butyl-2-cyclohexen-1-one (29),[33] and 6% 6-methyl-6-*n*-butyl-2-cyclohexen-1-one (30).[34] Column chromatography gave 1.2 g of a mixture of the two enones; this corresponds to a yield of 74% 29 and 6% 30.

Oxidation of 4,4-Diphenyl-1-cyclohexene (31).—Following the procedure used for 9, 4.5 g (0.02 mol) of 4,4-diphenyl-1-cyclohexene (31)[35] and 35 g (0.135 mol) of CrO_3–(pyridine)$_2$ complex gave 4.38 g of a viscous oil. Chromatography on silica gel yielded 2.46 g of starting olefin, 1.46 g (67%) of 4,4-diphenyl-2-cyclohexen-1-one[36] (33), and 0.27 g (13%) of 5,5-diphenyl-2-cyclohexen-1-one[37] (32).

Oxidation of 1-Phenyl-1-cyclohexene (34).—Following the procedure used for 9, 3.12 g (0.02 mol) of 1-phenyl-1-cyclohexene (34) and 55 g (0.21 mol) of CrO_3–(pyridine)$_2$ complex afforded 2.82 g of a viscous brown oil. Column chromatography gave 1.0 g of starting olefin and 1.65 g (71%) of 3-phenyl-2-cyclohexen-1-one (35) which was recrystallized from ethanol, mp 61–64° (lit.[38] mp 61–62°).

Oxidation of 3-(*p*-Fluorophenyl)-1-cyclohexene (36).—Following the procedure used for 9, 1.75 g (0.01 mol) of 3-(*p*-fluorophenyl)-1-cyclohexene (36)[39] and 55 g (0.21 mol) of CrO_3–(pyridine)$_2$ complex gave 1.43 g of a brown oil. Column chromatography afforded 0.68 g of starting material and 0.97 g (84%) of 3-(*p*-fluorophenyl)-2-cyclohexen-1-one (37): nmr (δ, ppm), 7.5 (2 H, multiplet), 7.0 (2 H, multiplet), 6.1 (1 H, triplet, J = 1 cps), 2.65 (2 H, multiplet), 2.25 (4 H, multiplet); mass spectrum, 190 (parent peak).

Oxidation of 1-Methyl-1-cyclopentene (38).—Following the procedure used for 9, 2.46 g (0.03 mol) of 1-methyl-1-cyclopentene (38) and 55 g (0.21 mol) of CrO_3–(pyridine)$_2$ complex afforded 1.73 g of a yellow liquid. Column chromatography gave 1.52 g of a mixture of two unsaturated ketones, shown by vpc analysis to be present in the ratio of 3.5:1. These values correspond to a yield of 41% 3-methyl-2-cyclopenten-1-one (39)[40] and 12% 2-methyl-2-cyclopenten-1-one (40).[41]

Oxidation of Allylbenzene (41).—Following the procedure used for 9, 2.4 g (0.02 mol) of allylbenzene and 35 g (0.135 mol) of CrO_3–(pyridine)$_2$ complex gave 1.95 g of a crude reaction product. Analysis by vpc showed the presence of 45% starting material and 55% cinnamaldehyde (63%).

Registry No.—1, 2099-26-5; 3, 604-35-3; 5, 570-74-1; 7, 20479-02-1; 9, 80-56-8; 11, 138-86-3; 14, 591-49-1; 17, 591-48-0; 19, 110-83-8; 21, 3856-25-5; 24, 14072-86-7; 28, 21544-97-8; 31, 21544-98-9; 34, 771-98-2; 36, 21545-08-4; 38, 693-89-0; 41, 300-57-2; chromium trioxide–pyridine complex, 20492-50-6.

Acknowledgment.—The authors are indebted to Dr. R. Teranishi for his interest and assistance in this study.

(33) The spectral properties were as follows: mass spectrum 166 (parent peak); ν_{max} 1680, 1625 cm^{-1}; nmr (δ, ppm), 6.28 (1 H, doublet, J = 10 cps), 5.85 (1 H, doublet, J = 10 cps), 1.3–2.3 (4 H, multiplet), 1.2 (6 H, broad peak), 1.1 (3 H, singlet), 1.0 (3 H, multiplet).

