the Bruker BVT-1000 variable-temperature control unit. Temperature measurements are accurate to ± 2 K. All NMR samples were prepared in precision NMR tubes on a vacuum line and degassed three times, and the NMR tubes were sealed.

Acknowledgment. C.H.B. is grateful to the National Science Foundation for support (Grants No. CHE78-21161, CHE79-26243, and CHE80-24931). We also acknowledge National Science Foundation Grant No. CHE79-16210 from the Chemistry Division in support of the Northeast Regional NSF-NMR Facility at Yale University. We appreciate the assistance of the University of Vermont Academic Computing Center staff in providing outstanding computational support. We are indebted to A. von Wartburg of Sandoz, Ltd., for a generous gift of podophyllotoxin and to Mervyn V. Leeding, ICIANZ, Victoria, Australia, for some preliminary estimates of ring current effects on chemical shift.

Registry No. 1, 518-28-5; 4, 40456-15-3; 5, 32970-80-2.

Some Aspects of Nitration of Aromatics by Lower Oxidation States of Nitrogen

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Received July 7, 1982

Nitration of benzene and toluene in trifluoroacetic acid (TFA) solution with sodium nitrite (N(III)) and nitrogen dioxide (N(IV)) occurs relatively slowly to produce mononitroarenes and oxidized byproducts. The yield of nitroarene improves as the ratio of nitrogen reagent to substrate increases over the stoichiometric requirement and can be good (greater than 90%) if the ratio is sufficiently high. Nitric oxide is the principal reduction product accompanying the conversion of N(III) or N(IV) to the N(V) state found in the nitroarene product. Evidence is presented against the intermediacy of nitrosoarenes, and the oxidation of nitrosobenzene with nitrogen dioxide in methylene chloride solution is found to produce a mixture of benzenediazonium nitrate and nitrobenzene. Palladium acetate and thallium trioxide have no detectable beneficial effect upon the rate of nitration or the yield of nitration by nitrogen dioxide in TFA. Wilkinson's catalyst does not effect reaction of nitrogen dioxide with benzene or toluene without solvent as reported.

Aromatic nitration is usually accomplished with nitric acid or some other form of nitrogen in oxidation state (V), and no redox change accompanies the formation of the resulting nitroaromatic product. However, the chemical literature is replete with fragmentary reports of the use of reagents containing nitrogen in lower oxidation state to form nitroaromatics. Although redox processes must accompany such reactions, little attention has been focused on the reduction products and the mechanisms by which they and the nitroarenes are formed. The efficiency of any procedure using lower oxidation states is directly related to the possibility of recycling the reduction product(s). When reduction products are nitrogen in oxidation states II or III, oxidation with air or oxygen is a feasible means of recycle. On the other hand, formation of still lower states of nitrogen, such as nitrous oxide or nitrogen, or substrate reduction products would make a process inefficient and unattractive unless other features were sufficiently attractive to offset the penalty of lost materials. Attention here is primarily upon the reactions of N(III) and N(IV) in acidic media.

Early reports of nitration with nitrogen dioxide have been summarized.¹ Coombes has reported that low concentrations of nitrogen dioxide in carbontetrachloride convert toluene slowly to nitrotoluenes with a high (44%) proportion of meta isomer while at higher concentrations a more normal isomer mix is obtained.² Diphenyl ether in 10.4 M perchloric acid was converted by a 100-fold

excess of nitrous acid to 2,4-dinitrophenol, and pnitrosophenol was converted to the same product under comparable conditions in the hands of of Challis, Higgins, and Lawson.³ Spitzer and Stewart⁴ found that benzene and toluene were converted in low yields (3% and 2%, respectively) to mononitro compounds by sodium nitrite in trifluoroacetic acid (TFA) in 4 h. Uemura, Toshimitsu, and Okano obtained considerably better results in the same system.⁵ Norman, Parr and Thomas⁸ also observed benzene nitration in TFA by sodium nitrite but found that passing nitrogen dioxide through the solution was more efficient. Moore and Lapp nitrated the methanesulfonamide of o-phenoxyaniline in 60% yield with sodium nitrite in TFA.⁶ and Crivello observed in a related process that trifluoroacetic anhydride in chloroform caused the formation of nitrobenzene from benzene and sodium nitrite.7

