rently exploring the steric perturbation of the α-fluorine effect on carbanion basicity and nucleophilicity.

Experimental Section

Caution! The compounds described in this work are explosives and may detonate on grinding or impact. Appropriate shielding should be used.

Preparation of Reagents. The potassium salts of the dinitromethide ions were prepared by the following procedures: trinitromethide ion,[8] carbomethoxydinitromethide ion,[34] dinitromethide ion from 2,2-dinitro-1,3-propanediol[35] and potassium hydroxide,[36] chlorodinitromethide ion,[10] and alkyl dinitromethide ions from the corresponding 1,1,1-trinitroalkanes by reduction with potassium iodide in methanol.[37] Due to the instability of fluorodinitromethide ion, stock solutions of fluorodinitromethane[38] were used and the pH of the reaction medium adjusted (borax buffers) so that the dinitroalkane was completely dissociated. Control runs, in the absence of methyl acrylate, showed that fluorodinitromethide ion is stable during the time required for the kinetic runs.

Methyl acrylate, dioxane, and other reagents and their stock solutions were prepared as described previously.[8]

Kinetic Procedures.[8] Generally, the appropriate aliquots of buffer components, methyl acrylate, and sodium perchlorate stock solutions were placed in a 100-ml low-actinic volumetric flask and additional solvent was added to a volume of about 90 ml. After thermostating for at least 30 min, a 3–10-ml aliquot of a thermostated dinitromethide ion stock solution was added, the mixture was made up to volume with thermostated solvent and mixed by shaking, and a 1-cm quartz cell was filled with the reaction mixture and placed in the thermostated cell compartment of a Cary Model 14 spectrophotometer. This operation generally took less than 2 min. The optical density of the reaction mixture was continuously monitored with time at λ_{max} for the dinitromethide ion until it had decreased to essentially zero. Pseudo-first- and second-order rate constants were evaluated as described in the Discussion.

For the kinetic runs in water using carbomethoxydinitromethide ion as a substrate, a small correction had to be applied to the pseudo-first-order rate constants due to a slow decomposition reaction at the higher $HOAc/OAc^-$ buffer ratios. For this purpose, an identical control run without methyl acrylate was made for each buffer ratio used in the kinetic study. The pseudo-first-order rate constant for the decomposition reaction was subtracted from the observed pseudo-first-order rate constant for the addition to methyl acrylate. At the lower pH's generated in 50% dioxane, carbomethoxydinitromethide ion was found to be stable throughout the kinetic runs.

Acknowledgment. This work was supported by the Independent Research Fund of the U. S. Naval Ordnance Laboratory, Task IR-44.

(34) C. O. Parker, *Tetrahedron*, **17**, 109 (1962).
(35) R. B. Kaplan and H. Shechter, *J. Amer. Chem. Soc.*, **83**, 3535 (1961).
(36) H. Feuer, G. B. Bachman, and J. P. Kispersky, *ibid.*, **73**, 1360 (1951).
(37) D. J. Glover and M. J. Kamlet, *J. Org. Chem.*, **26**, 4734 (1961).
(38) M. J. Kamlet and H. G. Adolph, *ibid.*, **33**, 3073 (1968).

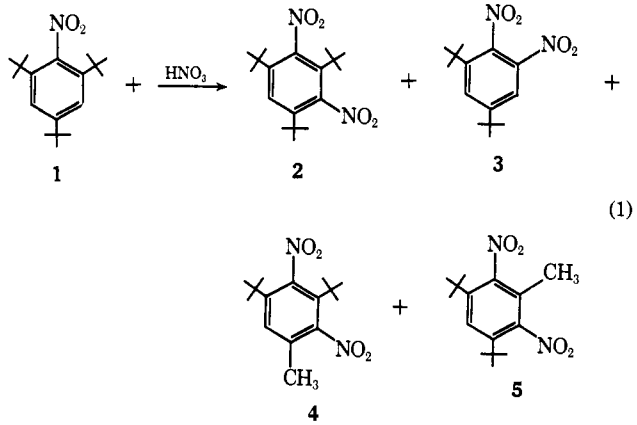
Rearrangement–Fragmentation in Aromatic Nitration

P. C. Myhre,*[1a] M. Beug,[1b] K. S. Brown,[1b] and B. Östman

Contribution from the Department of Chemistry, Harvey Mudd College, Claremont, California 91711, and the Research Institute of National Defense, Dept. 1, Sundbyberg 4, Sweden. *Received October 19, 1970*

Abstract: Two toluene derivatives, 2,4-dinitro-3,5-di-*tert*-butyltoluene (**4**) and 2,6-dinitro-3,5-di-*tert*-butyltoluene (**5**), are formed in 32 and 2% yields, respectively, by nitration of 2,4,6-tri-*tert*-butylnitrobenzene with fuming nitric acid. The paths leading to **4** and **5** are characterized as molecular rearrangements of the intermediate cyclohexadienyl cation **1a** followed by alkyl fragmentation. Deuterium labeling studies establish the intramolecular character of the methyl migration. Nitrogen-15 labeling studies permit identification of the *tert*-butyl group undergoing rearrangement–fragmentation to yield the major fragmentation product, **4**. These data, coupled with kinetic isotope effect data, serve as the basis for discussion of the detailed mechanism of rearrangement–fragmentation.

