

and 10 ml. of 47% hydriodic acid refluxing under an air condenser for 2 hr. The solvents were removed under reduced pressure leaving orange crystals which were recrystallized from water (Norite) to give 3,5-dihydroxy-*o*-xylene (XI), m.p. 136°, lit.<sup>32</sup> m.p. 136–137° (from water).

*3,5-Dimethylbenzyltrimethylammonium bromide* (VIIIb). 3,5-Dimethylbenzoic acid (30.0 g., 0.2 mole) was added slowly to a slurry of 10.0 g. (0.25 mole) of 95% pure lithium aluminum hydride in 500 ml. of anhydrous ether. The addition required about 1.5 hr. because of the unusually vigorous reaction. After 3 hr. of mechanical stirring the reaction was worked up by the usual procedure<sup>10</sup> to give 24 g. (88%) of 3,5-dimethylbenzyl alcohol, b.p. 115–117.5° at 10 mm., lit.<sup>33</sup> b.p. 218–221.°

This alcohol, 26.7 g. (0.16 mole), was treated with 27.1 g. (0.10 mole) of phosphorus tribromide in 500 ml. of ether. After the usual work-up the product was recrystallized once from methanol at –70° to give 31.2 g. (80%) of 3,5-dimethylbenzyl bromide, m.p. 37.5–38°, lit.<sup>33</sup> m.p. 37.5–38°.

Quaternary salt VIIIb, m.p. 238.5–239°, was prepared in 84% yield from 31.2 g. (0.157 mole) of this bromide and excess trimethylamine as described for Ia.

*Anal.* Calcd. for C<sub>12</sub>H<sub>20</sub>BrN·1/2 H<sub>2</sub>O<sup>34</sup>: C, 54.01; H, 7.92; N, 5.25. Found: C, 54.17, 54.05; H, 8.13, 7.98; N, 5.17, 5.14.

*Rearrangement of bromide VIIIb.* This rearrangement was carried out with 30.5 g. (0.114 mole) of quaternary salt VIIIb and 0.24 mole of sodium amide as described for the rearrangement of Ia to give 19.6 g. (97%) of 2,4,6-trimethylbenzylidimethylamine (IXb), b.p. 108–109° at 10.5 mm., *n*<sub>D</sub><sup>25</sup> 1.5109, lit.<sup>2</sup> b.p. 112–113° at 13 mm. The picrate melted

at 148–149°, lit.<sup>2</sup> m.p. 149–150°. The methiodide melted at 195–196°, lit.<sup>2</sup> m.p. 196–197° dec.

*Independent synthesis of amine IXb.* To a solution of 9.0 g. (0.2 mole) of dimethylamine in 50 ml. of benzene was added 9.3 g. (0.0436 mole) of 2,4,6-trimethylbenzyl bromide in 25 ml. of benzene. After 1 hr., the mixture was shaken with 300 ml. of 2*M* hydrochloric acid and the layers separated. The aqueous phase was made strongly basic with solid sodium hydroxide, cooled, and extracted with ether. The ethereal solution was dried, filtered, and evaporated. Vacuum distillation yielded 5.68 g. (74%) of 2,4,6-trimethylbenzylidimethylamine (IXb), b.p. 107–108° at 10 mm., *n*<sub>D</sub><sup>25</sup> 1.5109 (identical with that of the rearrangement product). The melting points of its picrate and methiodide were the same as those of the rearranged amine and mixed melting points were not depressed. In addition the infrared spectra of the two samples of amine were identical.

*Rearrangement of a mixture of benzyltrimethylammonium iodide and 3,5-dimethylbenzyltrimethylammonium bromide* (VIIIb). To a stirred suspension of 0.30 mole of sodium amide in 300 ml. of liquid ammonia was added during 1 min. a mixture of 25.8 g. (0.10 mole) of 3,5-dimethylbenzyltrimethylammonium bromide and 27.7 g. (0.10 mole) of benzyltrimethylammonium iodide in 1000 ml. of liquid ammonia. Most of the solid salts had dissolved in the ammonia before the addition. After 30 sec., 16 g. (0.3 mole) of ammonium chloride dissolved in liquid ammonia was added rapidly. The ammonia was replaced by ether and the mixture was filtered. The filtrate was distilled to give 8.72 g. (59%) of 2-methylbenzylidimethylamine, b.p. 80–85° at 14 mm. and 8.73 g. (49%) of 2,4,6-trimethylidimethylamine (IXb), b.p. 113–115° at 14 mm. Also a middle cut (2.16 g.), b.p. 85–113° at 14 mm., was obtained. These two amines were identified by comparison of their infrared spectra with those of authentic samples.

