrobenzene is small compared with the inductive effect, and it will be even smaller when the π electrons of the aromatic system are perturbed by an approaching electrophile.

The most satisfactory picture is given by considering the relative stabilities of the possible Wheland intermediates. Data relevant to this have been obtained by Colpa, Mackor, and Maclean[11] from nmr studies of the pentamethylcyclohexadienyl cation, which have been interpreted by Norman and Taylor.[12] In this representation, the Wheland intermediate has the positive change shared unequally between the *ortho* and *para* positions. Thus an electron-withdrawing group, whether of −I or −I, −M type, gives a $^1/_2\ o/p$ ratio of greater than 1.



V

Our results fit in well with this picture; the high *ortho* to *para* ratios for the mononitrodimethyl- and mononitrodiethylbenzenes show that twisting the nitro group out of the plane of the ring does not significantly reduce the amount of *ortho* relative to *para* substitution. This model also explains the nitration of 3,5-dimethoxy- and 3,5-diethoxypyridine in the 2 rather than the 4 position.[13]

However, Ridd's experiments on the nitration of the anilinium ion,[14] where the *para* position is the most reactive to nitration, and only traces of *ortho* substitution are observed, and on the trimethylanilinium ion,[15] which yields similar results, are inconsistent with this picture. These are examples which would be expected to follow the model of Norman and Taylor most accurately, since the ammonium and trimethylammonium substituent are very strongly deactivating, and in these cases therefore the Wheland intermediate would be a very close approximation to the transition state. Considerable steric hindrance in the *ortho* position, due to a large solvation shell firmly bound to the positively charged substituent, would not explain the large amount of *para* substitution observed. Moreover, similar solvation effects would also be expected in the case of the 3,5-dimethoxy- and 3,5-diethoxypyridinium cations.

The decreasing amount of *meta* (six) substitution must be due to the increased steric effect of the alkyl group buttressed by the 2-nitro group. The high proportion of *para* (five) substitution in the case of the di-*t*-butyl compound is undoubtedly due to distortions of the molecule other than twisting of the nitro group. This is readily shown by construction of a molecular model. The extra steric effect will be felt at the 3 and 6 positions, the 5 position being largely unaffected.

Experimental Section

Nitration of 2-Nitro-1,4-dimethylbenzene.—2-Nitro-1,4-dimethylbenzene (0.97 g) was dissolved in sulfuric acid (*d* 1.84, 100 ml). Nitric acid (*d* 1.50, 3.0 ml) in sulfuric acid (*d* 1.84, 10 ml) was added drop by drop with vigorous stirring, the temperature being kept between 25 and 30°. The solution was then stirred for additional 2 hr at 25°, and then poured onto ice. The precipitate was filtered off, thoroughly washed free of acid, and dried.

A similar procedure was followed for the other three nitrodialkylbenzenes. In the case of the diethyl and diisopropyl compounds, the temperature of the nitration mixture was 0° during addition of the nitric acid.

The nmr spectra were obtained on a Perkin-Elmer 60-Mcps permanent-magnet spectrometer (fitted with an integrator) with sample spinning. The solutions were made up to 10% by weight, and tetramethylsilane was used as an internal standard. The isomer ratios were calculated by integrating the singlet peaks due to the aromatic protons in the spectra in $CDCl_3$. An average from at least 12 separate integrations (which had a reproducibility of *ca.* ±5%) were obtained. In the case of the spectrum of the nitration product of 2-nitro-1,4-dimethylbenzene, integration of the peaks due to the methyl protons gave excellent agreement with the values obtained from the aromatic proton resonances.

2,6-Dinitro-1,4-dimethylbenzene, mp 125.5–126.5° (lit.[2] 124°), was obtained by successive recrystallizations of the nitration mixture from ethanol.

2,5-Dinitro-1,4-diethylbenzene, mp 84°, not previously reported, was obtained pure in one instance by successive re-

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[7] See Table I, footnote *a*.

