

in 2,2,5-trimethylhexane was treated with 17.0 ml. (0.12 mole) of triethylborane at 19–33°. The mixture was stirred at room temperature for 1.5 hours, then warmed to 65° for 0.5 hour. The solids were filtered from the cooled mixture and washed with several small portions of diethyl ether. The solvents were distilled from the combined filtrates at 100–110° and 0.2 mm. to give clear, viscous, liquid sodium *n*-butyltriethylboron which did not solidify on cooling to room temperature.

Anal. Calcd. for $C_{10}H_{14}BNa$: B, 6.09; Na, 12.91. Found: B, 6.10; Na, 14.30.

Sodium *n*-butyltriethylboron was also prepared from 1-chlorobutane, sodium and triethylborane in diethyl ether. The procedure was the same as for the ethyl chloride route to sodium tetraethylboron. The yield of $NaB(n-C_4H_9)(C_2H_5)_3$ was 75%.

Anal. Calcd. for $C_{10}H_{14}NBa$: B, 6.09; Na, 12.91. Found: B, 6.10; Na, 12.90.

Sodium *n*-Octyltriethylboron.—Sodium triethylborohydride (from 0.15 mole of sodium hydride and 0.18 mole of triethylborane) in diglyme was treated at room temperature with 24.2 g. (0.22 mole) of octene-1. The solution was refluxed for 2 hours, then cooled. Unconsumed octene (10.4 g., 43.0%) was distilled out. The excess triethylborane and diglyme were removed at reduced pressure to give a viscous oil which was a diglyme etherate of sodium *n*-octyltriethylboron, $NaB(n-C_8H_{17})(C_2H_5)_3 \cdot C_6H_{14}O_2$. The identity of this compound was confirmed by its chemical behavior.

Anal. Calcd. for $C_{20}H_{40}BNa_3$: Na, 6.24. Found: Na, 5.83.

Sodium Phenyltriethylboron.—Sodium sand (4.6 g., 0.2 g. atom) and 200 ml. of diethyl ether were stirred vigorously. Slowly, 11.2 g. (0.1 mole) of chlorobenzene and 15.0 ml. (0.1 mole) of triethylborane in 50 ml. of ether were added. The mixture was stirred for 1.5 hours and the solids were filtered off. The filtrate was evaporated at reduced pressure (finally at 100° and 1 mm. for 3.5 hours) to give solid, pale yellow sodium phenyltriethylboron. The identity was confirmed by its chemical behavior.

Anal. Calcd. for $C_{12}H_{20}BNa$: Na, 11.61. Found: Na, 12.10.

Disproportionation of Sodium Triethylborohydride.—A solution of 0.1 mole of sodium triethylborohydride was prepared in 50 ml. of diglyme and 20 ml. of diethyl ether. Distillation to a pot temperature of 50° at 10 mm. removed the ether and the excess triethylborane. The vacuum was broken with nitrogen. The solution was heated to a gentle reflux (169–171°) and there maintained for 2 hours. After the solution had cooled, water was added cautiously. Mass spectrometer analysis of the evolved gas showed that it was nearly pure hydrogen. The hydrolysis mixture was acidified with dilute hydrochloric acid to liberate hydrogen and ethane in approximately equal amounts. An unknown

quantity of the ethane remained dissolved in the hydrolysis solution.

Tetraethyllead. Method A.—At room temperature, 4.8 g. (0.12 mole) of sodium tetraethylboron in 100 ml. of water was added to 19.5 g. (0.06 mole) of lead acetate in 150 ml. of water with stirring. The addition was complete in 30 minutes. The mixture became dark as metallic lead separated. Gradually the lead agglomerated and two liquid phases could be observed. After an additional 30 minutes, 150 ml. of hexane was added, followed by 100 ml. of 10% aqueous potassium hydroxide. The organic phase was separated and extracted with two 50-ml. portions of hydroxide solution. The residual hexane solution was diluted to 250 ml. Analysis¹⁴ showed the tetraethyllead yield was 96.5%.

Method A-1.—The reaction procedure was the same except that potassium hydroxide was not used to separate the triethylborane. Instead the hexane phase was separated and the borane was distilled from it at reduced pressure (b.p. 56–57° at 220 mm.). Analysis of the residue showed an 85% yield of tetraethyllead.

