Copper Chloride–Ethanolamine Catalyzed Addition of Polyhaloalkanes to 1-Octene[1]

Donald J. Burton and Lawrence J. Kehoe

Department of Chemistry, The University of Iowa, Iowa City, Iowa 52240

The copper chloride–ethanolamine redox system initiates the addition of a variety of polyhaloalkanes to 1-octene, giving good yields of the 1:1 addition products. This redox system of radical initiation offers several advantages when compared with ordinary initiation techniques. The preparation and characterization of several new addition adducts are reported.

The extensive number of reports concerned with the free-radical addition of polyhaloalkanes to olefins have given close scrutiny to the scope and effectiveness of a variety of systems for the initiation of these reactions.[2] However, the redox system of radical initiation has received limited study. This redox system, as described by Asscher and Vofsi,[3,4] utilizes iron or copper salts to catalyze the addition of carbon tetrachloride and chloroform to olefins.

$$CCl_4 + PhCH{=}CH_2 \xrightarrow[\substack{\text{solvent,} \\ 120°}]{\text{CuCl}_2} PhCHClCH_2CCl_3$$
$$78\%$$
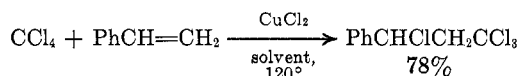
The redox system has several advantages when compared to ordinary initiation techniques: (a) telomerization reactions are minimized, with a corresponding increase in the yield of the 1:1 addition adduct; (b) the use of a large excess of alkyl polyhalide is no longer necessary to ensure a respectable yield of the 1:1 adduct, a distinct advantage as the haloalkane is generally the more expensive and more difficult reactant to obtain; (c) vigorous reaction conditions and the need for special apparatus can be avoided. Because of these advantages, the redox technique holds much promise for the preparation of many polyhalogenated compounds, and a study of the scope and utility of this system was of interest.

Results and Discussion

Many alkyl halide–olefin additions (utilizing conventional methods of radical initiation) have been described in the literature, and thus are provided convenient models for investigation of the applicability of the redox system.
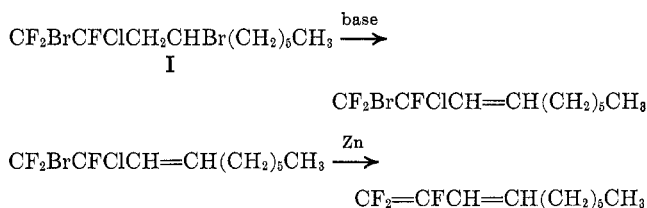
In this study, 1-octene was used as a model olefin for the initial survey of the scope of the reaction. The additions were carried out by refluxing the olefin, alkyl polyhalide, copper chloride, ethanolamine, and *t*-butyl alcohol, with stirring, for 24–48 hr. The results of these addition reactions are summarized in Table I.

An examination of the data in Table I reveals that this redox method successfully initiates the addition of polyhaloalkanes containing a reactive chlorine, bromine, or iodine atom to a number of olefins to give good yields

of the 1:1 addition products. Gas chromatography showed that in almost every reaction, in addition to the major product, small amounts (generally less than 5% of the total product) of isomeric compounds were formed. These by-products were not identified.

In order to determine the structure of the major products (and thereby obtain proof of the course of the addition reactions), it was necessary to establish two points: (a) which halogen atom was abstracted from the polyhaloalkane; (b) which carbon atom of the double bond underwent attack by the polyhaloalkane radical.

An example of a structure proof *via* chemical means has been reported by Tarrant and Gilman[5] for the $CF_2BrCFClBr$ + 1-octene adduct. The structure was shown to be I by the following reactions.

$$CF_2BrCFClCH_2CHBr(CH_2)_5CH_3 \xrightarrow{\text{base}}$$
$$\text{I}$$
$$CF_2BrCFClCH{=}CH(CH_2)_5CH_3$$

$$CF_2BrCFClCH{=}CH(CH_2)_5CH_3 \xrightarrow{\text{Zn}}$$
$$CF_2{=}CFCH{=}CH(CH_2)_5CH_3$$

This same series of dehydrohalogenation and dehalogenation reactions was employed in this study for structure elucidation. Additionally, the adducts synthesized in this study gave a pmr signal in the vicinity of δ 4.0 for the protons geminal to a single halogen atom. Thus, it was possible to determine if the halogen atom had become attached to the terminal or to the internal carbon of the double bond. For example, the methine proton in $CF_2BrCFClCH_2CHBr(CH_2)_5CH_3$ appeared as a multiplet centered at δ 4.4 and integrated for one proton. With the alternative structure, $CH_2BrCH(CFClCF_2Br)(CH_2)_5CH_3$, a signal with an intensity corresponding to two protons would be anticipated in the δ 4.0 region.