[8] G. S. Hammond, F. J. Modic, and R. H. Hedges, *J. Am. Chem. Soc.*, **75**, 1388 (1953).

[9] G. S. Hammond and K. J. Douglas, *ibid.*, **81**, 1184 (1959).

[10] J. H. Ridd and P. B. D. de la Mare, "Aromatic Substitution," Butterworth and Co. (Publishers) Ltd., London, 1959, p 82.

[11] J. P. Colpa, C. Maclean, and E. R. Mackor, *Tetrahedron*, **19**, 65 (1963).

[12] R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," C. Eaborn, Ed., Elsevier Publishing Co., London, 1965, p 307.

[13] H. J. den Hertog and J. W. van Weeren, *Rec. Trav. Chim.*, **67**, 980 (1948); C. D. Johnson, A. R Katritzky, and M. Viney, *J. Chem. Soc., Sect. B*, in press.

[14] M. Brickman and J. H. Ridd, *J. Chem. Soc.*, 6845 (1965).

[15] M. Brickman, J. H. P. Utley, and J. H. Ridd, *J. Chem. Soc.*, 6851 (1965).

crystallizations of the nitration mixture from ethanol. In subsequent attempts to obtain this compound, we were unable to remove small amounts of the 2,5-dinitro isomer (about 5% from the nmr spectrum).

2,5-Dinitro-1,4-di-*t*-butylbenzene, mp 191.5–192.5° (lit.[3] 191°), was obtained by successive recrystallizations of the nitration mixture from isopropyl alcohol.

The work was carried out during the tenure (by M. J. N.) of a Scientific Research Council Advanced Course Studentship.

Registry No.—I (R = Me), 89-58-7; I (R = Et), 10482-00-5; I (R = *i*-Pr), 10472-64-7; I (R = *t*-Bu), 3463-35-2; II (R = Me), 711-41-1; II (R = Et), 10472-67-0; III (R = Me), 712-32-3; III (R = Et), 10472-69-2; III (R = *t*-Bu), 10472-70-5; IV (R = Me), 609-92-7; IV (R = Et), 10472-72-7; IV (R = *t*-Bu), 10472-73-8.

The Reaction of Epihalohydrins with *n*-Butyl- and Allyllithium

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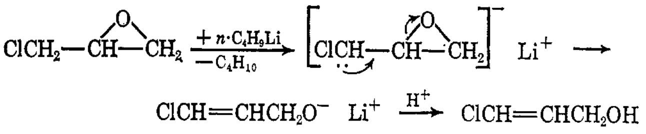
In connection with a search for new epoxides, it was of interest to examine the reaction of certain organolithium compounds with epihalohydrins.

Reactions of alkali metal organic compounds with chloroepoxypropane have been reported in the literature.[1-3] Although Gilman, *et al.*,[3] obtained the expected ring-opening product, 1-aryl-3-chloropropanol-2, from reaction of aryllithium with epichlorohydrin in ether at −78°, it was found in our laboratory that the more strongly basic *n*-butyllithium reacts in an anomalous manner.

When *n*-butyllithium in *n*-heptane was treated at −50° with the stoichiometric amount of *dl*-epichlorohydrin in dry diethyl ether, a mixture of *cis*- and *trans*-β-chloroallyl alcohols was isolated in 75% yield. The isomers could be separated by vapor phase chromatography,[4] and identified by comparison of their infrared spectra[5] with authentic samples prepared by hydrolysis of the corresponding 1,3-dichloropropenes.[6] In addition, a small amount (*ca.* 15%) of propargyl alcohol was found in the reaction mixture.

None of the seven-carbon compounds, heptene 1,2-epoxide, 1-chloro-2-hydroxyheptane, or hepten-2-ol-1 (from base-catalyzed rearrangement of the intermediate heptene epoxide[7]) were detected in the reaction mixture.

Formation of β-chloroallyl alcohol involves proton abstraction from the chlorine-bearing carbon atom followed by rearrangement of the carbanion.



The simultaneous formation of *n*-butane was verified by vapor phase chromatography.