Method B.—The reaction flask was equipped with a 6-inch Vigreux column and downward-directed condenser for distillation at reduced pressure. To a suspension of 13.4 g. (0.06 mole) of lead oxide and 100 ml. of water was added, with stirring, 18.75 g. (0.125 mole) of sodium tetraethylboron in 100 ml. of water. The pressure in the system had been reduced to 220 mm. and the oxide suspension had been heated to 80° prior to the addition. The addition rate was controlled so as to be approximately equal to the distillation rate. After a total reaction time of 45 minutes the mixture was allowed to cool and was returned to atmospheric pressure with nitrogen. The organic phase of the distillate was separated and diluted with 2,2,5-trimethylhexane. Triethylborane (51%) was distilled out at reduced pressure. The residual material was combined with a 2,2,5-trimethylhexane extract of the reaction flask contents. Analysis showed a 72% yield of tetraethyllead.

Method C.—The procedure was the same as that in method B except that the reaction was carried out at atmospheric pressure. The temperature was about 100°.

Acknowledgments.—The authors wish to thank Professor H. C. Brown of Purdue University and Dr. E. C. Ashby of this Laboratory for their suggestions. They also express their appreciation to Dr. R. P. Curry for infrared data, J. B. Chidester for mass spectrometric gas analysis, and the following members of the Analytical Group: R. A. Ashby, Ann K. Breaux, V. H. Dayan, W. J. Easley, J. W. Figgins, S. R. Henderson, J. L. Russell and G. Z. Smith.

(14) M. E. Griffing, A. Rozek, L. J. Snyder and S. R. Henderson, *Anal. Chem.*, **29**, 190 (1952).

[CONTRIBUTION FROM THE DIAMOND ALKALI CO. RESEARCH DEPARTMENT, PAINESVILLE, OHIO]

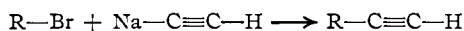
A Novel Synthesis of Polyacetylenes¹

BY JOHN H. WOTIZ, ROBERT F. ADAMS AND CHARLES G. PARSONS

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Novel non-conjugated, linear and cyclic polyacetylenes were prepared in a simple manner by the reaction of α,ω -dihalides with mixtures of mono- and disodium acetylides. Some physical and thermal properties are described.

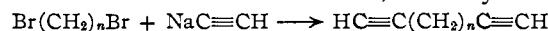
The alkylation of monosodium acetylide, $Na-C\equiv C-H$, with alkyl bromides in liquid ammonia is well known.² The reaction also proceeds in organic



(1) Presented in part at the 136th Meeting of the American Chemical Society, Sept. 1959, Atlantic City, N. J., Abstracts p. 91-P.

(2) T. L. Jacobs, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 1–78, and references therein.

solvents of high dielectric constant such as dimethylformamide.^{3,4} In this manner α,ω -dibromides were also converted to α,ω -diacetylenes^{2,3}



A "one-step" synthesis of dialkylacetylenes was described by Bried and Hennion⁵ who treated NaC

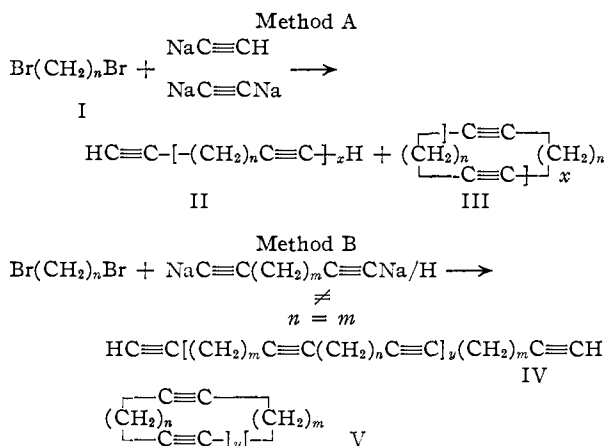
(3) M. Kracht and H. Pasdach, German Patent 944,311 (1956).

(4) T. F. Rutledge, U. S. Patent 2,846,491 (1958).

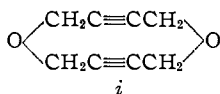
(5) E. A. Bried and G. F. Hennion, *THIS JOURNAL*, **59**, 1310 (1937).

$\equiv\text{CH}$, NaNH_2 and RBr , in the molar ratio of 1:1:2, simultaneously in liquid ammonia. They attributed the success of this reaction to the difference in solubility between sodium acetylide and sodamide, and the great reactivity of monoalkylacetylenes toward sodamide. An alternate explanation would consider the presence and alkylation of disodium acetylide, $\text{Na}-\text{C}\equiv\text{C}-\text{Na}$. This was verified by Henne and Greenlee⁶ who prepared 3-hexyne in 75% yield.