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(32) O. Simon, *Ann.*, **329**, 305 (1903).

(33) P. Wispek, *Ber.*, **16**, 1577 (1883).

(34) The yields of rearranged amine from salt VIIIb are nevertheless based on the anhydrous salt. The yields based on the hydrated form would be about 4% higher.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF FLORIDA]

## Tetraphenylbutatriene from the Reaction of 1,1-Diphenyl-2-nitroethylene with Potassium *t*-Butoxide<sup>1</sup>

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Treatment of 1,1-diphenyl-2-nitroethylene with potassium *t*-butoxide gives, in addition to products resulting from *beta*-addition of base, small amounts (up to 10%) of tetraphenylbutatriene II. Employing spectrophotometric techniques, it was shown that this reaction does not involve an intermediate carbene. A mechanism for this reaction involving *alpha*-addition of a vinyl carbanion to the nitroolefin is suggested.

In the course of some examinations of the scope and mechanism of *alpha*-eliminations from vinyl systems (the Fritsch-Buttenberg-Wiechell rearrangement)<sup>3,4</sup> we felt that it would be interesting

to investigate the reactions of 1,1-diphenyl-2-nitroethylene with strong base under typical *alpha*-elimination conditions. It was recognized from the outset that *beta*-addition of base to the nitroolefin<sup>5,6</sup> would certainly compete with *alpha*-elimination. We therefore selected the rather bulky base,

(1) Taken in part from the dissertation submitted by Charles D. Broaddus to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1960.

(2) Du Pont Teaching Fellow, 1959–60.

(3) P. Fritsch, *Ann.*, **279**, 319 (1894); W. P. Buttenberg, *Ann.*, **279**, 327 (1894); H. Wiechell, *Ann.*, **279**, 337 (1894). For a review of this type of reaction see T. L. Jacobs, *Org. Reactions*, **V**, 1 (1949). More recent references can be found in A. A. Bothner-By, *J. Am. Chem. Soc.*, **77**, 3293 (1955) and reference 4.

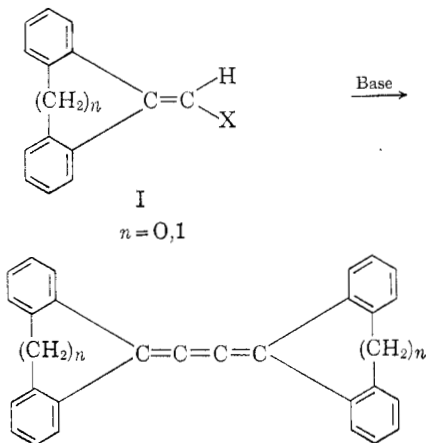
(4) J. F. Pritchard and A. A. Brothner-By, *J. Phys. Chem.*, **64**, 1271 (1960); D. Y. Curtin and E. W. Flynn, *J. Am. Chem. Soc.*, **81**, 4714 (1959).

(5) The addition of basic reagents to 1,1-diphenyl-2-nitroethylene is a well known reaction. *E.g.* see P. Lipp, W. Ludicke, N. Kalinkoff, and A. P. Pethoff, *Ann.*, **449**, 15 (1926); M. Konowalow and G. Jatzewitsch, *J. Russ. Phys. Chem. Ges.*, **37**, 542 in *Chem. Zent.*, **76**, II, 824 (1905).

(6) R. Anschütz and E. Romig, *Ann.*, **233**, 327 (1886).

potassium *t*-butoxide, for our initial investigations. It was found that, in addition to products which obviously arose from *beta*-addition to the nitroolefin, small amounts of 1,1,4,4-tetraphenylbutatriene II were consistently formed.

The formation of tetraphenylbutatriene from this reaction was particularly interesting to us in view of the recent observations by Hauser and Lednicer<sup>7</sup> as well as Curtin and Richardson<sup>8</sup> that certain vinyl halides give the dimeric product rather than the rearranged acetylene.