Nitration by way of nitroso intermediates is a commonly accepted mechanism for highly activated aromatics, but nitrosation of unactivated aromatics such as benzene and toluene has received relatively little attention. Challis, Higgins, and Lawson³ and Challis and Higgins⁹ have measured the rates of nitrosation of benzene, toluene,

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azulene, and 1-nitroazulene in moderately concentrated sulfuric and perchloric acids. More complex phenomena than straightforward nitrosation occur as shown by the work of Tedder and co-workers, summarized by Tedder and Theaker,¹⁰ and by the observations of Allan, Podstata, Snobl, and Jarkovsky.¹¹ In fairly concentrated solutions of N(III) in sulfuric acid such as those employed by Tedder et al. and by Allan et al., the presence of aromatics like benzene and toluene gives rise to a deep red color. Spectroscopic studies¹² suggest that N(III) in concentrated sulfuric acid exists as NO⁺, and Tedder and Theaker ascribe the red coloration to a complex of NO⁺ with the nitrosoarene while the Allan group favors a complex between NO^+ and the arene itself. Diazonium salts and/or products derived from them can often be isolated from these red solutions. Tedder and Theaker's results were consistent with formation of diazonium salts from nitrosoarene upon quenching of reaction mixtures in water, but some slow diazotization must also occur in concentrated acid for Allan et al. observed substantial diazonium salt formation upon long (months) standing.

A few publications describe the influence of metallic species on nitration by lower oxidation states of nitrogen. Uemura, Toshimitsu, and Okano^{5,13} found that treatment of toluene and other hydrocarbons with sodium nitrite and in a TFA solution of Tl(III) gave good yields of nitroarenes with isomer distributions suggestive of the intervention of metalation (toluene o/p = 0.15). However, oxidation of the intermediate nitroso compound also involved participation by the perchlorate ion that accompanied the thallium reagent. Palladium(II) was reported by Norman, Parr, and Thomas⁸ to catalize nitration in chloroacetic acid solution by either sodium nitrite or nitrogen dioxide. Quantitative formation of nitrobenzene from benzene and nitrogen dioxide in the presence of a reduced form of Wilkinson's catalyst was claimed by Mitchell and Tomezsko.¹⁴ In experiments described here, the nitration of aromatics with N(III) and N(IV) species in acidic media, especially with regard to stoichiometry, effects of metallic catalysts, and the mechanism by which the various products are formed, is further delineated.

Results

Several of the experiments described here have long reaction times. These times often reflect the demands of other projects but are on occasion informative.

N(V). A base-line experiment showing the behavior of nitrate (11.8 mmol) plus toluene (10.9 mmol) in TFA (15 mL) gave a 97% yield of nitrotoluenes. The ratio of o-/ p-nitrotoluenes was 1.38, and 1.2% of m-nitrotoluene was found. No unusual colors or other effects were seen. These observations are in accord with the results of Moodie, Schofield, and Tobin¹⁵ on the nitration of aromatics with nitric acid in TFA.

N(III). Sodium nitrite dissolves readily in TFA at room temperature with the rapid evolution of a small amount of gas. If air is excluded and the nitrite concentration is relatively low, this gas is colorless and was found by gas chromatography to be nitric oxide. The quantity of gas



Figure 1. Nitration in TFA. Yield of nitroarene vs. ratio of nitration reagent to arene: (∇) N(V) + toluene; (Δ) N(IV) + toluene; (\Box) N(III) + benzene; (O) N(III) + toluene.

evolved was measured after being allowed to stand for 70 days in one experiment and represented 8% of the nitrite charged.

