cc.) until evaporation of the last ether extract left no significant residue.

The residue (0.17 g.), m.p. 141–143°, from evaporation of the ether extracts had no nitro bands but did contain the following bands in its infrared spectrum: ν_{OH} 3310ms, $\nu_{C=O}$ 1680m cm.$^{-1}$ in Nujol. Recrystallization from methanol of a similar ether extraction residue from another run, having a m.p. of 172–177° but an infrared spectrum in Nujol identical with that of the preceding sample, yielded a sample, m.p. 204–207°, having an infrared spectrum in Nujol identical with that of anthraquinone, $\nu_{C=O}$ 1680 cm.$^{-1}$ Since the nitro compound is soluble in ether but insoluble in water, these ether extraction results indicate that none of the free nitro compound remained unchanged. Attempts to isolate the nitro compound salt in pure form by crystallization of the crude salt mixture from methanol were unsuccessful.

The aqueous solution of the nitro compound salt was added dropwise, with stirring, to a solution of acetic acid (30 cc.) in water (50 cc.), cooled in an ice bath, causing immediate formation of a cloudy white precipitate, which flocculated upon standing. The pale greenish white, granular product was filtered, washed with water (1000 cc.), and dried overnight in a vacuum desiccator, yielding a sample (5.41 g., 100%), m.p. 144–146°, and mixed melting point with starting material, 145–149°. The infrared spectrum in Nujol was identical with that of the starting material, but the ultraviolet spectrum suggested contamination by traces of anthracene (< 1.5%), as indicated by increased intensity at 252 mμ and faint bands at 356 and 374 mμ. Crystallization of 1.19 g. of the product from 95% ethanol yielded a sample (0.92 g.), m.p. 150.5–152°, shown to be identical with the starting material by mixed melting point and infrared and ultraviolet analysis. Chromatography of the mother liquor on alumina yielded an additional sample (0.16 g.), m.p. 149–150°, also shown to be identical with the starting material by mixed m.p. and infrared and ultraviolet analysis. The combined yield (1.08 g.) represents a 91% recovery of regenerated starting material.

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The Competitive Nitration of Toluene and *t*-Butylbenzene

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Recently, the origin of the Baker-Nathan effect has received considerable attention.[1] In an examination of the adherence of the relative rate data for the electrophilic substitution reactions of toluene[2] and *t*-butylbenzene[3] to a linear free energy relationship, the Baker-Nathan effect appeared to be dominant in governing the reactivity of the *para*-position. In contrast, the reactivity of the position *meta* to the alkyl groups was indicated to be in the inverse order. The experimental results for the substitution of the aromatics are straightforward regarding reaction in the *meta* position. In all cases, the *m*-*t*-butyl substituent enhances reactivity to a slightly greater extent than does the methyl group. On the other hand, the reactivity pattern for substitution in the *para* position of toluene and *t*-butylbenzene is not free of ambiguity. Most reactions provide the Baker-Nathan[3] order. However, certain substitution reactions have been reported to provide the inverse order for *para* substitution.[4] Significantly, the most popular model reaction, nitration, falls into this category.[5]

In view of the relevance of this observation to discussions of the Baker-Nathan effect a re-examination of the nitration was undertaken in this laboratory. However, the recent report of the relative rate and isomer distribution for the nitration of the alkylbenzenes[6] prompts this summary of our observations.

As described by Norman and his associates,[6] the competitive reaction technique and vapor phase chromatography provided a most satisfactory approach. Acetic anhydride was adopted as a solvent after preliminary experiments had demonstrated the nitration proceeded only very slowly in aqueous acid, the medium employed by Hughes and his coworkers.[5] The possible existence of a major solvent effect was investigated through study of the reaction in nitromethane.

The reaction between the aromatics and nitric acid in acetic anhydride was rapid as reported.[7–9] In the experiments outlined here the reaction was allowed to proceed to completion. The results for competitive reactions and isomer distributions for nitration in acetic anhydride are summarized in Table I.

The reaction between nitric acid and the aromatic in nitromethane proved to be somewhat more difficult to study quantitatively. Preliminary experiments revealed the amount of nitroaromatic obtained was minute unless a large excess of nitric acid was employed as suggested from the observations of Bird and Ingold.[7] Accordingly, nitric acid was kept in excess. Under these circumstances it was important to establish the presence of residual aromatic at the completion of the reaction. This

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(1) Much of the available information has been reviewed, *Tetrahedron*, **5**, 107 (1959).