The nitration of 2,4,6-tri-*tert*-butylnitrobenzene (**1**) yields a diverse set of products, eq 1. The identification of 2,4-dinitro-3,5-di-*tert*-butyltoluene (**4**) and 2,6-dinitro-3,5-di-*tert*-butyltoluene (**5**) among them necessitated a search for a rational mechanistic path.[2] This transformation of a *tert*-butyl group to a methyl group during aromatic nitration seemed most readily explained if one could permit the intermediate cyclohexadienyl cation **1a** to rearomatize to products by two competitive paths, one being molecular rearrangement with fragmentation to yield **4** or **5**, the other being a proton loss to yield 1,3-dinitro-2,4,6-tri-*tert*-butylbenzene (**2**), eq 2.



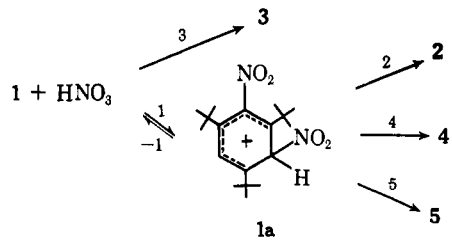
(1)

Rather special circumstances appear necessary for effective competition of rearrangement–fragmentation with proton loss. Most important of these is a slower than "normal" rate of proton transfer from **1a**. An increase in the barrier to proton transfer could be rea-

(1) (a) Address correspondence to this author at Harvey Mudd College; (b) National Science Foundation undergraduate research participants.

(2) At 40°, the observed distribution of products is: **2**, 49%; **3**, 17%; **4**, 32%; and **5**, 2%. More detailed discussion of the distribution data is available in ref 3.

(3) P. C. Myhre, M. Beug, and L. L. James, *J. Amer. Chem. Soc.*, **90**, 2105 (1968).



sonably associated with the increase in nonbonded repulsion attending the replacement of aromatic hydrogen by the larger nitro group in this very hindered reactant. The rate-limiting character of the proton transfer in the formation of **2** from **1** was established by isotope effect studies. These investigations revealed that the partition isotope effect, obtained from product distribution data, was smaller when the rate of formation of **3** was used as the reference reaction rather than the rate of formation of **4** or **5**. These differences could be anticipated on the basis of the kinetic form derivable from eq 2 and, thus, appeared to support the view that product **3** forms by a branching reaction which originates with reactants, while products **4** and **5** form by a partitioning of the intermediate cyclohexadienyl cation, **1a**.[3]

Several types of labeling experiments and related studies yield further information concerning the rearrangement–fragmentation observed in the nitration of **1**. We describe these results here and utilize them in an attempt to specify the mechanistic path of rearrangement–fragmentation in greater detail.

Results and Discussion

The intramolecular character of the rearrangement has been most clearly established by the following sequence of experiments. A nearly statistical distribution of isotopic isomers was obtained by mononitration of 1,3,5-tri-*tert*-butylbenzene-*1-tert-butyl-d*$_9$.[4] A sample of this mixture of 2,4,6-tri-*tert*-butylnitrobenzene-*2-tert-butyl-d*$_9$ and 2,4,6-tri-*tert*-butylnitrobenzene-*4-tert-butyl-d*$_9$ was nitrated at 0° with fuming nitric acid, and the mass spectra of the resulting products were recorded with the use of an LKB gas chromotograph–mass spectrometer. Mass spectral data in the region of the molecular ions are shown in Figure 1. After correction for residual protium present in the labeled alkyl groups, it is apparent that the toluene products have molecular ions with *m/e* values of either 303 or 297. The absence of other molecular ions at higher, lower, or intermediate *m/e* values eliminates intermolecular transfer of alkyl groups as a significant process and strongly implies intramolecular transfer of methyl from the fragmented *tert*-butyl group to the aromatic carbon to which the *tert*-butyl group was affixed.

The identification of the *tert*-butyl group in **1** which suffers rearrangement–fragmentation to yield **4** was made with the aid of a series of ^{15}N labeling experiments. 2,4,6-Tri-*tert*-butylnitrobenzene-^{15}*N-3,5-d*$_2$ was prepared by nitration of the deuterium-labeled hydrocarbon with nitric acid containing greater than 97 atom % ^{15}N.[5] The purified product was then subjected to nitration in fuming nitric acid at 0°, and the ^{15}N-labeled product **4** was isolated by column and gas–liquid partition chromatography. An authentic sample of 2,4-dinitro-3,5-di-*tert*-butyltoluene-*2*-^{15}*N* was prepared as a reference compound by nitration of 4-nitro-3,5-di-*tert*-butyltoluene with nitric acid-^{15}*N*, eq 3.