Addition of benzene or toluene to such a solution results in the immediate formation of a deep red color. In most instances, the hydrocarbon was added by vacuum-line transfer, and the red color first appeared when the mixture was still solid and well below the melting point of TFA. If the ratio of nitrite to substrate was less than the 3:1 value required by eq 1 and employed by Uemura et al.,⁵ the red

$$ArH + 3HNO_2 \rightarrow ArNO_2 + 2NO + 2H_2O \qquad (1)$$

color persisted over long periods. At higher ratios of nitrite to hydrocarbon, the color would gradually fade to yellow. In an early experiment conducted without exclusion of air, an attempt was made to discover the stoichiometry of reaction by employing a nitrite/toluene ratio <1. The initial brown color persisted until aqueous workup, and no recognizable products were formed.

When the ratio of nitrite to toluene was varied from 2.5 to 7.8, the yield of nitrotoluenes increased from 17% to 91.5% as indicated in Figure 1, in sharp contrast to the results of Uemura and co-workers who obtained a high yield at 3:1 ratio. Oxidative byproducts identified were 4,6-dinitro-o-cresol, 2,6-dinitro-p-cresol, and (in one case) p-hydroxybenzoic acid. In one instance when the ratio of nitrite to toluene was 6.3, the dinitrocresols were isolated in 45% yield and the nitrotoluene yield was 47.6% on the basis, as all yields in this paper, of the arene charged. Analysis for unreacted toluene was generally not conducted, but the high material balance obtained in this experiment strongly suggests that oxidized products are formed in nearly all cases. Times of reaction varied from 0.7 to 268 days (in the case of the lowest yield).

The ratio of o-/p-nitrotoluene varied from 1.32 to 1.38 with one exception, which was 0.99. The proportion of m-nitrotoluene ranged from 1.3% to 4.3%. Only traces of dinitrotoluene were ever observed.

Results with benzene were comparable to those with toluene. As seen in Figure 1, the yield of nitrobenzene was also sensitive to the ratio of nitrite to substrate. In the experiment employing the ratio 4.8, the 77.6% yield of nitrobenzene was accompanied by 0.9% of 2,4-dinitrophenol and 10.8% of picric acid. To ensure that oxidation of the product was not a source of phenolic products, nitrobenzene was treated with sodium nitrite (6.9/1) for 13 days in TFA; no phenolic products were found. Additional details are given in the supplementary material (see paragraph at the end of the paper).

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N(IV). Nitration of toluene with nitrogen dioxide in TFA was conducted over a toluene concentration range 0.07-1 M and with nitrogen dioxide to toluene ratios 1.7-7.7. Part of the results are indicated in Figure 1, and although the yields are clearly better than those obtained with nitrite, the requirement of a ratio above the 1.5 value suggested by eq 2 is obvious. The red color described

$$2ArH + 3NO_2 \rightarrow 2ArNO_2 + NO + H_2O \qquad (2)$$

above in nitrite reactions was also observed in these reactions. It faded to yellow, or green in more concentrated cases, as reaction ran to completion at a rate roughly an order of magnitude faster than with N(III). Other than the color, the results at higher concentrations were identical with those at lower concentrations. The ortho/para isomer ratios fell in the range 1.20 to 1.38, and *m*-nitrotoluene content was always 1.1-1.9%. Again only traces of dinitrotoluenes were seen.

The high acidity of TFA is a key element in the successful production of nitroaromatics by nitrogen dioxide. Reaction mixtures prepared under otherwise parallel conditions to the higher concentration runs described above but with acetic acid as solvent produced only small (0-5%) yields of nitrotoluene in 3 days. The colors of the mixtures were light green rather than dark red, and oxidation products such as benzaldehyde, benzamide, and nitrobenzonitrile were identified by GC/MS. Additional details are available as supplementary material.