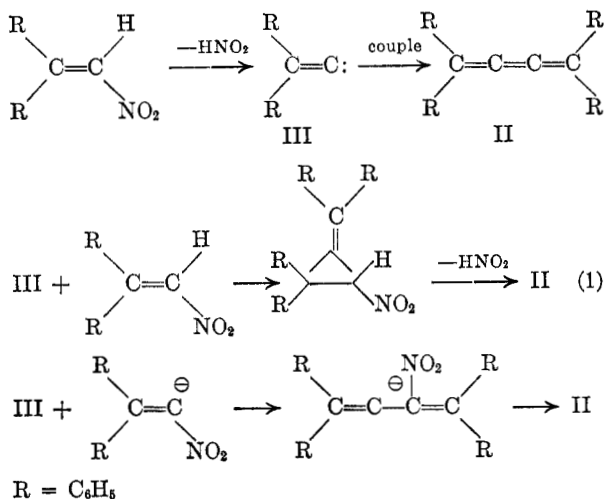
However, the characteristic which was common to all of these investigations was that the two phenyl rings were bonded together in such a way as to inhibit rearrangement. In fact, Curtin and Richardson<sup>8</sup> found that when the length of the chain bonding the two phenyls together was long enough (I.  $n = 2$ ), again, rearrangement was observed. In the case of the nitroolefin, however, the dimeric product was formed despite the fact that the two phenyls were free to migrate. Furthermore, the crude product from this reaction was examined with gas chromatography and it was found that no detectable amount of diphenylacetylene had been formed.

In view of this interesting difference in the course of the reaction and in view of the possible theoretical implications, this reaction was studied in some detail. This paper will be confined to the reaction involving the *alpha*-carbon.

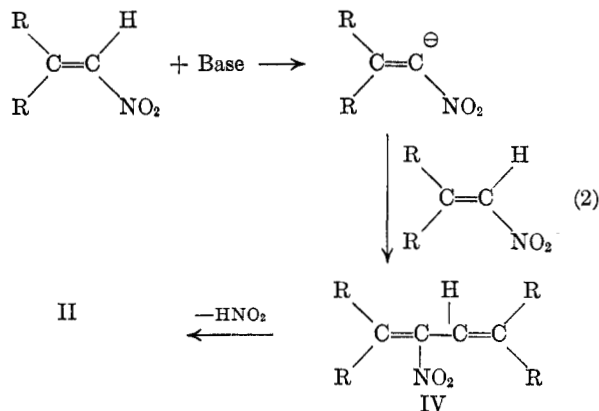
The two mechanisms suggested by both Hauser<sup>7</sup> and Curtin<sup>8</sup> for the formation of triene from the substituted methylenefluorenes and related compounds certainly appeared to apply to the system under investigation. Thus, the reaction could proceed *via* initial formation of the carbene III followed by various reaction paths leading to formation of the triene (Equation 1) or it could proceed by attack

(7) C. R. Hauser and D. Lednicer, *J. Org. Chem.*, **22**, 1248 (1957).

(8) D. Y. Curtin and W. H. Richardson, *J. Am. Chem. Soc.*, **81**, 4719 (1959).



of the vinyl carbanion on the *alpha*-carbon of 1,1-diphenyl-2-nitroethylene<sup>9</sup> to give the nitrobutadiene IV. This, in turn, could *beta*-eliminate to give the observed product (Equation 2).



In the attempt to distinguish between these two reaction paths, two approaches were employed. First, attempts were made to isolate intermediate IV. Isolation of this material followed by elimination under the reaction conditions would exclude carbene coupling as the sole source of triene. However, in view of the small proportion of this reaction which proceeded by reaction at the *alpha*-carbon (at most 9.4%) it was not too surprising that all attempts to isolate such an intermediate failed.

As a second method to distinguish between these two reaction paths, attempts were made to capture the carbene with an appropriate trapping agent and isolate and characterize such a product. The trapping agents which were employed were cyclohexene and diethylamine. Again all attempts failed.