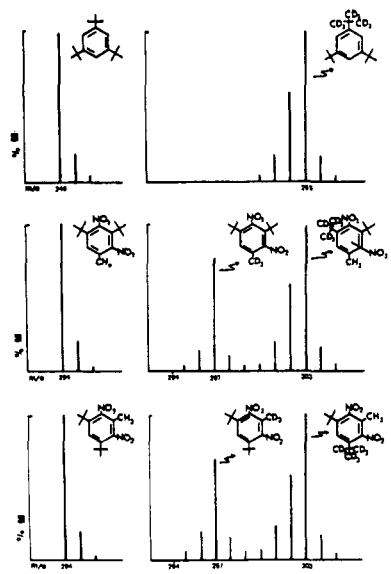
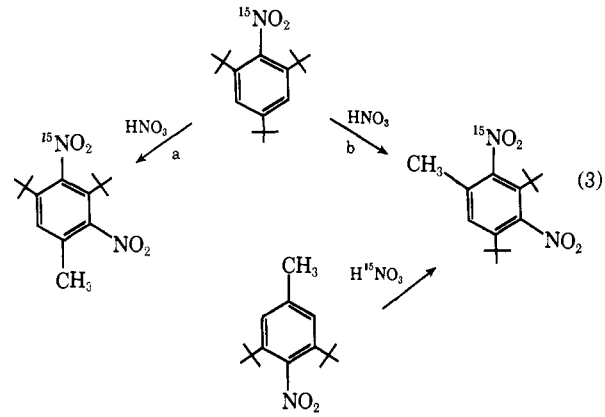


Figure 1. Mass spectra (molecular ion region) of parent hydrocarbons and the rearrangement–fragmentation products resulting from dinitration of 1,3,5-tri-*tert*-butylbenzene and 1,3,5-tri-*tert*-butylbenzene-*1-tert-butyl-d*$_9$.



The ^{15}N-nmr spectrum of each of the three labeled nitro compounds was recorded with the use of the Varian digital frequency sweep spectrometer.[6] Each compound exhibited a singlet ^{15}N absorption line. As shown in Figure 2, the difference in ^{15}N chemical shifts of the compounds was sufficient to establish that product **4** isolated from nitration of 2,4,6-tri-*tert*-butylnitrobenzene-^{15}*N was not* 2,4-dinitro-3,5-di-*tert*-butyltoluene-*2*-^{15}*N*. Hence, the rearrangement product must be the isotopic isomer with ^{15}N attached at C-4. This result strongly suggests that formation of 2,4-dinitro-3,5-di-*tert*-butyltoluene by nitration of 2,4,6-tri-*tert*-butylnitrobenzene occurs with predominant rearrangement–fragmentation of the 4-*tert*-butyl group of the reactant, path a, eq 3.

To confirm this conclusion, each of the ^{15}N-labeled samples of **4** was selectively reduced to the corresponding meta nitroaniline. At −60°, exchange of the amine protons was sufficiently slow, and authentic 2-amino-4-nitro-3,5-di-*tert*-butyltoluene-*2*-^{15}*N* exhibited

(4) P. C. Myhre and L. L. James, unpublished work.

(5) Deuterium-labeled reactant was used as starting material in order to maximize the yield of **4** in the second nitration step; see ref 3.

(6) The spectrometer has been described: F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967).

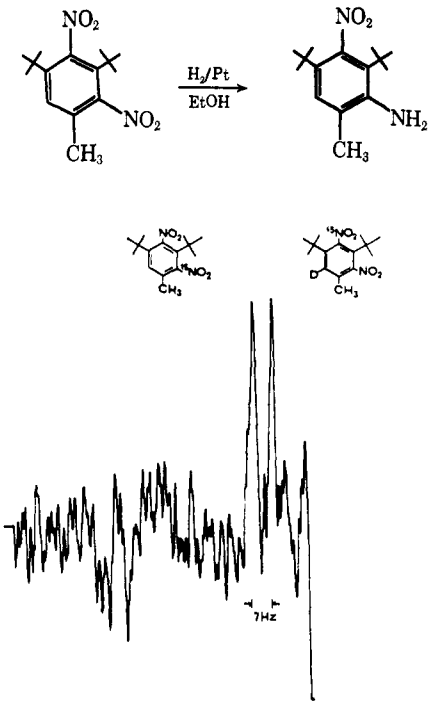


Figure 2. ^{15}N-nmr spectrum of a prepared mixture consisting of equal amounts of authentic 2,4-dinitro-3,5-*tert*-butyltoluene-2-^{15}N (left) and the 2,4-dinitro-3,5-di-*tert*-butyltoluene (right) isolated from the nitration of 2,4,6-tri-*tert*-butylnitrobenzene-^{15}N-3,5-d_2.

the anticipated ^{1}H-nmr spectrum with an amine proton doublet ($J_{^{15}N-H}$ = 89 Hz). In contrast, the presumed 2-amino-4-nitro-3,5-di-*tert*-butyltoluene-4-^{15}N (derived from nitration of 1-^{15}N) exhibited a singlet amine proton line with no evidence of spin coupling with ^{15}N, Figure 3. The deliberately prepared mixture of isotopic isomers used to record the ^{15}N spectrum shown in Figure 2 was also selectively reduced and gave the ^{1}H nmr spectrum shown in Figure 4. We conclude that at least 90–95% of **4** formed in the nitration of **1** must result from rearrangement–fragmentation of the 4-*tert*-butyl group.