The intermediacy of nitroso compounds in the process of nitration by lower oxidation states of nitrogen is an interesting possibility. Gas chromatography of samples from a partially reacted mixture of toluene and NO_2 in TFA revealed no trace of nitrosotoluenes and showed a steady increase in the amounts of nitrotoluenes. Thus, if nitrosotoluenes are intermediates, their oxidation by nitrogen dioxide was sufficiently rapid to prevent detectable concentrations from building up. To assess this possibility, the reaction of nitrosobenzene with nitrogen dioxide was examined. In TFA solution, tarry, unrecognizable products were produced, and they were not further investigated. In methylene chloride solution, a precipitate formed and later dissolved. Examination by GC/MS without workup showed the presence not only of nitrobenzene and dinitrobenzene but also of chlorobenzene, benzonitrile, and benzaldehyde. Insufficient resolution of dinitrobenzene isomers was obtained in a 25-m silicone capillary column to identify the dinitrobenzene formed with certainty, but a ready separation by thin-layer chromatography showed it to be the para isomer. Since the unexpected products suggested a free radical reaction with the solvent and since nitrosobenzene is known to react with nitric oxide to form benzenediazonium nitrate,¹⁶ the solid which precipitated and redissolved was presumed to be that salt, formed by the reactions of eq 3-5.

$$2ArNO + 2NO_2 \rightarrow 2ArNO_2 + 2NO$$
 (3)

$$ArNO + 2NO \rightarrow ArN_2^+ + NO_3^-$$
(4)

$$3ArNO + 2NO_2 \rightarrow 2ArNO_2 + ArN_2^+NO_3^- \qquad (5)$$

Ku and Barrio have recently found that diazonium salts do lead to aromatic halides when decomposed in polyhalomethanes.¹⁷ In additional experiments, the formation of diazonium salt was further confirmed by quenching in ice water when the green color of nitrosobenzene had disappeared, but before the solid dissolved again, and then treating the aqueous layer with α -naphthylethylenediamine, which couples with diazonium salts to form purple product(s). The yield was determined by spectrophotometry vs. a calibration curve obtained under identical conditions from diazotized aniline. The nitrobenzene yield was determined by gas chromatography of the organic layer.

In three experiments yields of nitrobenzene from nitrosobenzene calculated by the stoichiometry of eq 5 were in the range of 70–86%. The yield of diazonium salt was measured in two experiments and was quantitative, again according to eq 5. In one of these the nitrogen dioxide was labeled with ¹⁵N, and by GC/MS the nitrobenzene was unlabeled and the dinitrobenzene was singly labeled. Additional details are available as supplementary material.

Effects of Metals. Mixed-acid nitration of benzene or toluene occurs at mass-transfer-limited rates, so any practical alternative must also be fast. For this reason, the catalysis of reaction of lower oxidation states of nitrogen with aromatics was of great interest. Extrapolating from the results of Norman and co-workers,8 toluene was reacted with nitrogen dioxide in TFA containing palladium(II) acetate. The results are shown in entry 1 of Table I. In a run that was identical except for the absence of palladium and a reaction time of 2 days, a quantitative yield of nitrotoluenes was obtained (entry 11 in Table II of supplementary material). The small amount of gas produced suggests that the low yield resulted from Pdcatalyzed oxidation of either substrate or products to nonvolatile or acidic materials, which would have been removed during workup. With this poor result in hand, experiments were made that more closely approximated the conditions used by Norman et al., who bubbled nitrogen dioxide into a chloroacetic acid solution at 100 °C. These were conducted in heavy-walled glass tubes closed by Rotaflow valves, and the results are shown in entries 2-4 of Table I. Again, the results were disappointing, especially in comparison with the control without palladium. Finally, reported conditions were reproduced as closely as possible with results as given in entry 5 of Table I.

Uemura and co-workers have demonstrated nitroso- and nitrodethallation of aromatics in TFA.^{5,13} If Tl(I) resulting from a dethallation reaction would be oxidized back to Tl(III) by nitrogen dioxide in TFA, only a catalytic amount of thallium would be required. Reaction mixtures with and without a small amount of Tl(III) were prepared and observed side by side. The red color disappeared in both the same time and identical results were obtained upon analysis as indicated in entries 6 and 7 of Table I.

Attempts were made to reproduce the quantitative yield described by Mitchell and Tomezsko¹⁴ of nitrobenzene from benzene and nitrogen dioxide in the presence of Wilkinson's catalyst, which had been prereduced with hydrogen to a yellow form. A hydrogen atmosphere was maintained as described, but only small amounts of nitroarene were obtained from either benzene or toluene. Data are given as entries 8–10 in Table I.