(2) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 3323 (1959).

(3) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 5621 (1959).

(4) For example, deuterium exchange, W. M. Lauer, G. W. Matson, and G. Stedman, *J. Am. Chem. Soc.*, **80**, 6433, 6437 (1958); tritium exchange in trifluoroacetic acid, C. Eaborn and R. Taylor, *Chem. & Ind.*, 949 (1959); and mercuridesilylation, R. A. Benkeser, T. V. Liston and G. M. Stanton, *Tetrahedron Letters*, No. **15**, 1 (1960).

(5) H. Cohn, E. D. Hughes, M. H. Jones, and M. G. Peeling, *Nature*, **169**, 291 (1952).

(6) J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

(7) M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938).

(8) C. K. Ingold, A. Lapworth, E. Rothstein, and D. Ward, *J. Chem. Soc.*, 1959 (1931).

(9) For a recent discussion of the nature of the reagent under these conditions, F. G. Bordwell and E. W. Garbisch, *J. Am. Chem. Soc.*, **82**, 3588 (1960).

condition was demonstrated by vapor phase chromatography. Moreover, dinitrotoluenes were shown to be absent. The relative rate determined in two experiments was found to be independent of the concentration of nitric acid also indicative that the rate measurements represent the true relative reactivity. The relative rates and isomer distributions are presented in Table I.

TABLE I

RELATIVE RATES, ISOMER DISTRIBUTIONS AND PARTIAL RATE FACTORS FOR THE NITRATION OF TOLUENE AND *t*-BUTYLBENZENE

Reaction with Nitric Acid in Acetic Anhydride at 25°
Competitive Relative Rate $k_T/k_{t\text{-BuB}}$[a] 2.0 ± 0.3

	Toluene	*t*-Butylbenzene
	Product Distributions	
% *o*-	63.3 ± 2.8	10.3 ± 1.3
% *m*-	2.8 ± 0.8	10.3 ± 1.3
% *p*-	33.9 ± 2.3	79.4 ± 1.8
	Partial Rate Factors[b]	
o_f	46.5	3.8
m_f	2.1	3.8
p_f	48.5	57.7

Reaction with Nitric Acid in Nitromethane at 25°
Competitive Relative Rate $k_T/k_{t\text{-Bu}}$[c] 1.4 ± 0.1

	Toluene	*t*-Butylbenzene
	Product Distributions	
% *o*-	61.7 ± 3.0	12.2 ± 2.0
% *m*-	1.9 ± 0.5	8.2 ± 0.8
% *p*-	36.4 ± 3.0	79.6 ± 3.0
	Partial Rate Factors[d]	
o_f	38.9	5.5
m_f	1.3	3.7
p_f	45.8	71.6

[a] Calculated from expression derived by C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927). [b] Based on a toluene to benzene rate ratio of 23, ref. 8. [c] Estimated from ratio of products obtained. [d] Based on a toluene to benzene rate ratio of 21, ref. 8.

The three experimental examinations of the nitration reaction are in good agreement regarding the proportion of *ortho* and *para* isomers formed for each alkylbenzene.[5,6,8] Somewhat greater uncertainty is apparent for substitution in the *meta* position but the discrepancy between the two recent studies is minor. The relative rates examined in the three laboratories are also in essential agreement considering the various experimental approaches and the different conditions adopted for the experiments.

This investigation confirms the results of two previous studies and extends the work to a third reaction solvent. In summary, the partial rate factors obtained demonstrate $m_f^{t\text{-Bu}}$ to be greater than m_f^{Me} in agreement with the observations for other substitution reactions.[3] The results of this study together with the data of Norman and his associates[6] confidently establish $p_f^{t\text{-Bu}}/p_f^{\text{Me}}$ for nitration to be greater than 1.0. The value of the ratio is not dependent on the solvent and is 1.3 for reaction in acetic anhydride[6] at 0°; 1.2 for the same solvent at 25°; 1.2 in nitromethane at 25° and 1.3 for nitration in aqueous acetic acid[5] at 45°. The selectivity of the nitration reagent is not significantly influenced by the reaction medium.