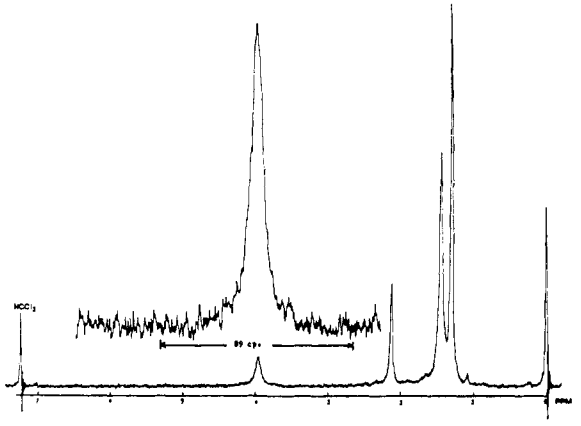


Figure 3. ^{1}H-nmr spectrum of 2-amino-4-nitro-3,5-di-*tert*-butyltoluene-4-^{15}N-6-*d* obtained by nitration of 2,4,6-tri-*tert*-butylnitrobenzene-1-^{15}N-3,5-d_2 and subsequent reduction. The spectrum was recorded in $DCCl_3$ at −60°.

Results with isotopically labeled reactants may then be summarized. The previously reported isotope

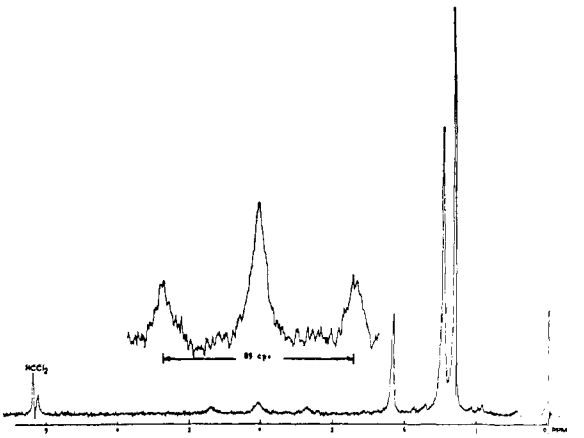
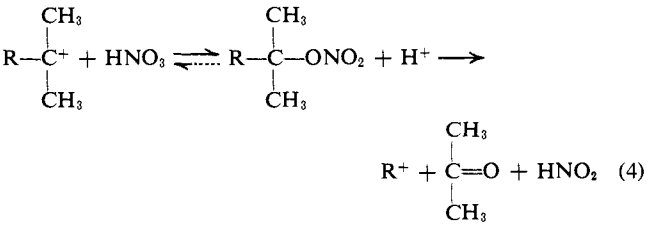


Figure 4. ^{1}H-nmr spectrum ($DCCl_3$ at −60°) of equal amounts of 2-amino-4-nitro-3,5-di-*tert*-butyltoluene-2-^{15}N and 2-amino-4-nitro-3,5-di-*tert*-butyltoluene-4-^{15}N-6-*d* prepared by selective reduction of the sample of **4** whose ^{15}N spectrum is shown in Figure 2.

effect studies implicate the cyclohexadienyl cation **1a** as the species undergoing rearrangement–fragmentation.[3] The existence of an isotope effect in the formation of **2** provides a rationale for the intrusion of the rearrangement–fragmentation. Studies with alkyl-labeled reactant reported here restrict the rearrangement to one in which the methyl replacing the *tert*-butyl group comes directly from the lost *tert*-butyl group. Study of the nitration with the use of ^{15}N-labeled reactant identifies the particular *tert*-butyl group which undergoes rearrangement to yield the major toluene isomer, **4**. On the basis of these data it is possible to describe the rearrangement–fragmentation in some detail. Sequences of steps involving rearrangement of the three different *tert*-butyl groups are shown in Chart I.

Consideration of these sequences prompts questions which deserve comment. In the discussion to follow, we will be concerned with possible mechanisms of alkyl fragmentation, the preference for rearrangement *via* path 1 (Chart I), and energetic considerations which may explain the particular importance of rearrangement–fragmentation in this aromatic nitration reaction.