Discussion

With the exception of a few preliminary experiments and the reaction of N(V), all of the work described here was conducted by vacuum-line techniques, and effects of adventitious oxygen are absent. Thus reduction products must accompany every mole of nitro compound observed. For the present discussion, I make the assumption that these reduction products are nitrogen species, but the possibility of organic reduction products cannot be totally

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				cus of metals on	NILFALION WILL INU2 IN 1	r A			
						vield	isomer	ratios	
entry	substrate (mmol)	reagent (mmol)	solvent (amount)	time, temp	catalyst (mmol)	ArNO ₂ , %	d o	<i>m</i> %	remark
TI	toluene (1.13)	NO ₂ (8.7)	TFA (15 mL)	6 days, rt	Pd(OAc), (1.6)	38	1.85	1.5	0.15 mmol of gas
63	toluene (2.66)	$NO_{3}(5.0)$	ClAcOH (2.5 g)	5 h, 100 °C	Pd(OAc), (0.2)	q pu			5.3 mmol of gas
er.	toluene (2.86)	$NO_{2}(5.0)$	ClAcOH (5.0 g)	16 h, 75 °C	Pd(OAc), (0.2)	54	1.14	3.5	4.3 mmol of gas
4	toluene (2.64)	$NO_2(2.5)$	ClAcOH (2.5 g)	7 h, 75 °C	none	80	1.21	2.7	2.7 mmol of gas
5	toluene (10.9)	NO ² ^c	ClAcOH (10 g)	3.5 h 100 °C	Pd(OAc), (0.4)	42	0.85	10	D
9	toluene (1.06)	$NO_{2}(2.8)$	TFA^{d} (10 mL)	1 h, rt	Tl,O, (0.03)	102	1.40	1.2	
7	toluene (1.10)	$NO_{2}(2.8)$	TFA^{d} (10 mL)	1 h, rt	none	105	1.40	3.3	
ø	toluene (9.96)	NO ₂ /H ₂ (19.7) (2.2)	none	1 h, 100 °C	(Ph ₃ P) ₃ RhCl (0.028)	10	nd ³	nd^{e}	α -nitrotoluene. benzaldehvde
6	toluene (9.82)	NO ₂ /H ₂ (19.4) (2.3)	none	2 h, 50 °C	(Ph.P),RhCl	10	nd^e	nd^{e}	a-nitrotolnene henzaldehvde
10	benzene (9.92)	$NO_{2}/H_{2}(19.4)(2.5)$	none	1 h, 100 °C	(Ph ₃ P) ₃ RhCl	10			0.35% picric acid
^a ClAc(to dissolv	OH = chloroacetic ac e Tl2O3. e nd = not	cid. rt = room temperat t determined.	ure. b nd = not deter	mined, too man	y products by GC to ide	ntify indivic	luals, ^c	NO2 bub	bled in. ^{d} TFA contained 1% H ₂ O

ignored except possibly in those cases in which a quantitative or near quantitative yield of nitroaromatic was obtained. Nitroso intermediates would appear a likely choice in N(III) nitrations at least. Nitrosation of aromatic hydro-

carbons is known,⁹ and there is evidence that nitrosonium ion is abundant in TFA solutions of N(III).⁴ In N(IV) processes N(II) reduction product would disproportionate with excess N(IV) to generate N(III) and thus nitrosonium ion promptly after reaction began. However, three lines of evidence argue against a significant pathway involving nitroso intermediates. First, they cannot be directly observed. The results of Uemura and co-workers clearly demonstrate that nitrosoarenes are observable in TFA.⁵ Because the oxidation of nitrosobenzene to nitrobenzene is not instantaneous, it is difficult to argue that nitroso intermediate is too rapidly consumed to be detected. Second, the products obtained from nitrosobenzene and nitrogen dioxide in TFA were tarry and inconsistent with the high yields obtainable under proper conditions. Third and most important is the fact that the same isomer distribution is obtained in nitration of toluene whether the reagent is N(V), N(IV), or N(III). In all known systems nitrosation is more selective toward the para position than nitration. Thus if nitrotoluene from N(III) and/or N(IV) were formed via nitrosation, the ortho/para ratio would be smaller than that obtained with N(V). The ortho/para ratio data are remarkably consistent, and one forms a conclusion that one product-determining step is common to all three systems.