The rates of chlorination of toluene and *t*-butylbenzene for reaction in the *para* position are, in contrast to the nitration results, in the Baker-Nathan order. This result is valid for chlorination in aqueous acetic acid, acetic anhydride, and nitromethane.[10] Accordingly it does not appear reasonable to identify the reversal in the nitration reaction broadly with a "solvent effect." The appearance of a Baker-Nathan effect is presumably associated with the detailed nature of the transition state for the substitution process. Further discussion of this point will be delayed until the full details of the chlorination study are available.[10]

EXPERIMENTAL

Materials. Toluene was fractionated and stored over drierite, n_D^{20} 1.4962. *t*-Butylbenzene (Phillips research grade) was used without further purification, n_D^{20} 1.4921. The nitrotoluenes purified by recrystallization (*para*, m.p. 51.5–52.0°) or by fractionation followed by recrystallization from the melt (*ortho*-n_D^{20}, 1.5460 and *meta*-, n_D^{20} 1.5469). The purity of the nitrotoluenes was checked by the examination of vapor phase chromatograms. Nitration of *t*-butylbenzene[11] yielded a mixture of isomers from which the *para* product was isolated by careful fractionation. Chromatographic analysis indicated the *p*-nitro-*t*-butylbenzene, n_D^{20} 1.5331, contained 2–3% of the *meta* isomer. In subsequent experiments utilizing this material as a reference allowance was made for the presence of the contaminant.

Acetic anhydride was fractionated through a glass packed column. Nitromethane (Eastman spectrograde) was fractionated in a glass column and dried over calcium sulfate, n_D^{20} 1.3829. Anhydrous nitric acid was prepared by a method previously described.[12]

Competitive reactions in acetic anhydride. Preliminary experiments demonstrated the reaction to be rapid as reported. Equimolar amounts of toluene and *t*-butylbenzene, 0.16 and 0.18*M* in duplicate experiments, were dissolved in the anhydride and the solution brought to thermal equilibrium. To this solution a reagent solution of nitric acid in acetic anhydride, 0.087 and 0.17*M* in the duplicate experiments, was rapidly added. The utilization of dilute solutions avoided the major temperature variations reported in earlier studies.[7,8,13] Seven days were allowed for the reaction to reach completion. The reaction mixture was quenched in aqueous carbonate and the anhydride hydrolyzed. The organic materials were extracted into methylene chloride and the extraction solvent stripped to provide the analytical sample. In view of the partial water solubility of the nitro compounds caution was exercised to insure a complete extraction.

Competitive reaction in nitromethane. The reaction of low concentrations of nitric acid with equimolar amounts of toluene and *t*-butylbenzene in dilute solutions of nitro-

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(10) Work in progress with Mr. Albert Himoe.

(11) D. Craig, *J. Am. Chem. Soc.*, **57**, 195 (1935).

(12) E. D. Hughes, C. K. Ingold, and R. J. Reed, *J. Chem. Soc.*, 2440 (1950).

(13) The nitric acid solution was prepared at 0°. It was faint yellow at 25° just prior to use.

methane proceeded only very slowly. To carry out the reaction it was necessary to adopt a large excess of nitric acid.[14] Reactions with 0.5 to 0.8 *M* aromatic and 2 to 4 *M* nitric acid were carried out over a 12-hr. interval. The analytical samples were obtained after treatment of the mixture with aqueous base and extraction into methylene chloride. The vapor phase chromatograms demonstrated the presence of residual aromatic and the absence of dinitrotoluenes. The relative rate was calculated on the basis of the relative amounts of nitrotoluenes to nitro-*t*-butylbenzenes rather than the more valid logarithmic expression. The error introduced by this approximation is minor for compounds differing only by a factor of two. In point of fact, the procedure adopted underestimates the relative rate by a maximum of 10%.

Analytical procedures. The vapor-phase chromatography method will not be detailed in view of the previous presentation of the procedure.[6] The methods utilized in the two laboratories were extraordinarily similar.

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(14) Experiments relating to this problem are reported by Ingold and Bird, ref. 7.

Cyanamide Derivatives. LIX.[1] Preparation and Polymerization of Alkylenedicyanamide[2]

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During the course of our studies on alkyl derivatives of cyanamide, an attempt was made to prepare alkylenedicyanamides. In regard to this problem, one patent,[3] which turned out to be erroneous, has been reported. In that patent, only hexamethylenedicyanamide was recorded as a viscous liquid having a boiling point of 150–155° at 50 mm.

It seemed to us that the synthesis of alkylenedicyanamides might be performed by the reaction of alkylenediamine with cyanogen halide[4] or by the reaction of alkylenedihalide with cyanamide. We chose the former route and succeeded in obtaining alkylenedicyanamides almost quantitatively.