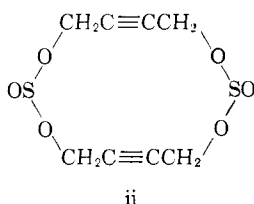
The present paper deals with the reaction of a mixture of mono- and disodium acetylides with α,ω -dibromides (I) and the preparation of non-conjugated linear (II, IV) and cyclic (III, V) polyacetylenes.



The preparation of non-conjugated polyacetylenes has received only scant attention. Lespieau treated "dimagnesium of acetylene"⁷ with *sym*-dichlorodimethyl ether and reported a minute quantity of



From the reaction of butynediol and thionyl chloride, Reppe⁸ isolated



There is only one report of a preparation of a carbocyclic polyacetylene containing nonconjugated triple bonds; this is by Cram and Allinger⁹ who prepared 1,7-cyclododecadiyne (III) ($n = 4$, $x = 1$), m.p. 37° , in a seven-step synthesis in less than 1% over-all yield. A linear polyacetylene, hexadecatriyne-5, 8, 11, was described,^{10a} and linear poly-

(6) A. Henne and K. Greenlee, *THIS JOURNAL*, **67**, 484 (1945); K. Greenlee, Ph.D. Dissertation, Ohio State University, 1942.

(7) M. Lespieau, *Compt. rend.*, **188**, 502 (1929); *C. A.*, **23**, 2716 (1929), refers to the material as a Grignard derivative of acetylene.

(8) W. Reppe, *Ann.*, **596**, 57 (1955).

(9) D. J. Cram and N. L. Allinger, *THIS JOURNAL*, **78**, 2518 (1956).

(10a) W. J. Gensler and A. P. Mahadevan, *ibid.*, **78**, 167 (1956).

(10b) W. J. Bailey and E. J. Fujiwara, *J. Org. Chem.*, **24**, 545 (1959).

acetylenes of polymeric nature (II), ($n = 2$) were recently reported by Bailey and Fujiwara^{10b} who treated 1-chloro-4-bromo-2-butyne with magnesium.

In our reactions, α,ω -dibromides (I) were used to alkylate a mixture of mono- and disodium acetylides; the $\text{NaC}\equiv\text{CH}$ acts as a chain stopper and decreases the yield of polymeric material. The ratio of mono- to disodium acetylide was established by passing an appropriate volume of acetylene into a known quantity of sodium amide (prepared from a weighed amount of sodium) in liquid ammonia.



Thus, for example, to obtain a reaction mixture containing 1 mole of mono- and 2 moles of disodium acetylide, 5 moles of sodium amide was treated with 3 moles of acetylene. In a similar manner was prepared a mixture of acetylides from α,ω -diacetylenes, $\text{HC}\equiv\text{C}(\text{CH}_2)_n\text{C}\equiv\text{CH}$. In the latter, alkylation with I yielded products IV and V which contained only an even number of triple bonds. This provided for a simplified separation and purification of products. In order to decrease the amount of halogen-containing by-products, e.g., $\text{HC}\equiv\text{C}-[(\text{CH}_2)_n\text{C}\equiv\text{C}]_x(\text{CH}_2)_n\text{Br}$, it was found desirable to employ an excess of sodium acetylides over that stoichiometrically required by the quantity of dibromide. Since alkylation of sodium acetylide in anhydrous ammonia at -33° is known to proceed with satisfactory speed only in cases of alkyl bromides and iodides,¹¹ dibromides were allowed to react in NH_3 at -33° . The reactants and products representative of reactions are listed in Table I.

Experimental

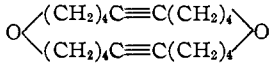
Dibromides I were purchased from the Columbia Organic Chemical Co., Columbia, S. C., and were used without further purification.