In the course of this study, however, it was observed that as long as the conditions of the reaction (including the time interval between the prepara-

(9) This type of reaction has been discussed fully by Hauser and Lednicer<sup>7</sup> and Truce and his co-workers (*J. Am. Chem. Soc.*, **78**, 2743, 2748 (1956); **80**, 1916, 6450 (1958)).

tion and use of the base) were held reasonably constant, the reaction gave consistent yields of the triene which could be determined quite accurately by employing spectrophotometric techniques. For example, see the first two entries in Table I. The yield of triene was therefore determined in the presence of various carbene trapping agents. In Table I it will be seen that the addition of a large excess of either cyclohexene or diethylamine caused no detectable change in the amount of triene formed (as compared with blanks run at the same time). These experiments make the carbene mechanism very unlikely for this particular reaction.

TABLE I

1,1,4,4-TETRAPHENYLBUTATRIENE FROM THE REACTION OF 1,1-DIPHENYL-2-NITROETHYLENE WITH POTASSIUM *t*-BUTOXIDE<sup>a</sup>

Moles of Nitroolefin	Moles of Reagent Added	Reaction Time, Hours	Nitroolefin Unreacted, %	Yield of Triene, %
$2.2 \times 10^{-4}$	None	2	14	3.5 <sup>b</sup>
$2.2 \times 10^{-4}$	None	2	13	3.4 <sup>b</sup>
$8.8 \times 10^{-5}$	None	0.5	13	2.3
$8.8 \times 10^{-5}$	$1 \times 10^{-2}$ Cyclohexene	0.5	14	2.3
$2.2 \times 10^{-4}$	None	2	14	2.1 <sup>c</sup>
$2.2 \times 10^{-4}$	$1 \times 10^{-3}$ Diethylamine	2	17	2.1 <sup>c</sup>
$2.2 \times 10^{-4}$	None	2	18	4.0
$2.2 \times 10^{-4}$	$3.2 \times 10^{-3}$ Methyl iodide	2	16	2.2
$2.2 \times 10^{-4}$	None	1.5	21	5.4
$2.2 \times 10^{-4}$	$3.2 \times 10^{-3}$ Methyl iodide	1.5	18	3.0 <sup>d</sup>
$2.2 \times 10^{-4}$	None	12	11	9.4 <sup>e</sup>

<sup>a</sup> The reactions were made up to 10 ml. with heptane. Unless otherwise stated the potassium *t*-butoxide was added as a solution (0.8M) in 1 ml. of *t*-butyl alcohol. <sup>b</sup> These two runs were made under identical conditions for the purpose of comparison of triene yields. <sup>c</sup> The difference in yield between these two runs and the first two is typical of the differences observed when different batches of base were used. It was not determined why this reaction was so sensitive to either changes in batch or the length of time a single sample was stored before use. This difficulty was obviated in individual runs by comparison with blanks. <sup>d</sup>  $4 \times 10^{-3}$  moles of base. <sup>e</sup>  $9 \times 10^{-4}$  moles of freshly prepared dry potassium *t*-butoxide added to a solution of the olefin in heptane.

Finally, it should be mentioned that the formation of a carbanion intermediate was demonstrated by effecting the reaction in the presence of a tenfold excess of methyl iodide, a reagent that should be effective as a carbanion trapping agent (Table I). This mixture showed a 40–50% drop in the amount of triene formed. In another pair of runs, there was included in the reaction mixture containing the methyl iodide enough excess potassium *t*-butoxide to completely react with the methyl

iodide and still retain the same mole ratio of 1,1-diphenyl-2-nitroethylene to potassium *t*-butoxide as was present in the blank. These conditions gave the same 40–50% drop in the amount of triene formed.

It is therefore suggested that the most likely path for the formation of the four-carbon chain is initial formation of the vinyl carbanion followed by *alpha*-addition to the nitroolefin (Equation 2).