Curiously, other workers have not mentioned the intense red color formed in solutions of aromatics and lower valent forms of nitrogen in TFA. A few attempts to observe an absorption band from which this color arose were not successful. To the extent that the results of Allan et al.¹¹ in concentrated sulfuric acid can be translated to TFA solution, the color results from an absorption beginning in the visible and rising monotonically into the ultraviolet. As noted earlier, Allan et al. ascribe this color to a complex of the nitrosonium ion with the aromatic hydrocarbon while Tedder and Theaker¹⁰ considered it to arise from a complex of nitroso product with nitrosonium ion. The conclusions above about the low probability of nitroso intermediates in these systems argue against the Tedder and Theaker view. The eventual disappearance of the red color is consistent with the view that when arene has been exhausted, none of the products form sufficiently strong complexes to give a visible color.

The considerations above are consistent with the mechanism shown in Scheme I. Oxidation of the red nitrosonium-arene complex by nitrogen dioxide to yield the nitronium complex, which immediately collapses to nitro product through cyclohexadienyl intermediate, is the key step. Competing with this process is oxidative reaction or reactions upon the free hydrocarbon, which is shown formally as a reaction of N_2O_3 , yielding two molecules of nitric oxide. When a very large excess of reagent is present, the arene is fully complexed with nitrosonium ion and unavailable to the competing oxidative route, explaining the shift from oxidized to nitrated products as the ratio of reagent to substrate is increased. In N(III) systems the amount of nitrogen dioxide available to bring about oxidation of nitrosonium complex to nitronium complex is limited by disproportionation equilibria and/or rates resulting in slow reaction, but in N(IV) systems nitrogen dioxide is abundant, resulting in fast reaction.

Insufficient data are available to specify the nature of the oxidative process in more detail. Virtually, every



aromatic nitration reaction is accompanied by the formation of phenolic byproducts ranging in amount from parts per million to 50% or more. No one mechanism can account for all of the results. The work of Myhre, Fisher, Hahn, and others¹⁸ has shown that in many cases oxidation accompanying nitration takes place by addition-elimination mechanisms involving attack of the nitronium ion at an ipso position. However, in the present instance, addition elimination of nitrogen oxides as observed many years ago by Titov¹⁹ in nonpolar media may be adequate, and in any event the relatively large amounts of phenolic products obtained from benzene cannot be derived from ipso substitution.

The low rate of nitration found in acetic acid compared to TFA combined with the lack of color is a strong indication of a low degree of conversion to nitrosonium ion. The side-chain nitration and oxidation products observed here were not generally seen when reaction was conducted in TFA.

Two simple mechanisms are possible for the conversion of nitroso benzene to nitrobenzene by nitrogen dioxide as shown in Scheme II. The experiment with labeled nitrogen dioxide clearly shows that no more than 1-2% of nitrobenzene is formed by the ipso substitution route for at that level the 124 m/z peak obtained upon GC/MS would have been noticeably larger than the normal ¹³C satellite of the parent peak. The facile reaction observed contrasts sharply with the result reported by Bamberger^{16c} in chloroform solution. He found no reaction at all of nitrosobenzene with rigorously dried nitrogen dioxide. Since nitrogen dioxide was distilled from the supply cylinder in the present experiments into the vacuum line at relatively low partial pressure, the presence of significant amounts of water is unlikely even if the liquid in the cylinder were quite wet. That the difference should reside

Scheme II





in changing from chloroform to methylene chloride is also unlikely, and more information is needed to explain the discrepancy. The results of reaction of nitrosobenzene with nitrogen dioxide in TFA are even more perplexing. Ogata and Tezuka have made a careful study of the kinetics of oxidation of nitrosoarenes to nitro compounds by nitric acid in aqueous dioxane.²⁰ Their finding of half-order dependence upon both nitrate ion and nitrous acid concentrations implicates nitrogen dioxide in the oxidation process by which smooth oxidation takes place. The formation of unrecognizable products in TFA from nitrosobenzene and nitrogen dioxide is not easy to explain. Even if the reaction paralleled that in methylene chloride and the diazonium salt was not stable in TFA, the nitrobenzene that needs to be formed to generate nitric oxide should survive.