Preparation and Alkylation of Sodium Acetylides. **General Description.**—Sodium (7 moles) was treated with 4 liters of anhydrous ammonia at -33° in the presence of an iron-containing catalyst.¹² Purified acetylene was then metered into the suspension of sodium amide in ammonia until the desired ratio of mono- to disodium acetylide was reached. The dibromide was added dropwise and the reaction mixture stirred under reflux for 4 hours using a Dry Ice-acetone condenser. After removing of the condenser, the opening was covered with a Cellophane film and ammonia was permitted to evaporate. The residue was diluted with water and, if the organic portion was not sufficiently liquid, it was dissolved in ether. The organic layer was washed in succession with dilute hydrochloric acid, 10% sodium carbonate solution, water, and dried over magnesium sulfate. The products were separated by fractional distillation. In reactions where n equaled 5, distillation was temporarily interrupted after this diyne (II, $x = 1$) was collected. On cooling, cyclic diyne III ($n = 5$, $x = 1$) crystallized and was removed by filtration. Fractional distillations at 0.1 mm. were continued until a pot temperature of 300° was reached. The pot residue was frequently tan-colored and of jelly-like consistency. Fractions of narrow boiling range were redistilled or crystallized from appropriate mixtures of ether-petroleum ether. The products were characterized by their boiling points, melting points, indexes of refraction and infrared spectra. Structure assignment was on the basis of elementary analyses, molecular weight determinations and infrared spectra. The linear polyacetylenes II and IV had the strong and characteristic hydrogen absorption

(11) T. H. Vaughn, G. F. Hennion, R. R. Vogt and J. A. Nieuwland, *ibid.*, **2**, 1 (1938).

(12) K. W. Greenlee and A. L. Henne, "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, 128.

TABLE I

POLYACETYLENES																
Method	Type	n	m	x	y	Carbon, %		Hydrogen, %		Mol. weight		°C.	B.p. Mm.	M.p. °C.	n _D	t _c
						Calcd.	Found	Calcd.	Found	Calcd.	Found					
A	II	4	..	2	..	90.3	90.3	9.7	9.6	186	188	111	1.0	-3	1.4775	25
A(B)	II(IV)	4	(4)	3	(1)	90.2	89.9	9.8	9.8	266	276	167	0.3	19	1.4918	25
A	II	4	..	7	..	90.1	88.5	9.9	10.2	586	587	36
A	II	4	..	8	..	90.1	86.9	9.9	10.2	666	666	55
A	II	5	..	2	..	89.5	88.3	10.3	10.3	214	203	113	0.8	8	1.4791	26
B	IV	5	5	..	1	89.6	89.1	10.4	10.6	308	279	170	.1	33
A	II	6	..	2	..	89.3	89.9	10.7	10.3	242	237	131	.2	24	1.4806	25
B	IV	6	4	..	1	89.9	88.5	10.2	10.2	294	286	168	.6	..	1.4900	22
B	V ^a	4	4	..	1	90.0	89.5	10.0	10.2	160	161	87	.2	39
B	V	4	5	..	1	89.7	89.0	10.3	10.3	174	171	83	.08	7	1.5060	25
A(B)	III(V)	5	(5)	1	(1)	89.3	89.6	10.7	10.6	188	182	100
B	V	6	4	..	1	89.3	89.0	10.7	10.5	188	186	98	0.7	..	1.5010	24
B	V	6	5 ^b	..	1	89.0	88.2	11.0	11.0	202	193	103	.1	40
B	V	4	4	3	2	90.0	89.5	10.0	9.8	320	276	215	.2	71
A	HC≡C(CH ₂) ₄ O(CH ₂) ₄ C≡CH					81.0	79.4	10.1	9.9	178	165	128	30	..	1.4577	20
A						79.0	79.1	10.5	10.6	304	279	178	0.08	75

^a Previously reported by Cram (ref. 9); m.p. 37°; spectrum identical. ^b Prepared by W. H. Pittman.

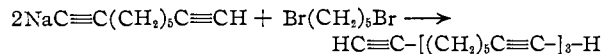
band, H—C≡ at 3300 cm.⁻¹, and the terminal triple bond H—C≡C at 2130 cm.⁻¹. The absorption band for an internal triple bond C—C≡C—C, when present, was of very low intensity at 2240 cm.⁻¹.¹³ The cyclic polyacetylenes III and V showed only the internal triple bond absorption band (doublet) at 2220 and 2270 cm.⁻¹.¹⁴ The intensity of this band was weak but somewhat stronger than the internal triple bond absorption band in the linear polyacetylenes. Of considerable diagnostic importance was the strong absorption band near 1330 cm.⁻¹ which was assigned to a methylene group next to a triple bond, —CH₂C≡C.¹⁴ Thus in compounds where no internal triple bond absorption band was found, the presence of the 1330 cm.⁻¹ band was used to confirm the acetylenic structure.