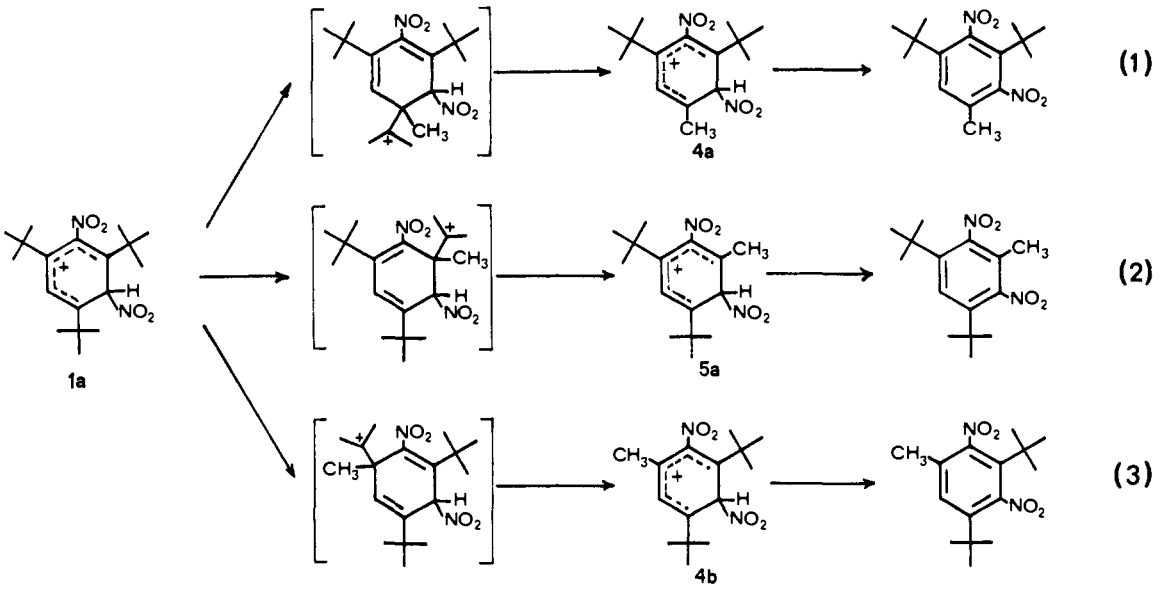
Alkyl Fragmentation. We prefer to formulate the fragmentation occurring in the nitration of **1** in 90% HNO_3 as a process proceeding by formation of a nitrate ester and subsequent acid-catalyzed fragmentation to yield a new cyclohexadienyl cation (**4a**, **5a**, or **4b**), acetone, and nitrous acid, eq 4, where R^+ = **4a**, **5a**, or **4b**.



$$R^+ + \underset{CH_3}{\overset{CH_3}{C}}{=}O + HNO_2 \quad (4)$$

Experimental evidence to support this proposal is limited. Release of alkyl fragments in the strongly oxidizing reaction medium will lead, eventually, to carbon dioxide and nitrogen oxides. These end products have been isolated or detected. Of somewhat greater relevance is the detection of acetone upon partial nitration of **1** and subsequent distillation of the neutralized reac-

Chart I. Paths of Rearrangement–Fragmentation



tion filtrate. Finally, a fairly direct relationship exists between the amount of rearrangement–fragmentation product and the amount of free nitric acid in the reaction system.[7] In addition, our preference is substantially influenced by the analogy of this formulation with operative mechanisms of related oxidation–reduction reactions,[8] the few reports concerning products of reaction of nitrate esters in strong acid media,[9] and the observed tendency of systems to undergo alkyl fragmentation when stabilized carbonium ions result as products.[10]

Migratory Preference. Product distribution data show that the rate of formation of **4** is 10–20 times faster than the rate of formation of **5**.[3] The data presented here demonstrate that **4** is formed by predominant rearrangement of the 4-*tert*-butyl group of **1**. The reasons for predominance of path 1 with respect to paths 2 and 3 (Chart I) are not clear. Proper discussion of this question should be based on a reasonable model for the rearrangement transition state. However, a variety of configurations lying between **1a** and the set of cations, **4a**, **5a**, and **4b**, exist as possible candidates. In addition, it seems quite possible that a rearrangement following path 3 could undergo an apparent crossover, by loss of nitronium ion at **4b** with subsequent preferential nitration to yield **5**.[11] Thus, it is possible that a major portion of the minor product, **5**, could form by the rearrangement designated as path 3. In spite of these intriguing secondary issues, the major problem centers about rationalizing the marked predominance of path 1 over either paths 2 or 3.

Selection of **1a** as a model close in structure and energy to the rearrangement transition state may be a reasonable one. If this is the case, a distribution of charge in **1a**, which is greater at C-4 than at C-2 or C-6, could account for the preferential migration of methyl by path 1. In principle, charge distributions in such intermediates can be estimated by molecular orbital calculations. In practice, we find it necessary to very pointedly assume the answer before calculated values reflect the experimental results.

Some representative ω-technique molecular orbital calculations (ω = 1.25) indicate that a marked asymmetry in charge distribution is obtained only by building such a distribution into the calculation with the assumption of larger coulomb integrals at C-2 and C-6 than at C-4. The assumption may well be a reasonable one, but the necessity of making it renders the estimates of charge distribution of questionable value in any attempt to more clearly understand the preferred path of methyl migration.

An alternate and perhaps more reasonable line of argument would involve consideration of the degree of relief of nonbonded interaction attending methyl migration to aromatic C-2, -4, or -6. On this basis, rearrangement to C-6 would clearly be the *least*-favored process. The choice between rearrangement to C-2 or C-4 is more difficult. Without making a detailed review of the considerations, we can summarize by noting that rearrangement to C-2 will remove the most hindered *tert*-butyl group, but the achievement of this will require passage through considerably more hindered configurations than will the corresponding rearrangement at C-4. Presumed intermediate configurations for these two migrations are shown in Figure 5. It can be seen that rearrangement to C-2 will necessarily involve nonbonded interaction with the nitro group attached at C-1. If a nucleophile (such as nitrate) participates, the steric preference for rearrangement to C-4 would seem even greater. Thus, if the structures shown in Figure 5 can be taken as representative of the transition-state configurations (with the possible inclusion of a nucleophilic participant), the preferential migration to C-4 could be rationalized on steric grounds.