Effects of Metals. The catalytic effect of palladium on nitration by nitogen dioxide under any conditions used in this study is unclear. Discounting an anticatalytic effect, the only possible explanation of the low yield found in the presence of palladium when an excellent one was obtained in its absence (in TFA) is oxidation of the toluene and/or nitrotoluene catalyzed by palladium. Thus any catalytic effect on the nitration reaction itself has been obscured. The results in chloroacetic acid solution at 75 °C are less clear cut, but the facts that a better accountability of starting material and less gaseous products were obtained without palladium in a shorter period of time suggest that a practical application of any catalytic effect would be difficult. In a competitive experiment between benzene and toluene under the conditions of entry 5 of Table I, Norman, Parr, and Thomas⁸ found 113%, 11%, 50%, and 57% yields (based on Pd(II)) of nitrobenzene and o-, m-, and *p*-nitrotoluenes, respectively. This unusual distribution of nitrotoluene isomers was especially interesting and is in fact approached by that observed in entry 5 of Table I where the yield based on Pd(II) calculated in the manner of Norman, Parr, and Thomas⁸ is 1000%. However, within the context of the other results given here, selective oxidation of o- and p-nitrotoluenes over their meta isomer is a more probable explanation of the results than a directive catalytic effect of palladium. While a small catalytic effect, of say 2- or 3-fold, cannot be excluded, an effect of one or more orders of magnitude certainly is.

Catalysis by thallium clearly was not observed in the reaction of nitrogen dioxide with toluene in TFA. This finding merely says that thallation, if any under these particular conditions, is slower than nitration. The results of Uemura et al. on the other hand demonstrate that nitrosodethallation in TFA is faster than nitration by N(III) in that medium, for thallated arenes were regiospecifically

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(19) Titov, A. I. Zh. Obshch. Khim. 1952, 22, 1329.

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converted to the corresponding nitroso- and/or nitroarenes.

The evolution of a small amount of nitric oxide when sodium nitrite dissolves in trifluoroacetic acid is a fairly reproducible phenomenon and deserves comment. The extent of this reaction does not appear to depend upon the nitric oxide pressure, although detailed measurements have not yet been made. Thus the equilibria that control the formation of NO probably do not involve it. The simplest explanation is suppression of nitrous acid decomposition by water formed in the dehydration of nitrous acid, eq 6-8.

$$NaNO_2 + CF_3CO_2H \rightarrow HNO_2 + Na^+CF_3CO_2^- \quad (6)$$

$$2HNO_2 \rightarrow H_2O + NO + NO_2 \tag{7}$$

$$HNO_2 + CF_3CO_2H \rightarrow H_2O + NO^+CF_3CO_2^- \quad (8)$$

Experimental Section

Experiments except as noted above were conducted or prepared on a vacuum line in which all parts exposed to the reactants were glass, Teflon, Viton, or stainless steel. Pressures were measured by means of an MKS Baratron capacitive pressure gauge that had been calibrated against a laboratory aneroid barometer. The volumes of the various manifolds were determined by pressure, volume, temperature measurements against a calibrated volume sealed into the system. Nitrogen dioxide was measured out by filling a known volume to a pressure calculated by a program for a hand-held calculator that took into account the dimerization to dinitrogen tetroxide and the variation of the equilibrium constant with temperature and then condensing into the reaction mixture. Temperature of a gas was measured by taping a thermocouple to the manifold in which its pressure was measured.

Materials. Trifluoroacetic acid and chloroacetic acid were purchased from Aldrich Chemical Co. Toluene and benzene were ACS reagent grade. These materials were degassed and usually vacuum transferred into the reaction vessel prior to use. Nitrogen dioxide was obtained from Air Products and Chemicals, Inc., and labeled nitrogen dioxide was obtained from Prochem Isotopes. Sodium nitrite was ACS reagent grade purchased from Fisher Scientific and had an assay of 96% by permanganate titration. Palladium acetate and thallium trioxide were obtained from Alfa Inorganics and were used as supplied.