Discussion

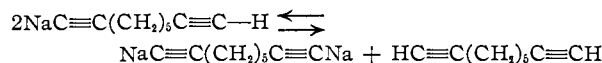
By keeping an excess of sodium acetylide over the amount of dibromide, the ethynylation reactions proceeded in high yields (at least 90%). However, the distribution, according to molecular weight, of linear and cyclic products depended to a great extent on the ratio of mono- to disodium acetylides. For example, the reaction of NaC≡CH and NaC≡Na (1:1 molar ratio) with I (*n* = 4) in liquid ammonia produced II (*x* = 1, 2, 3, 7, 8) in yields of 23, 12, 8, 0.6 and 0.3%, respectively. The rest were higher boiling products, possibly of types II and III. In this reaction it was not possible to isolate from the distillate the cyclic diyne III (*x* = 1), although a mass spectrum analysis showed the presence of a small quantity. However, this compound was isolated in 5% yield from the reaction of equimolar quantities of NaC≡C(CH₂)₄C≡CNa with I (*n* = 4). Its melting point and infrared spectrum showed it to be identical with the compound prepared by Cram and Allinger.⁹

The alkylation of a mixture of NaC≡CNa and NaC≡CH (1:1 molar ratio) with I (*n* = 5) produced II (*x* = 1) and III (*x* = 1) in 18 and 25% yields, respectively. The alkylation of a mixture of di- and monosodium acetylide in a 1:2 molar ratio produced II (*x* = 1) and III (*x* = 1) in 40 and 12% yields, respectively. The cyclic diyne III (*n* = 5, *x* = 1) was found in most reactions regard-

less of ratio of reactants, nature of halide, metal or solvent employed. In an attempt to prepare a pure specimen of II (*n* = 5, *x* = 3), the reaction



was undertaken. Even in this reaction the cyclic diyne III (*n* = 5, *x* = 1) was isolated in 30% yield, suggesting the possible disproportionation



In the examples reported here, it is seen that the optimum chance for an intramolecular reaction leading to a "small" cyclic polyacetylene, as evidenced from the yield of products, is in the reactions which produced a cyclotetradecadiyne. However, the nature of the metal in the acetylide also had an influence on the distribution of products. This is observed in the alkylation with pentamethylene dibromide of an equimolar mixture M—C≡C—M and M—C≡C—H (Table II).

TABLE II

M MC=CM/HC=CM (1:1)	Product (<i>n</i> = 5, <i>x</i> = 1) % of yield	
	II	III
Li	51	6
Na	18	25
K	30	..
Ba	9	10

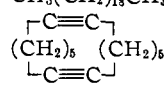
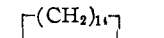
As expected, reactions which did not contain the chain-stopping NaC≡CH or NaC≡C—(CH₂)_{*n*}C≡CH, resulted in the formation of large quantities of high molecular weight product which did not distill at a pot temperature of 300° at 0.1 mm. pressure. The nature of such polymers as well as the chemistry of the novel polyacetylenes will be described in future publications.

The nonconjugated polyacetylenes are colorless liquids or solids which show a rather surprising thermal stability. For example, 1,7,13,19-eicosatetrayne, HC≡C—[(CH₂)₄C≡C]₃—H, II (*n* = 4, *x* = 3) distilled without decomposition at 167° at 0.3

(13) J. H. Wotiz and F. A. Miller, *THIS JOURNAL*, **71**, 3441 (1949).

(14) J. J. Mannion and T. S. Wang, Diamond Alkali Co. Spectrographic Laboratory, unpublished.

TABLE III
 THERMOCHEMICAL PROPERTIES OF POLYACETYLENES

Structure	M.p., °C.	Density, g./ml. (°C.)		Heat of combustion ^a		-ΔH ^o c at (°C.)	
				Kcal./mole	Cal./g.	Cal./ml.	
HC≡C[(CH ₂) ₄ C≡C] ₂ -H	-3	0.865(25)	0.807(105)	2025(25)	10887(25)	9417(25), 8786(105)	
CH ₃ (CH ₂) ₂ CH ₃	6 ^b	.769(25) ^c	2262(25)	11402(25)	8654(25),	
HC≡C[(CH ₂) ₄ C≡C] ₃ -H	19	.883(25)	.834(105)	2898(25)	10896(25)	9621(25), 9087(105)	
CH ₃ (CH ₂) ₁₈ CH ₃	37	.785(25) ^d	0.777(40)	.735(105)	3206(25) ^d	11350(25) ^d	8819(40), 8342(105)
	100	1.040(25) ^d	.872(105)	1906(25) ^d	10140(25) ^d	10546(25), ^d 8842(105)	
	58	0.942(25) ^d	0.834(60)	.809(105)	2215(25) ^d	11302(25) ^d	9426(60), 8613(105)