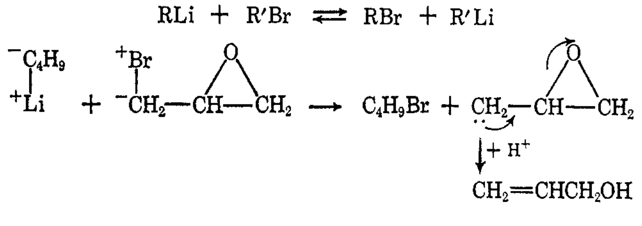
Proton abstraction appears to be restricted to the chlorine-bearing carbon since none of the two isomeric carbonyl compounds, chloroacetone and 3-chloropropanal, which would be expected from attack on the carbon atoms of the oxirane ring could be detected in a vapor phase chromatogram.

Similar base-catalyzed isomerizations of alkylene oxides have been encountered by Culvenor, *et al.*,[7] in the rearrangement of glycidonitrile and phenylglycidylsulfone to the corresponding allyl alcohols by alkali and by Letsinger, *et al.*,[8] in the rearrangement of cyclohexene oxide to cyclohexen-3-ol in the presence of *n*-butyllithium.

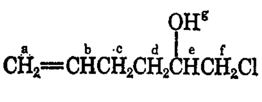
Formation of propargyl alcohol from epihalohydrins in strongly basic medium has been observed by Eglinton, *et al.*,[9] when epichlorohydrin was treated with sodium amide in liquid ammonia.

The reaction of *n*-butyllithium with epibromohydrin takes a different course. Halogen–metal interchange takes place exclusively and 1-bromobutane and allyl alcohol are the sole identifiable reaction products. The exchange reaction which is normally reversible and whose equilibrium position depends strongly on the relative electron-attracting power of the R groups[10] is in this case driven to completion by rearrangement of the initially formed carbanion to the more stable alkoxide ion (Scheme I).

SCHEME I

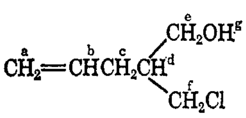


The less basic allyllithium takes a position between aryllithium[3] and butyllithium in its reactivity toward epichlorohydrin. When treated at −5 to 0° in ether–hexane, 48% of the corresponding ring-opening product was isolated.



$CH_2{=}CHCH_2CH_2CH(OH)CH_2Cl$

I



$CH_2{=}CHCH_2CH(CH_2OH)CH_2Cl$

II

In addition, 43% of a mixture of the geometrical isomers of β-chloroallyl alcohol was obtained.

Opening of the oxirane ring by the allyl anion can give either 1-chloro-2-hydroxy-hexene-5 (I) or its isomer (II).

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[1] G. Volema and J. F. Arens, *Rec. Trav. Chim.*, **78**, 140 (1959).

[2] L. J. Haynes, I. Heilbron, E. R. H. Jones, and F. Sondheimer, *J. Chem. Soc.*, 1583 (1947).

[3] H. Gilman, B. Hofferth, and J. B. Honeycutt, *J. Am. Chem. Soc.*, **74**, 1594 (1952).

[4] All vapor phase chromatograms were obtained on an Aerograph instrument equipped with a 5-ft diethylene succinate-on-firebrick column and thermoconductivity detector at a gas flow of 30 ml of He/min.

[5] Infrared spectra were obtained on a Perkin-Elmer Model 237 grating infrared spectrophotometer.

[6] L. F. Hatch and A. C. Moore, *J. Chem. Soc.*, 2873 (1952).

[7] C. C. J. Culvenor, W. Davies, and W. E. Savage, *ibid.*, 2198 (1949).

[8] R. L. Letsinger, J. G. Traynham, and E. Bobko, *J. Am. Chem. Soc.*, **74**, 399 (1952).

[9] G. Eglinton, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2873 (1952).

[10] See, *e.g.*, R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951).

[11] H. Schaltegger, *Helv. Chim. Acta*, **45**, 1368 (1962).