The Occurrence of Rearrangement–Fragmentation. Several studies concerned with aromatic substitutions proceeding with rate-limiting proton transfer reveal a

(7) See ref 3, Table II.
(8) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, New York, N. Y., 1964.
(9) (a) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955); (b) J. W. Baker and A. J. Neale, *J. Chem. Soc.*, 608 (1955); (c) R. T. Merrow and G. C. Whitnack, *J. Org. Chem.*, **23**, 1224 (1958); (d) S. D. Ross, E. R. Coburn, and M. Finkelstein, *ibid.*, **33**, 585 (1968).
(10) (a) N. C. Deno and E. Sacher, *J. Amer. Chem. Soc.*, **87**, 5120 (1965); (b) K. Conrow, *ibid.*, **81**, 5461 (1959); (c) S. Patai and S. Dayagi, *J. Chem. Soc.*, 726 (1962).
(11) The intermediate **4b** is very similar to **1a** in terms of the degree of hindrance around the reaction site. Since the latter is known to lose nitronium ion at a rate comparable to the rate of proton loss, a similar result might be anticipated with **4b**.

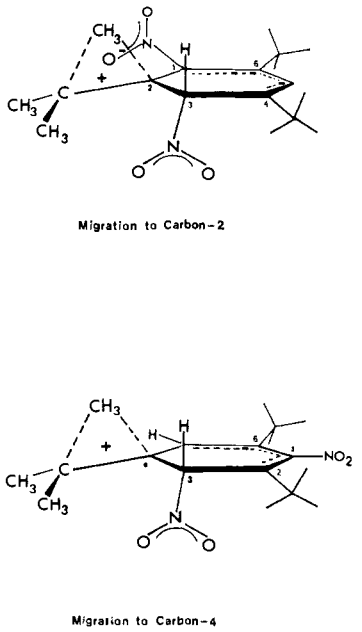


Figure 5. Possible transition-state configuration in rearrangement–fragmentation.

dominant theme. When proton transfer becomes rate limiting, alternative processes involving the intermediate cyclohexadienyl cation become observable. The intrusion or dominance of any one of them will depend upon the structure of the reactant and the nature of the reaction medium. For example, addition reactions (followed by elimination) can be anticipated if the reaction system is adaptable to significant concentrations of nucleophilic species.[12] Reversal to reactant and subsequent substitution at other sites may be anticipated if these alternative reactions have lower or comparable energy barriers. Structural modification by molecular rearrangement and fragmentation of substituent groups provides another means of permitting competitive conversion of the cyclohexadienyl cation to final product.

It is pertinent to ask why the rearrangement–fragmentation is prominent in the nitration of **1** but is not significant in other nitrations, even those which proceed with rate-limiting proton transfer. The answer would appear to be related to the large activation energy associated with this unusual formal transformation of a cyclohexadienyl cation to a tertiary alkyl cation. The intrusion of such a process could only be anticipated in those systems where all other reaction paths have similarly large activation energies. The resistance of aromatic nitro compounds to electrophilic attack is well known. Sites ortho and para to the nitro group are notably unfavorable. Attack at a meta carbon represents the most favorable alternative. However, the formation of **1a** from **1** is not the rate-limiting step. Proton loss represents the kinetically important hurdle to formation of **2**. Because of the high energy of the intermediate **1a**, the remaining barrier to formation of normal nitration product, and the absence of alternative sites of electrophilic attack, diversion of the intermediate through an unusual rearrangement–fragmentation can emerge as one of the more favorable paths of product formation. This situation can be contrasted with other sterically hindered systems which have been found to yield the normal nitrodeprotonation product with rate-limiting proton transfer. In these latter cases, the rates of nitration reflect lower activation energies and, in addition, favorable alternative sites of substitution exist.[3] It would appear that rearrangement–fragmentation processes attending aromatic substitution will appear only in systems such as **1** where the energy demands are very high. Studies of products resulting from the nitration of systems such as 2,4,6-tri-*tert*-butylanilinium ion provide a possible area for further investigation of these unusual rearrangement processes.

(12) P. C. Myhre, G. S. Owen, and L. L. James, *J. Amer. Chem. Soc.*, **90**, 2115 (1968).

Experimental Section

The preparations of 1,3,5-tri-*tert*-butylbenzene-*2,4,6-d*$_3$ and 4-nitro-3,5-di-*tert*-butyltoluene have been described.[3] 1,3,5-Tri-*tert*-butylbenzene-*1-tert-butyl-d*$_9$ and the corresponding mononitration product were available from another study.[4] Nitric acid-^{15}N was purchased from the Volk Chemical Company.

Proton nmr spectra were recorded on a Varian A-60 spectrometer. Chemical-shift data are reported in δ values with respect to TMS. Nitrogen-15 nmr spectra were obtained with the use of the Varian DFS-60 spectrometer.[6] Chemical-shift data for the ^{15}N-nmr spectra are reported in hertz with respect to the methyl proton resonance line of toluene solvent at 60,006,000 Hz. Mass spectral data were obtained with the use of a LKB chromatograph mass spectrometer, Model 9000. Elemental analyses were performed by Mr. C. F. Geiger, Ontario, Calif.