(34) The spectral properties were as follows: mass spectrum, 166 (parent peak); ν_{max} 1682 cm^{-1}.

(35) The starting olefin was prepared by Wolff–Kishner reduction of 4,4-diphenyl-2-cyclohexen-1-one (W. A. Spitzer, unpublished results).

(36) E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

(37) The spectral properties were as follows: ν_{max} 1665, 1559 cm^{-1}; mass spectrum, 248 (parent peak); nmr (δ, ppm), 7.15 (10 H, singlet), 6.75 (1 H, multiplet), 5.9 (1 H, doublet of triplets), 3.1 (4 H, multiplet).

(38) D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 517 (1951).

(39) The olefin was kindly supplied by Richard J. Shavitz and was prepared by coupling of *p*-fluorobromobenzene and 3-cyclohexenyl-1-magnesium bromide [A. Berlande, *Compt. Rend.*, **213**, 437 (1941)].

(40) R. M. Acheson and E. R. Robeinson, *J. Chem. Soc.*, 2127 (1952).

(41) G. Singh, *J. Amer. Chem. Soc.*, **78**, 6109 (1956).

The Condensation of Internal Olefins with Paraformaldehyde and Hydrogen Chloride

PAUL R. STAPP AND DAVID S. WEINBERG

Phillips Petroleum Company, Bartlesville, Oklahoma 74003

Received December 3, 1968

The condensation of *cis*- and *trans*-2-butene with paraformaldehyde and hydrogen chloride at −65° gives predominantly the diastereomeric and chloro alcohols, *threo*-3-chloro-2-methyl-1-butanol and *erythro*-3-chloro-2-methyl-1-butanol, respectively, with 80–90% isomeric purity. The structures of the products were established by a nuclear magnetic resonance study.

In a previous article[1] we have described a novel modification of the Prins reaction in which 1 olefins are condensed with paraformaldehyde and hydrogen halides at low temperatures to give good yields of 3-alkyl-4-halotetrahydropyrans. Extension of this modified Prins reaction to include the condensation of 2-butenes with paraformaldehyde and hydrogen chloride at −65° is described in this report. In contrast to the 1-olefin reactions, the principal products were found to be a mixture of chloro alcohols and their formals (45–60% yield). Small amounts of alkylchlorotetrahydropyrans and uncharacterized 1,3-dioxanes were formed as by-products.

It has been previously demonstrated that conventional Prins reactions of cyclohexenes proceed exclusively with *trans*[2,3] diaxial[4] addition, but condensation of *trans*- and *cis*-4-octene with formaldehyde was stereoselective only for the *trans* isomer under the conditions employed.[5] To determine the stereochemistry in our modification of the Prins reaction, *trans*- and *cis*-2-butene were condensed separately with paraformaldehyde and hydrogen chloride at −65°. Distillation of the reaction mixtures gave, after removal of the lower boiling dioxanes and chlorotetrahydropyrans, mixtures of chloro alcohols and formals in proportions dependent on the olefin/formaldehyde molar ratio. Treatment of these mixtures with methanol and hydrochloric acid to hydrolyze the formals produced two diastereomeric chloro alcohols which were indistinguishable by glpc, but which were determined to be of high isomeric purity by nuclear magnetic resonance (nmr) analysis (Chart I). If the chloro alcohols are formed by *trans* addition in this system, then *trans*-2-butene would produce *erythro*-3-chloro-2-methyl-1-butanol and

(1) P. R. Stapp, *J. Org. Chem.*, **34**, 479 (1969).