Analysis. Except as noted in the supplementary results, reaction mixtures were worked up by quenching in water, extraction with methylene chloride, reextraction with water to remove TFA, extraction with 1% sodium carbonate to remove acidic byproducts, and drying with calcium sulfate. The sodium carbonate extracts were acidified to pH 1 with sulfuric acid and extracted three or four times with ether. The dried ether solutions were examined by thin-layer and/or liquid chromatography. Nitroarene products were analyzed by gas chromatography on a 25-m dimethylsilicone capillary column using nitrobenzene as internal standard for nitrotoluenes and p-nitrotoluene as internal standard for nitrobenzene. Response factors were measured from mixtures approximating the compositions of those analyzed. The internal standard was generally added to the initial reaction mixture. A Finnigan Model OWA GC/MS was used by the Air Products Corporate Research Services Department.

Acknowledgment. I am indebted to Drs. Brian C. Challis and James F. White for helpful discussions and to Fred B. Leh for his capable laboratory assistance. Permission by Air Products and Chemicals, Inc., to publish this work is also gratefully acknowledged.

Registry No. Benzene, 71-43-2; toluene, 108-88-3; nitrosobenzene, 586-96-9; sodium nitrite, 7632-00-0; nitrogen dioxide, 10102-44-0; nitric oxide, 10102-43-9; palladium acetate, 3375-31-3; Wilkinson's catalyst, 14694-95-2; dithallium trioxide, 1314-32-5; benzenediazonium nitrate, 619-97-6; trifluoroacetic acid, 76-05-1.

Supplementary Material Available: Tables of data on the nitration of toluene in TFA, concentration effects on nitration in TFA and acetic acid, and oxidation of nitrosobenzene and a figure (5 pages). Ordering information is given on any current masthead page.

1,1-Dicyclopropylallene: Cycloadditions and Dimerization. Dependence of the Regioselectivity on Solvent Polarity and Lewis Acid Catalysis in the Reactions with Alkoxycarbonyl-Activated Olefins¹

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Received November 29, 1982

1,1-Dicyclopropylallene (1a) was found to react with a number of activated olefins (2) in a [2 + 2] manner. The reactions with monoactivated 2, as well as those with 1,2-disubstituted 2, proceeded at reasonable rates at 200 °C, whereas the reactions with 1,1-disubstituted 2 occured at much lower temperatures. Moreover, the dependence of regioselectivity on the structure of 2 was noted in these reactions. Thus, at 200 °C, methyl acrylate (2a), acrylonitrile (2f), dimethyl fumarate (2b), dimethyl maleate (2c), fumaronitrile (2g), and maleonitrile (2h) yielded the adducts 4 predominantly, if not exclusively. In contrast, the reaction with methylenemalononitrile (2i), as well as that with ethenetetracarbonitrile (2j), occured at room temperature with overwhelming production of the adducts 3. The reaction of 1a with diethyl methylenemalonate (2d) required heating to some degree, and its regioselectivity was influenced by solvent polarity. Namely, 4d predominated in refluxing benzene whereas 3d was a major product in refluxing acetonitrile. It was further revealed that the Lewis acid catalysis greatly reduced the necessary temperature for the reactions of la with alkoxycarbonyl-activated olefins and brought about a total reversal of the regioselectivity. Thus, 2a-d gave 3 exclusively at room temperature in the presence of aluminum chloride. These cycloadditions should be stepwise processes since all the reactions that were carried out with 2c were nonstereospecific. The thermal reaction yielding 4 predominantly appears to be a diradical stepwise process whereas the reaction producing 3 as the principal cycloadduct will involve an intermediate possessing a polar character. Finally, 1a was found to dimerize at 200 °C. Among the two dimers produced, less crowded 9 rearranged slowly to a spiro compound 11 under the reaction conditions.

The chemistry of allenes has attracted considerable attention for some decades mostly because the allenes exhibit peculiar chemical reactivities.² In particular, mechanistic interests have focused on rare, thermal [2 +