It was found that redox-initiated additions proceeded in the same manner as that described for additions initiated by ordinary techniques. Therefore it was valid to make direct comparisons of reaction yields and products to previously reported information.

The series of reactions utilizing 1-octene as a model olefin provides some straightforward data on the relative reactivity of several polyhalides. The data in Table I indicate that increasing reactivity of the halogenated alkane directly parallels the ease with which a halogen atom is abstracted from the molecule. An examination of the experimental results does indeed show increased reactivity of bromo compounds over

(1) (a) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; (b) abstracted from the Ph.D. thesis of L. J. Kehoe, University of Iowa, Feb 1967; (c) preliminary report in *Tetrahedron Lett.*, 5163 (1966). (d) This investigation was supported in part by the U. S. Public Health Service, Grant GM 11809.

(2) For an extensive review of this work, *cf.* (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 6; (b) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, Chapter 2.

(3) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1887 (1963).

(4) M. Asscher and D. Vofsi, *ibid.*, 3921 (1963).

(5) P. Tarrant and E. Gilman, *J. Amer. Chem. Soc.*, 76, 5423 (1954).

TABLE I
DATA ON ADDITION ADDUCTS

Reaction	Halide	Adduct	% yield[a]	% conversion[b]	Ratio of halide: olefin	Reaction time, hr	Bp, °C (mm)	$n^{20}D$	Calcd % C	Calcd % H	Found % C	Found % H
I	CH₂Br₂		0	0	1:1	48						
II	CF₂Br₂	CF₂BrCH₂CHBr(CH₂)₅CH₃	68	47	2:1	53	42 (0.1)	1.4583	33.6	4.97	33.7	5.26
III	CHClBr₂	CHClBrCH₂CHBr(CH₂)₅CH₃	99	57	2:1	79	100 (0.55)	1.5021	33.8	5.32	33.6	5.01
IV	CHBr₃	CHBr₂CH₂CHBr(CH₂)₅CH₃	95	41	2:1	48	98 (0.2)	1.5192	29.6	4.67	29.9	4.73
V	CHCl₃	CHCl₂CH₂CHCl(CH₂)₅CH₃	37	25	2:1	53	63 (0.15)	1.4654	46.8	7.36	46.9	7.53
VI	CCl₄	CCl₃CH₂CHCl(CH₂)₅CH₃	77	52	2:1	24	107 (2)	1.4763	40.6	6.02	40.6	5.97
VII	CCl₃Br	CCl₃CH₂CHBr(CH₂)₅CH₃	96	100	2:1	24	70 (0.05)	1.4942	34.9	5.17	34.6	4.90
VIII	CF₂BrCF₂Br	CF₂BrCF₂CH₂CHBr(CH₂)₅CH₃	77	57	2:1	48	84 (1)	1.4380	32.3	4.31	32.6	4.60
IX	CF₂BrCFClBr	CF₂BrCFClCH₂CHBr(CH₂)₅CH₃	95	96	2:1	24	88 (0.4)	1.4612	30.9	4.13	30.7	4.19
X	CF₂ClCFCl₂	CF₂ClCClClCH₂CHCl(CH₂)₅CH₃	62	45	2:1	48	79 (0.95)	1.4305	40.2	5.35	40.4	5.59
XI	CF₃CHBr₂	CF₃CHBrCH₂CHBr(CH₂)₅CH₃	97	80	2:1	48	54 (0.05)	1.4475	33.9	4.80	34.2	5.03
XII	CF₃CClBr₂	CF₃CClBrCH₂CHBr₂(CH₂)₅CH₃	98	97	2:1	48	68 (0.1)	1.4619	30.9	4.13	30.7	4.00
XIII	CF₃CBr₃	CF₃CBr₂CH₂CHBr(CH₂)₅CH₃[c]	74	100	2:1	43	80 (0.15)	1.4776	27.7	3.69	27.5	3.68
XIV	CF₃CCl₃	CF₃CCl₂CH₂CHCl(CH₂)₅CH₃	83	100	2:1	48	54 (0.15)	1.4304	40.2	5.35	40.0	5.07
XV	CCl₂BrCCl₂Br		0	0	1:1	30						
XVI	CCl₃CCl₃		Trace	8	1:1	45						
XVII	CF₂ClCFClCII	CF₂ClCFClCH₂CHI(CH₂)₅CH₃	73	51	1:1	43	82 (0.25)	1.4722	30.7	4.19	30.6	4.03
XVIII	CF₃CF₂CF₂I	CF₃CF₂CF₂CH₂CHI(CH₂)₅CH₃	57	36	1:1	24	54–55 (0.4)	1.4116	32.4	3.92	32.6	3.77
XIX	CF₃CFICF₃	(CF₃)₂CFCH₂CHI(CH₂)₅CH₃	66	54	1:1	24	43 (0.2)	1.4132	32.4	3.92	32.2	4.07
XX	CF₃CFBrCFBrCF₃		0	0	1:1	48						