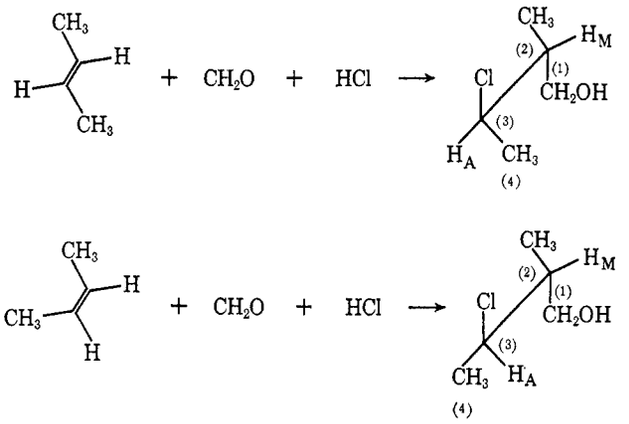
(2) E. E. Smissman and R. A. Mode, *J. Amer. Chem. Soc.*, **79**, 3447 (1957).

(3) A. T. Blomquist and J. Wolinsky, *ibid.*, **79**, 6025 (1957).

(4) E. E. Smissman and D. T. Witiak, *J. Org. Chem.*, **25**, 471 (1960).

(5) N. A. LeBel, R. N. Liesemer, and E. Mehmedbasich., *ibid.*, **28**, 615 (1963).

CHART I



cis-2-butene would give the diastereomeric *threo*-3-chloro-2-methyl-1-butanol; that this was indeed the case was determined by a nmr study of the isomeric alcohols.

The configurations of the two diastereoisomers were assigned on the basis of the relative values of the coupling constants between the H_A and H_M protons. A first-order analysis of the nmr spectrum of the isomer obtained from *trans*-2-butene yields J_{AM} = 3.0 Hz. The spectrum of the isomer obtained from *cis*-2-butene is more difficult to analyze because of overlapping peaks, but irradiation of the C-4 methyl group in a double-resonance experiment collapses the peak produced by H_A to a doublet and yields J_{AM} = 6.5 Hz.

The diastereomer which has the larger population of conformers with *gauche* protons will exhibit the smaller coupling constant because protons in *gauche* conformations exhibit smaller coupling constants than those in *anti* conformations.[6,7]

Consideration of nonbonded interactions in the rotational isomers of *erythro*-3-chloro-2-methyl-1-butanol (Chart II), where the substituents are designated as small (S), medium (M), and large (L) suggests that conformers **1b** and **1c** would be more stable than **1a**.[8] In addition, intramolecular hydrogen bonding between the hydroxymethyl group and the *gauche* chlorine atom in **1b** and **1c** would lead to enhanced stability of these isomers.[9] Similar considerations suggest that conformer **2c** of the *threo* isomer would be more stable than **2a** or **2b**.

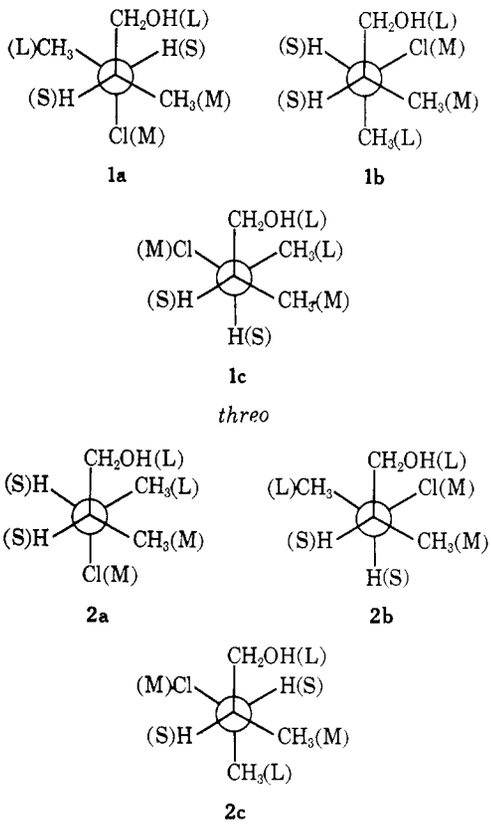
Since the protons are *gauche* in **1b** and **1c** and *anti* in **2c**, and the difference of the coupling constants is large, the diastereomer obtained from *cis*-2-butene must have the *threo* configuration and that from *trans*-2-butene must have the *erythro* configuration.[10]