2,4,6-Tri-*tert*-butylnitrobenzene-^{15}N-*3,5-d*$_2$. A solution composed of nitric acid-^{15}N (1.88 g, 14 *M*, 97 atom % ^{15}N), acetic acid (5 ml), and acetic anhydride (5 ml) was added dropwise to a cold, magnetically stirred mixture of 1,3,5-tri-*tert*-butylbenzene-*2,4,6-d*$_3$ (3.98 g, 15.9 mmol), acetic acid (5 ml), and acetic anhydride (10 ml). After addition, the cooling bath was removed and the reaction was allowed to proceed for 4 days at room temperature. The product was isolated by hydrolysis of the acetic anhydride with water and filtration to yield 4.89 g of crude product. Glpc indicated 92% conversion. Recrystallization from ethanol–cyclohexane (1:1) afforded 3.03 g of nitration product with a purity judged to be 99.5% (glpc). The ^{1}H-nmr spectrum (CCl_4) showed two singlets at δ 1.38 and 1.32 with an integral ratio of 2:1. The ^{15}N-nmr spectrum (toluene) showed a single line (0.8 Hz half-width) at 6,082,677.8 Hz.

2,4-Dinitro-3,5-di-*tert*-butyltoluene-2-^{15}N. Nitric acid-^{15}N (200 μl, 14 *M*, 97 atom % ^{15}N) was added to a stirred mixture of 4-nitro-3,5-di-*tert*-butyltoluene (0.29 g, 1.1 mmol), acetic acid (2 ml), acetic anhydride (3 ml), and concentrated sulfuric acid (0.5 ml). Reaction was continued with stirring at room temperature for 4 hr and then terminated by the addition of 5 ml of water. After hydrolysis of the acetic anhydride, the nitration product was extracted with cyclohexane, and the cyclohexane layer was carefully washed with water and dried over anhydrous sodium sulfate. Evaporation of cyclohexane yielded 0.33 g (96%) of crude product. Glpc analysis indicated that the material was the desired product, **4**, with a purity of greater than 99%. The ^{1}H-nmr spectrum was identical with that of unlabeled **4**.[3] The ^{15}N-nmr spectrum (toluene) showed a single absorption line (1.3 Hz half-width) at 6,082,649.2 Hz.

Nitration of 2,4,6-Tri-*tert*-butylnitrobenzene-^{15}N-*3,5-d*$_2$. Fuming nitric acid (15 ml) was added to 2.5 g of ^{15}N-labeled **1**, and the reaction was allowed to proceed with magnetic stirring for a period of 12 hr at -5 to 0°. The reaction was stopped by the addition of 200 ml of water, and the crude product was collected by suction filtration, 3.5 g. Trituration of the filter residue with hot absolute ethanol and subsequent evaporation of the ethanol filtrate yielded 1.88 g. This material was redissolved in the minimum amount of cyclohexane and applied to a column of acid-washed alumina (Merck). The column was eluted with purified *n*-pentane, and 30-ml fractions were taken after elution of the first traces of material. Complete separation of ^{15}N-labeled **4** was not achieved; however, fractions 5–9 contained 2,4-dinitro-3,5-di-*tert*-butyltoluene of greater than 90% purity, 0.58 g. A portion of this material was further purified by preparative glpc to yield 0.24 g (98% pure by glpc). The ^{1}H-nmr spectrum (CCl_4) consisted of three

singlets at δ 2.23, 1.43, and 1.36, with an integral ratio of 1:3:3. The ^{15}N-nmr spectrum (toluene) showed a single line (0.9 Hz half-width) at 6,082,641.8 Hz.

2-Amino-4-nitro-3,5-di-*tert*-butyltoluene-*4*-^{15}*N*-*6*-*d*. A sample of **4** (0.24 g) dissolved in 25 ml of ethanol was reduced with hydrogen in the presence of prereduced platinum oxide at atmospheric pressure. The uptake of the requisite amount of hydrogen was rapid, and reaction was complete after 1 hr. The deep yellow crystalline product was isolated by filtration and evaporation of ethanol solvent, 0.20 g. Glpc indicated almost complete conversion of reactant to a single product. The ^{1}H-nmr spectrum (CCl_4) consisted of two *tert*-butyl singlets at δ 1.32 (9 H) and 1.49 (9 H), an aromatic methyl singlet at 2.18 (3 H), and a broad amine proton band at about 3.8 (2 H). The spectrum of this sample at −60° ($DCCl_3$) is shown in Figure 3.

Reduction of an unlabeled sample of **4** was carried out in an identical manner. Recrystallization of the product from hexane and sublimation (110° (1 mm)) afforded an analytical sample, mp 104–106°.

Anal. Calcd for $C_{15}H_{24}N_2O_2$: C, 68.14; H, 9.15; N, 10.60. Found: C, 68.22; H, 9.20; N, 10.89.