In the method, an alcoholic solution of alkylenediamine was treated with a solution of cyanogen bromide in a mixture of ether and alcohol and the crystals of alkylenediamine dihydrobromide formed were filtered off. Concentration of the resulting solution followed by the addition of water gave alkylenedicyanamide crystals in a good yield. The crystals of hexa-, hepta-, octa-, nona-, and decamethylenedicyanamide were successfully prepared by this method.

These compounds have relatively low melting points and are soluble in alcohol and acetone, but sparingly soluble in water, ether or benzene. To keep them unchanged for a long time, it may be better to preserve them in a cooled place, preferably in the refrigerator.

It is very interesting to note that the alkylenedicyanamides produced transparent insoluble-infusible homopolymers when they were polymerized with each other. It is thought that these polymers may have the structure of polydicyandiamide or polymelamine, probably the former. They were found to be very useful in the manufacture of adhesives, films, fibers, and other plastics. We also found that alkylenedicyanamides could be copolymerized with alkylenediamines to obtain ion exchange resins which may have the structure of polyguanidine.

EXPERIMENTAL[5]

Hexamethylenedicyanamide. A solution of 11.0 g hexamethylenediamine (0.095 mole) in 33 cc. of isopropyl alcohol was added dropwise with stirring to a solution of 10.6 g. of cyanogen bromide (0.10 mole) in a mixture of 35 cc. of ether and 32 cc. of isopropyl alcohol, keeping the temperature at 5–10°. The reaction was almost completed[6] after the last portion of hexamethylenediamine solution had been added. The crystals of hexamethylenediamine dihydrobromide formed were filtered off and washed with isopropyl alcohol. The filtrate combined with the wash was concentrated at diminished pressure below a temperature of 50°. The resulting concentrate was added gradually with stirring in 30 cc. of water and then cooled with ice, resulting in the separation of the crystals of hexamethylenedicyanamide almost completely.[7] The crystals were filtered, washed with cold water and dried in a vacuum desiccator. Yield 7.0 g., 89%, m.p. 61–63°. After recrystallization from alcohol, the melting point rose to 64–65°.

Anal. Calcd. for $C_8H_{14}N_4$: C, 57.80; H, 8.49; N, 33.71. Found: C, 57.82; H, 8.71; N, 33.71. Mol. wt., Calcd.: 166. Found: 163, 170 (cryoscopic in *tert-butyl alcohol*).

An infrared spectrum indicated a very distinct adsorption at 2200 cm.$^{-1}$, pointing to the presence of nitrile group. It also indicated the presence of imino group bands at 3220–3240 cm.$^{-1}$ and of methylene group bands at 2920, 2860, 1470, and 740 cm.$^{-1}$

Identity was further confirmed by converting it to hexamethylenediurea by hydrolysis with acid, m.p. 197–198°.

Hepta-, octa-, nona-, and decamethylenedicyanamide were prepared by the same procedure. The yields, melting points and nitrogen analyses for these compounds are listed in Table I.

Polymerization. The crystals of alkylenedicyanamides (hexa-, hepta-, octa-, nona-, or deca-) were once melted and then kept in molten state at a suitable temperature.[8] A transparent glassy mass resulted which was infusible and insoluble

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(1) Part LVIII, K. Shirai and K. Sugino, *J. Org. Chem.*, **25**, 1046 (1960).

(2) This paper was prepared for delivery before the annual meeting of the Chemical Society of Japan held on Apr. 1960.

(3) H. Dreyfus, British Pat. **549,368**, Nov. 18, 1942. [*Chem. Abstr.*, **38**, 878 (1944)]; U. S. Pat. **2,349,851**, May 30, 1944 [*Chem. Abstr.*, **39**, 1174 (1945).]

(4) For monofunctional cyanamides, see R. Kitawaki, M. Yamashita, and K. Sugino, *J. Chem. Soc. Japan* (Pure Chem. Sec.), **78**, 567 (1957).

(5) All melting points are uncorrected.

(6) At the end of the reaction, the resulting mixture should be kept slightly acidic.

(7) In the cases of hepta- and nonamethylenedicyanamide, the rates of crystallization were very slow.

(8) Attention is required to keep the reaction temperature at a desired range (for example: 50–55° for hexa-) by preventing spontaneous heat evolution.