Analysis of the methyl region in the nmr spectrum of each isomer indicates that the methyl protons have slightly different chemical shifts in the two compounds and that each compound is contaminated by an estimated 10–20% of its diastereoisomer. However,

CHART II

STAGGERED ROTATIONAL ISOMERS OF THE DIASTEREOMERIC 3-CHLORO-2-METHYL-1-BUTANOLS

erythro



threo

the sharp melting points of the crystalline 3,5-dinitrobenzoate esters are improved very little by repeated recrystallization, and this suggests that isomeric purity is in the upper end of this range.

The nature of the by-products in each reaction was investigated briefly. The presence of minor amounts (<5%) of a mixture of 1,3-dioxanes was deduced both from the earlier identification of 1,3-dioxanes from 1-alkenes[1] as well as comparison of infrared spectra of enriched fractions with those of several alkyl-1,3-dioxanes available as standards. No attempt was made, however, to identify the various isomers. Gas chromatographic analysis of the chloro ether fraction from each reaction showed it to consist of three (and possibly four) isomers, having infrared spectra similar to the spectra of 3-alkyl-4-chlorotetrahydropyrans. Sodium and methanol reduction of the isomeric chlorotetrahydropyran mixture from both *cis*- and *trans*-2-butene afforded 3-methyltetrahydropyran in greater than 95% purity in each case. Pure samples of *cis*- and *trans*-4-chloro-3-methyltetrahydropyran were obtained by preparative gas chromatography of the *cis–trans* mixtures from 1-butene[1] and identified by application of the von Auwers–Skita rules[11] and their nmr spectra (see Experimental Section). Comparison of the pure samples with the mixtures obtained from both *cis*- and *trans*-2-butene established that in each case the *trans–cis* isomer ratio was about 4:1. The structure of the other isomers reducible to 3-methyltetrahydropyran remains uncertain.

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 381.

(7) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Engelwood Cliffs, N. J., 1965, p 117.

(8) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., p 13.

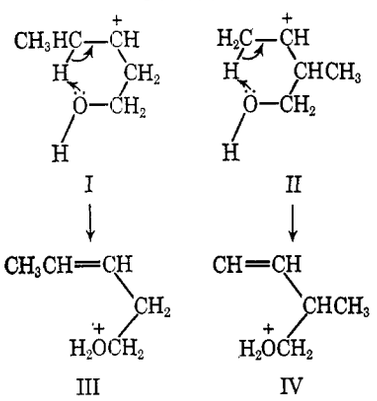
(9) Reference 6, p 18.

(10) C. A. Kingsbury and W. B. Thornton, *J. Org. Chem.*, **31**, 1000 (1966), provides a more detailed discussion of this general technique.

(11) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1707 (1950).

In consideration of explanations to account for the difference in product ratios (*e.g.*, cyclics or chloro alcohols) from 1 olefins and internal olefins, some hypothesis must be proposed which would rationalize a difference in either electronic factors in the transition state or relative thermodynamic stabilities of the product. If the assumption that 4-chlorotetrahydropyrans are formed from homoallylic alcohols generated by a cyclic deprotonation is correct,[1] the respective intermediates from 1-butene and 2-butene would be as depicted in Chart III. It is immediately obvious that

CHART III



chloro alcohols are not produced by hydrogen chloride addition to the homoallylic alcohol. If such were true, III would undoubtedly lead to mixtures of 3- and 4-chloro-1-pentanols, and IV would form 3-chloro-2-methyl-1-butanol with complete loss of stereochemical integrity. The observed high degree of stereospecificity implies either that, in a stepwise reaction, the charged intermediate must be associated (as in an ion pair) in such a manner as to retain its geometry or that a concerted reaction is involved. Again, the most puzzling aspect of the modified Prins reaction is why the formation of cyclics from 2-butenes is unfavorable. On the surface it might appear that deprotonation of II to IV, a thermodynamically less stable terminal olefin, would not be favorable; however, this cannot be the sole factor since the condensation of propylene, paraformaldehyde, and hydrogen chloride gives primarily 4-chlorotetrahydropyran *via* intermediate 3-buten-1-ol. At the present time not enough information is available to decide whether the inductive effect alone of the α-methyl group would influence chloride ion capture by II to the extent actually observed.