Nitration of 2,4,6-Tri-*tert*-butylnitrobenzene-*2*(*and 4*)-*tert*-butyl-d_9 and Mass Spectral Analysis. Parallel nitrations of 50-mg samples of unlabeled **1** and **1**-*2*(*and 4*)-*tert*-butyl-d_9 were carried out by mixing the nitro compounds with 2-ml portions of fuming nitric acid at 0°. After a 40-min reaction time, water was added, and the organic products were extracted with toluene. The toluene extracts, after thorough extraction with water and drying over sodium sulfate, were analyzed by direct injection into a gas chromotograph mass spectrometer (LKB Model 9000). Mass spectral data for the products of interest are shown in Figure 1.

Acknowledgment. We wish to thank Professor J. D. Roberts and Dr. F. J. Weigert for their interest and for recording the ^{15}N magnetic resonance spectra reported here. The assistance of Mrs. Inger Lindgren in performing the analysis on the LKB mass spectrometer is gratefully acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Reactions and Nuclear Magnetic Resonance Studies of Allylic Wittig Ylides

Robert K. Howe

Contribution from the Monsanto Co., Agricultural Division, Research and Development Department, St. Louis, Missouri 63166.
Received October 31, 1970

Abstract: Nmr studies of (3-ethoxycarbonyl-2-methylallylidene)triphenylphosphorane (**9**) reveal that this Wittig ylide exists mainly as two conformers **9a** and **9b** in rapid equilibrium, with the cis form **9a** as the major isomer. The ylide condenses with benzaldehyde to give ethyl 3-methyl-5-phenyl-2,4-pentadienoate in which cis-2 isomers predominate. Protonation of the ylide, formed from phosphonium salts *cis*-**3** and *trans*-**4**, with aqueous hydrogen bromide regenerates the salts in an 88:12 ratio of **3** and **4**. Hydrolysis of **9** produces triphenylphosphine oxide and a 92:8 mixture of ethyl 3-methyl-3-butenoate and ethyl 3-methylcrotonate. (3-Ethoxycarbonylallylidene)-triphenylphosphorane (**8**) exists as the two conformers **8a** and **8b**, with the trans form **8a** as the major isomer. Ylide **8** condenses with benzaldehyde to produce predominantly trans-2 isomers of ethyl 5-phenyl-2,4-pentadienoate.

The phosphonium ylide from either the methyl or ethyl ester of (3-carboxy-2-methylallyl)triphenylphosphonium bromide has been reported to condense with β-ionylidenealdehyde in ethanol to give predominantly trans-2 isomers of vitamin A ester.[1] Thus, the observation in the present work that the ylide condenses with benzaldehyde to give mainly cis-2 isomers of ethyl 3-methyl-5-phenyl-2,4-pentadienoate prompted further studies of the ylide.

The phosphonium salts **3** and **4** were each obtained in pure form by fractional crystallization of the salt mixtures produced from the reaction of triphenylphosphine with enriched samples of **1** and **2**, respectively. Treatment of either **3** or **4** with base and benzaldehyde gave, within experimental error, the same product ester mixture **5** in which the sum of cis-2 isomers amounted to 57–60% (Scheme I). The product mixture was analyzed by integration of the nmr signals of the vinyl methyl groups, which are sufficiently separated in the spectra to allow reasonably accurate assays. The nmr spectra of all the individual esters have been determined and reported in detail previously.[2-4] Under similar conditions the ylide from **6**[5] reacted with benzaldehyde to produce ethyl 5-phenyl-2,4-pentadienoate (**7**) that consisted of 94% trans-2 isomers.

The ylide **8** formed from **6** and the ylide **9** formed either from **3** or **4** were prepared and isolated as solids. The infrared spectrum of **8** has strong absorption at 1636 cm^{-1} and very strong absorption at 1530 cm^{-1}, and the ylide **9** has strong absorption at 1632 cm^{-1} and very strong absorption at 1492 cm^{-1}, indicative of extensive delocalization of the carbanionic charge into the carbonyl group of the ylides. The ylides **8** and **9** are

(1) (a) G. Wittig and H. Pommer, German Patent 950,552 (1956); (b) H. Pommer, *Angew. Chem.*, 72, 811 (1960).

(2) R. H. Wiley, T. H. Crawford, and C. E. Staples, *J. Org. Chem.*, 27, 1535 (1962).

(3) R. H. Wiley, H. C. van der Plas, and N. F. Bray, *ibid.*, 27, 1989 (1962).

(4) G. Pattenden and B. C. L. Weedon, *J. Chem. Soc. C*, 1997 (1968).

(5) The corresponding methyl ester derivative, (3-methoxycarbonylallyl)triphenylphosphonium bromide, and its ylide have been prepared: (a) F. Bohlmann, *Chem. Ber.*, **90**, 1519 (1957); (b) E. Buchta and F. Andree, *ibid.*, **92**, 3111 (1959); (c) G. Kresze, J. Firl, and H. Braun, *Tetrahedron*, **25**, 4481 (1969). Bohlman prepared methyl 5-aryl-2,4-pentadienoates of unspecified stereochemistry *via* the reaction of the ylide with aromatic aldehydes. Kresze, *et al.*, found the product mixture from reaction of 9-anthraldehyde and the ylide to consist of 70% methyl 5-(9-anthryl)-*trans*,*trans*-2,4-pentadienoate and 30% methyl 5-(9-anthryl)-*trans*,*cis*-2,4-pentadienoate.