There remains unanswered, however, the question of why the nitroolefin couples to give the triene whereas the corresponding halogenated olefin,<sup>3,4</sup> when possible, *only* rearranges to the corresponding diphenylacetylene. Since there is little doubt but that both reactions proceed *via* an anionic intermediate<sup>4</sup> this difference is particularly striking. One obvious contributing factor to this difference in reaction routes is the difference in electron density at the *alpha*-carbon to which the anion must couple. This, however, hardly seems to be sufficient to explain the difference in reaction routes since Curtin and Flynn<sup>4</sup> found that the vinyl halide anionic species were much too short-lived to expect appreciable coupling. For example, it was found that the anionic species generated from the reaction of 1,1-diphenyl-2,2-dibromoethylene underwent 80% rearrangement to the acetylene in just 30 seconds at  $-35^\circ$ . Furthermore, in contrast to the nitroanalog, all attempts to trap the intermediate anion failed. Thus, there apparently exists within the anions inherent differences in tendencies to rearrange. One is tempted to conclude that this difference indicates that the *alpha*-elimination from vinyl type systems proceeds by migration of a phenyl without its electrons and that the nitro group retards this migration by dispersing the negative charge of the anion away from the carbon to which migration occurs (at least by an inductive effect and probably also by rehybridizing the carbon and placing the nonbonding electrons into a conjugated *p*-orbital). However, it is also possible that the *alpha*-elimination proceeds by migration of the phenyl with its electrons with concomitant loss of the halide and that the difference in these two reactions is simply due to the difference in ease of loss of the halide versus the nitro groups. The real difference must remain a mystery until further investigations which are under way are completed.

EXPERIMENTAL<sup>10</sup>

*1,1-Diphenyl-2-nitroethylene.* 1,1-Diphenyl-2-nitroethanol was prepared from 1,1-diphenylethylene<sup>11</sup> by the method of Anschutz and Romig.<sup>8</sup> The substituted ethanol was then dehydrated by the method of Wittig and Gauss<sup>12</sup> to give 1,1-diphenyl-2-nitroethylene, yellow crystals from hexane (33%), m.p. 86–87° (lit.<sup>5</sup> m.p. 86–87°).

(10) Melting points are uncorrected. Microanalyses were done by Galbraith Laboratories.

(11) C. F. H. Allen and S. Converse, *Org. Syntheses*, Coll. Vol. I, 226 (1951).

(12) G. Wittig and W. Gauss, *Ber.*, 80, 372 (1947).

*Authentic 1,1,4,4-Tetraphenylbutatriene* Authentic tetraphenylbutatriene was synthesized from 1,1,4,4-tetraphenyl-2,3-dihydroxybutyne-2 by the method of Kuhn and Wallenfells,<sup>13</sup> m.p. 236–237° (lit.<sup>13</sup> m.p. 236.5–237°).

*Reaction of 1,1-diphenyl-2-nitroethylene with dry potassium t-butoxide.* Dry potassium *t*-butoxide was prepared by adding *t*-butyl alcohol to a refluxing mixture of potassium in dry toluene or xylene. After 2 hr. reflux, the mixture was filtered under nitrogen and the residue of potassium *t*-butoxide was washed thoroughly with dry ether. The best yields of triene were obtained when this material was used as soon after preparation as possible. In a typical run, 1,1-diphenyl-2-nitroethylene (2.0 g., 8.8 mmoles) was dissolved in 150 ml. of dry heptane. The system was flushed with dry nitrogen and heated to reflux. To the refluxing solution was added in small portions 2.0 g. (18 mmoles) of dry potassium *t*-butoxide. After each addition, a red color developed in the reaction mixture. The mixture was refluxed for 5 hr. after completion of the addition. It was then filtered, while hot, through a Buchner funnel. Upon cooling, the heptane filtrate deposited 0.12 g. (7.6%) of yellow crystals, m.p. 236–237°; admixture with authentic 1,1,4,4-tetraphenylbutatriene showed no melting point depression.

*Anal.* Calcd. for C<sub>28</sub>H<sub>20</sub>: C, 94.37; H, 5.63. Found: C, 94.12; H, 5.60.

The infrared spectrum was identical with that of authentic tetraphenylbutatriene.

Evaporation of the heptane filtrate almost to dryness afforded 0.34 g. (17%) of the starting material.

Both the residue from the above filtration of the hot reaction mixture and the filtrate (after evaporation to dryness) were analyzed for diphenylacetylene. This was effected by gas chromatography of samples of each (chloroform extract of the residue) employing a six-foot column of Tide at 198° and 15 p.s.i. internal pressure in a Perkin-Elmer

model 154-B vapor fractometer. Neither sample showed any peak near 7.4 min., the retention time of authentic diphenylacetylene.