Experimental Section[12]

Reaction of *trans*-2-Butene with Paraformaldehyde and Hydrogen Chloride.—Dry hydrogen chloride was introduced into a mixture of 62 g (2.0 mol) of 97% paraformaldehyde, 84 g (1.5 mol) of *trans*-2-butene, and 200 ml of methylene chloride at −65° for 2 hr and the reaction mixture was allowed to warm to room temperature overnight. The methylene chloride solution was washed with water and sodium bicarbonate solution, dried ($MgSO_4$), and filtered, and the solvent was removed. The residue was fractionated through an efficient column to give 5.6 g of 1,3-dioxane mixture, bp 25–51° (18 mm), 40.3 g of methylchlorotetrahydropyran mixture, bp 51–68° (15 mm), and 89.6 g, bp 68° (15 mm) to 115° (1 mm), of a mixture of chloro alcohol and formal. Additional large-scale experiments using 4 mol of paraformaldehyde and 2.5–3.5 mol of olefin gave chloro alcohol/formal yields ranging from 45 to 60%.

Isolation of *erythro*-3-Chloro-2-methyl-1-butanol.—The chloro alcohol–formal mixture above was refluxed for 3 hr with 400 ml of methanol and 20 ml of concentrated hydrochloric acid. After isolation *via* dilution and ether extraction, the product was distilled to give 62.7 g of chloro alcohol, bp 80–83° (15 mm), $n^{20}D$ 1.4510.

Anal. Calcd for $C_5H_{11}ClO$: C, 49.0: H, 9.0 Found: C, 49.2; H, 8.9.

The 3,5-dinitrobenzoate ester was obtained as colorless platelets, mp 93–94°, after two recrystallizations from 95% ethanol.

Anal. Calcd for $C_{12}H_{13}ClN_2O_6$: C, 45.5; H, 4.1; N, 9.0. Found: C, 45.4; H, 4.2; N, 8.8.

Reaction of *cis*-2-Butene with Paraformaldehyde and Hydrogen Chloride.—The reaction was performed as before using an identical quantity of *cis*-2-butene. There was obtained 2.8 g of 1,3-dioxane mixture, bp 27–54° (18 mm), 43.0 g of methylchlorotetrahydropyran mixture, bp 50–68° (15 mm), and 78.7 g of chloro alcohol–formal, bp 41–132° (3 mm).

Isolation of *threo*-3-Chloro-2-methyl-1-butanol. Methanolysis of the chloro alcohol–formal mixture gave 58.6 g of chloro alcohol, bp 78–83° (15 mm), $n^{20}D$ 1.4520.

Anal. Calcd for $C_5H_{11}ClO$: C, 49.0; H, 9.0. Found: C, 49.3; H, 9.0.

The 3,5-dinitrobenzoate after three recrystallizations from heptane melted at 61–62°.

Anal. Calcd for $C_{12}H_{13}ClN_2O_6$: C, 45.5; H, 4.1; N, 9.0. Found: C, 45.6; H, 4.1; N, 8.9.

Sodium and Methanol Reduction of Methylchlorotetrahydropyran By-products from *trans*-2-Butene.—Treatment of 45.9 g (0.34 mol) of cyclic chloride mixture in 250 ml of methanol with 39.1 g (1.7 g-atoms) of sodium gave a 55% yield of product, bp 105–110°. Glpc analysis on a 10-ft Ucon column operated isothermally at 100° showed this material to contain greater than 95% 3-methyltetrahydropyran. A similar reduction of the cyclic by-products from *cis*-2-butene gave essentially identical results.