^a Herron Testing Laboratories, Cleveland, Ohio. ^b R. R. Dreisbach, "Physical Properties of Chemical Compounds. Vol. II," Advances in Chem. Series, No. 22, Am. Chem. Soc., 1959. ^c F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," Circular C461, National Bureau of Standards, 1947, pp. 40, 41, 57, 143-155. ^d Solid.

mm. When heated at atmospheric pressure it did not decompose below 316°.

The triple bonds in the polyacetylenes are responsible for the higher densities of these compounds compared with the corresponding saturated hydrocarbons. Some thermochemical properties of representative polyacetylenes are listed in Table III. Three saturated compounds tetradecane, eicosane, and cyclotetradecane are included for comparison purposes. Since some of the polyacetylenes are solids at room temperature, density measurements were also made near the melting points and at 105°.

An examination of heat of combustion data (kcal./mole and cal./g.) shows lower values for

acetylenes than the corresponding saturated hydrocarbons. This is due to the fewer hydrogen atoms in the acetylene molecules. However, since the densities of the polyacetylenes are greater than those of saturated hydrocarbons, the heats of combustion expressed in cal./ml. are greater for the linear polyacetylenes. An anomalous result was found in the case of 1,8-cyclotetradecadiyne which has a lower experimental heat of combustion value than its saturated analog, cyclotetradecane, giving a greater negative heat of formation than cyclotetradecane. A possible explanation is that a transannular effect of the two triple bonds may give rise to a lower energy content of the molecule.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIF.]

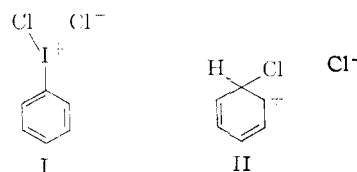
Acetic Acid as an Inhibitor in Trifluoroacetic Acid-catalyzed Aromatic Halogenations and in Halogen Addition Reactions

BY R. M. KEEFER AND L. J. ANDREWS

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The influence of acetic acid on the trifluoroacetic acid-catalyzed rate of reaction of halogens with alkylbenzenes or substituted alkenes in carbon tetrachloride has been investigated. A wide range of effects, from strong inhibition to mild acceleration, has been observed. The capacity of trifluoroacetic acid to solvate the electronegative portion of the polar activated complexes in the reactions presumably is reduced through interaction with acetic acid to form a mixed dimer. In cases in which only this type of solvation is highly critical to the activation process, acetic acid has the maximum effect. It is assumed that in reactions in which the inhibitory effect of acetic acid is small or non-existent, solvation of the electropositive end of the dipole which develops is also an important feature of the activation process. This interpretation has been satisfactorily applied in explaining the experimental results, which include the observations that in the presence of trifluoroacetic acid the electrophilic reactivity of bromine is less inhibited by acetic acid than is that of chlorine and iodine monochloride and also that the reactions of α, β -unsaturated acids are unusually insensitive to added acetic acid.

Trifluoroacetic acid catalyzes the chlorination of aromatic hydrocarbons in carbon tetrachloride¹ and also promotes the dissociation of iodobenzene dichloride and its substitution products in this solvent.² The activated complexes (I and II) for these two types of reaction are presumed to be appreciably polar in character. The activity of the catalyst is attributed to its capacity to function as an electron acceptor in solvating the negatively polarized chlorine atoms of these complexes through hydrogen bond formation. The effectiveness of the catalyst



in the aromatic chlorination reaction falls off sharply as acetic acid is added to the medium, probably because of the interaction of the two acids to form a mixed dimer. This substance undoubtedly is less suited for solvation of the negative end of a dipole than is trifluoroacetic acid.

It has been found, however, that the rate of trifluoroacetic acid-catalyzed dissociation of the di-

(1) R. M. Keefer and L. J. Andrews, *THIS JOURNAL*, **82**, 4547 (1960).

(2) L. J. Andrews and R. M. Keefer, *ibid.*, **82**, 3057 (1960).