*Quantitative determination of tetraphenylbutatriene and unchanged 1,1-diphenyl-2-nitroethylene.* The concentration of the triene and unchanged starting material were determined quantitatively by utilizing the Beckman DK-2 Spectrophotometer. Absorptions at 420 m $\mu$  (triene) and 360 m $\mu$  (starting material) were employed. Both compounds obeyed Beer's Law and no absorption from products resulting from *beta*-addition to the nitroolefin appeared at these wave lengths. It was therefore possible to analyze the reaction products for triene and nitroolefin directly. A typical run is given below. The other results are summarized in Table I.

*Reaction of 1,1-diphenyl-2-nitroethylene with a t-butyl alcohol solution of potassium t-butoxide in the presence of cyclohexene.* 1,1-Diphenyl-2-nitroethylene (0.02 g., 8.8  $\times 10^{-5}$  moles) was dissolved in 8 ml. of dry heptane. To this solution was added 1 ml. (1  $\times 10^{-2}$  moles) of cyclohexene. The three-necked flask was flushed well with dry nitrogen and 1.0 ml. of a *t*-butyl alcohol solution of potassium *t*-butoxide (8.0  $\times 10^{-4}$  moles) was added dropwise by means of a syringe. The solution was refluxed, with constant agitation, for 30 min. at which time the hot mixture was poured into 30 ml. of boiling chloroform. The solution was washed twice with 50-ml. portions of saturated salt solution and dried over anhydrous magnesium sulfate. The solution was made up to volume with chloroform in a 50-ml. volumetric flask followed by dilution with chloroform of 1:10. The amount of triene and starting material were then calculated directly from the ultraviolet spectrum to be 2.3% and 14%, respectively.

A blank, differing from the above reaction only in that 9 ml. of heptane was used as the solvent rather than 8 ml. of heptane and 1 ml. of cyclohexene also gave a 2.3% yield of triene.

(13) R. Kuhn and K. Wallenfells, *Ber.*, 71, 783 (1938).

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[CONTRIBUTION No. 31 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LIMITED]

## Aryldiazonium Tetrachloroborates and Tetrabromoborates

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Aryldiazonium tetrachloroborates and tetrabromoborates were prepared from (1) the corresponding aryldiazonium halides and boron trihalides, (2) primary aromatic amines and nitrosonium tetrachloroborate, (3) the reaction of N<sub>2</sub>O<sub>2</sub>·BCl<sub>3</sub> and N<sub>2</sub>O<sub>2</sub>·BBr<sub>3</sub> with primary aromatic amines.

The first reference to diazonium tetrafluoroborates is that of Bart<sup>1</sup> in 1913 who prepared them by treating aromatic diazo compounds with complex fluoroboric acids and their salts. Owing to the great stability and practical application of the diazonium tetrafluoroborates, considerable research has since been carried out on these compounds.<sup>2</sup> As intermediates in the Schiemann reaction, aryldiazonium tetrafluoroborates are prepared either by diazotizing aromatic primary amines and then treating the prepared diazonium compounds with fluoroboric acid or fluoborates or by carrying out the diazotiza-

tion directly in aqueous fluoboric acid.<sup>3</sup> Wannagat and Hohlstein<sup>4</sup> in an improved method prepared aryldiazonium tetrafluoroborates from primary aromatic amines and nitrosonium tetrafluoroborates. No aryldiazonium tetrachloroborates or tetrabromoborates, however, have been reported previously.

Tetrachloroborate and tetrabromoborate complexes are considerably less well known than the corresponding tetrafluoroborates. Muettterties<sup>5</sup> ob-

(1) H. Bart, Ger. Patent 281,055 (Oct. 7, 1913) [*Chem. Abstr.*, 9, 1830 (1915)].

(2) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," Wiley, New York, 1949.

(3) G. Balz and G. Schiemann, *Ber.*, 60B, 1186 (1927); E. Wilke-Dorfurt and G. Balz, *Ber.*, 60, 115 (1927); A. Roe, *Org. Reactions*, 193–228 (1949).

(4) U. Wannagat and G. Hohlstein, *Chem. Ber.*, 88, 1839 (1955).

(5) E. L. Muettterties, *J. Am. Chem. Soc.*, 79, 6563 (1957).