Synthesis of 3-Methyltetrahydropyran.—2-Methyl-1,5-pentanediol was prepared in 70% yield by lithium aluminum hydride reduction of diethyl 2-methylglutarate according to the procedure for preparation of 2-*n*-amyl-1,5-pentanediol.[1] Cyclodehydration of the diol with 85% phosphoric acid[13] gave an 80% yield of 3-methyltetrahydropyran, bp 106–107°, $n^{20}D$ 1.4210 (lit.[14] bp 109°, $n^{20}D$ 1.4210).

***cis*-4-Chloro-3-methyltetrahydropyran and *trans*-4-Chloro-3-methyltetrahydropyran.**—These were separated in greater than 99% purity by preparative gas chromatography on a 40 ft × 0.75 in Ucon column at 150° with the lower boiling *trans* isomer eluting first. The nmr spectra of both isomers were consistent with the 4-chloro-3-methyltetrahydropyran structure. A quartet centered at τ 5.6 in the higher boiling isomer was assigned to the proton α to the chlorine atom. The other isomer gave a complex spectrum in the region between τ 5.9 and 7.3 which corresponded to a total of five protons. The proton α to the chlorine necessarily falls within this region; therefore, a difference in chemical shift of at least τ 0.3 must exist for these protons in each isomer. It has been established previously[15] that an equatorial proton α to a chlorine in a six-membered ring occurs at lower field by τ 0.3–0.5 than the corresponding axial proton. The lower field chemical shift observed for the proton α to the chlorine in the higher boiling isomer suggests a conformational distribution that has a higher equatorial contribution than does the lower boiling isomer. Inspection of the chair conformers available to each isomer suggests that in the *trans* isomer this proton is axial, while in the *cis* isomer an equilibrium distribution between axial and equatorial positions is probable. Thus, the lower

(12) All melting and boiling points are uncorrected. Olefins used were Phillips Petroleum Co. Pure Grade materials. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. Glpc analyses were carried out on a Perkin-Elmer Model 720 gas chromatograph using a 10 ft × 0.25 in column of 20% Ucon LB-550-X on Chromosorb P. Nmr data were obtained on a Varian Model A-60 spectrometer in carbon tetrachloride with tetramethylsilane as an internal standard. The nmr measurements on the diastereomeric 3-chloro-2-methyl-1-butanols were made on neat liquids; the spin decoupler employed in the double-resonance experiment was constructed in these laboratories by Dr. R. Bayer and Mr. F. L. Tilley.

(13) J. Colonge and R. Marey, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 350.

(14) E. Hanschke, *Chem. Ber.*, **88**, 1043 (1956).

(15) R. V. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **80**, 6098 (1958).

boiling isomer is the *trans* compound. The chemical shifts of both methine protons in the *cis* isomer are found at lower field.

Registry No.—Hydrogen chloride, 7647-01-0; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *erythro*-3-chloro-2-methyl-1-butanol, 21430-05-7; 3,5-dinitrobenzoate ester of *erythro*-3-chloro-2-methyl-1-butanol, 21430-06-8; *threo*-3-chloro-2-methyl-1-butanol, 21430-07-9; 3,5-dinitrobenzoate ester of *threo*-3-chloro-2-methyl-1-butanol, 21430-08-0; *cis*-4-chloro-3-methyltetrahydropyran, 18755-76-5; *trans*-4-chloro-3-methyltetrahydropyran, 18755-77-6.

Acknowledgments.—We wish to thank Mrs. Joy Buell for recording the nmr spectra, Mr. F. L. Tilley for carrying out the double-resonance experiments, and Mr. C. G. Long for carrying out the preparative gas chromatographic separations.

Substituent Effects on the Reactivity of Arynes. Product Distributions as an Index of Relative Reactivities of Arynes in Methylamine and Dimethylamine Solvents[1a]

EDWARD R. BIEHL, EDWARD NIEH,[1b] AND K. C. HSU[1b]

Department of Chemistry, Southern Methodist University, Dallas, Texas 75222

Received April 1, 1969

The competition between the anion of acetonitrile and methyl- or dimethylamine for various substituted arynes has been studied. The product distribution, per cent amine/per cent nitrile, was found to increase in all cases as the substituent was varied along a series, H, CH_3, OCH_3, Cl, and F, with a more marked increase in the product distribution being observed for 3-arynes than for 4-arynes. In addition, a linear free-energy relationship has been found between the log $(\%\ \text{amine}/\%\ \text{nitrile})_G/(\%\ \text{amine}/\%\ \text{nitrile})_H$, where the subscripts G and H represent the substituted and unsubstituted benzyne intermediates, respectively, and the absolute value of the polar substituent constant, σ'. Therefore, it is concluded that both +I and −I substituents destabilize arynes by inductively polarizing the "triple bond" of benzyne.

There is ample evidence that the highly reactive aryne intermediates do possess some degree of selectivity.[2] For example, arylation of anions of active hydrogen compounds by phenyl halides occurs in high yields even though the reactions are carried out in the presence of amide ion and a large excess of the nucleophilic solvent, ammonia.[3] However, only one study on substituent effects on aryne selectivities has been reported.[4] In that investigation, the selectivities of 3-substituted benzynes were determined by studying the relative rates of addition of phenyllithium *vs.* lithium piperidide to the arynes in ether. The results indicated that −I (electron withdrawing by induction) substituents [OCH_3, $N(CH_3)_2$, and CF_3], by facilitating nucleophilic addition, decreased the selectivity of the aryne intermediate. By contrast, the +I (electron releasing by induction) substituent (CH_3), by retarding nucleophilic addition, increased the selectivity of the aryne intermediate. Experimental data concerning effects of 4 substituents on aryne selectivities were not reported. Recently, Zoltewicz and Bunnett[5] have obtained indirect evidence that the 4-methyl substituent may actually decrease the stability of the aryne intermediate generated not in ether but in liquid ammonia by the action of potassium amide on 4-chlorotoluene-3-*d*.

During the course of our investigation of the extension of the general aryne–carbanion arylation reaction, initiated by sodium amide in liquid ammonia, we have noted that the yields of arylated carbanions gradually decreased with a gradual increase in the yields of arylated amines as the substituent of the substituted phenyl halide was varied along the series H, CH_3, OCH_3, and Cl.[6] It has been demonstrated[7] that the predominant amine nucleophile in sodium amide initiated aryne reactions is the solvent molecule, ammonia. These results, therefore, indicate that the gradual increase in the amine yield with the above substituent variation was due to a gradual increase in the reactivity of the aryne intermediate toward the less reactive but more abundant ammonia molecule as compared with the carbanions.

Accordingly, the product distribution should serve as a measure of the influence of substituents on aryne reactivity. Therefore, a systematic study of the product distributions obtained from competition between carbanions and ammonia for various arynes was initiated.

Quantitative determinations of product distributions obtained from aryne reactions carried out in liquid ammonia were hampered by the formation of polyarylated amine and acetonitrile compounds. More recently, Hsu[8] has observed that the competition reactions between acetonitrile anion and the solvent, methyl- or dimethylamine, for various arynes (generated from the corresponding haloaromatic compound and sodium amide) yielded predominantly monoarylated products (80–90%) with only small amounts (10–20%) of polyarylated product being formed. Quantitative material balances, however, were not attempted in that study.

This paper reports on the study of the quantitative determinations of the various product distributions

(1) (a) Supported in part by Grant No. N-118 from the Robert A. Welch Foundation, Houston, Texas; (b) Robert A. Welch Predoctoral Fellows.

(2) R. W. Hoffman, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, pp 246–250.

(3) For reviews, see J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); H. Heaney, *Chem. Rev.*, **62**, 81 (1962).

(4) R. Huisgen, W. Mack, and L. Mobius, *Tetrahedron*, **9**, 29 (1959); R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(5) J. A. Zoltewicz and J. F. Bunnett, *J. Amer. Chem. Soc.*, **87**, 2640 (1965).

(6) Unpublished results.

(7) E. R. Biehl, E. Nieh, H. Li, and C. Hong, *J. Org. Chem.*, **34**, 500 (1969).

(8) K. C. Hsu, Master's Thesis, Southern Methodist University, 1967.