[a] Yield (*via* glpc) = moles of adduct formed/moles of olefin consumed. [b] Conversion (*via* glpc) = moles of olefin consumed/moles of olefin charged. [c] The structure of this adduct was not unequivocally determined.

chloro compounds. For example, the dibromoalkane CF_2BrCF_2Br gave a 77% yield (57% conversion) of the addition adduct, while the closely related chloro compound $CF_2ClCFCl_2$ gave only a 62% yield (45% conversion). Compare also reactions VI and VII.

With the iodo compounds, however, seemingly anomalous results are observed. In these instances, the relatively low yields of addition adducts were traceable directly to the formation of large amounts of olefins, the product formed by the loss of HI from the adduct. The reaction of $CF_3CF_2CF_2I$, for example, gave a product mixture composed of 57% $CF_3CF_2CF_2CH_2CHI(CH_2)_5CH_3$ and 42% $CF_3CF_2CF_2CH=CH(CH_2)_5CH_3$.

The susceptibility of these iodo compounds to loss of HI under the redox reaction conditions points out one other aspect of this catalysis system. The adduct, as well as the reactants, must be stable in the presence of the copper salt and the ethanolamine for addition to be successful. In the case of the iodo compounds, the ethanolamine is probably a strong enough base to remove HI from the product. Approximately 0.05 mol of olefin was formed, and 0.05 mol of ethanolamine was used to initiate the addition.

If a bulkier atom is added to each of a series of alkyl polyhalides, each successive compound would be expected to be more reactive (owing to both steric considerations and to the activating influence of each added halogen atom) than the one preceeding it in the series. The series CF_3CHBr_2 (80% conversion), CF_3CClBr_2 (97% conversion), CF_3CBr_3 (100% conversion) is a case in point.

While most of the polyhalo compounds examined did undergo successful addition, several others are worthy of note. For example, the tetrachloro compound CCl_2BrCCl_2Br gave only tetrachloroethylene under these conditions, and no addition adduct. The closely related tetrafluoroethane CF_2BrCF_2Br however, added readily to 1-octene. The failure of $CF_3CFBrCF-BrCF_3$ to react was somewhat unexpected, since debromination of this halide was not observed.

One final comparison of halide reactivities is between CH_2Br_2 and CF_2Br_2. While CH_2Br_2 gave no addition,

CF_2Br_2 formed the desired adduct in a 68% yield, an indication of the ability of the fluorine atoms to activate the bromine atom toward radical attack.

Several reaction parameters were examined. One interesting reaction series revealed that the addition of very reactive polyhalides, such as $CF_2BrCFClBr$, can be catalyzed by ethanolamine alone, while the less reactive halides, such as CF_2BrCF_2Br and $CF_2ClCF-Cl_2$, undergo successful addition *only* in the presence of both copper salt and amine. These results are summarized in Table II.

TABLE II
EFFECT OF COPPER ON REACTION

Olefin	Halide	% conversion	% yield
A.	1 mmol of CuCl + 50 mmol of Ethanolamine		
1-Octene	CF₂BrCFClBr	96	95
	CF₂BrCF₂Br	57	77
	CF₂ClCFCl₂	45	62
B.	No Added CuCl–50 mmol of Ethanolamine		
1-Octene	CF₂BrCFClBr	88	73
	CF₂BrCF₂Br	4	100
	CF₂ClCFCl₂	0	0

When CuCl was utilized in the absence of ethanolamine, $CF_2BrCFClBr$ gave no addition. It was also found that the initial oxidation state of the copper salt did not affect the yield of adduct. Both CuCl and $CuCl_2 \cdot 2H_2O$ gave a 62% yield of adduct (45% conversion) with $CF_2ClCFCl_2$.

Butylamine was substituted for the ethanolamine with no loss in reactivity. However, both aniline and triethylamine were considerably less effective.

One final parameter was considered, this being the effect of solvent on the yield of adduct. The results are summarized in Table III and are indicative of some type of solvent effect since all three solvents have approximately the same boiling point and the reaction temperature was therefore the same in each case.

While the immediate goal of this study was an evaluation of the scope of this redox system of radical
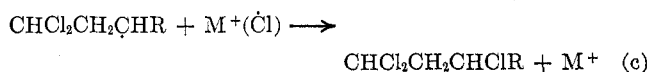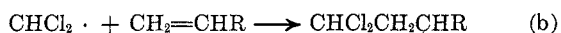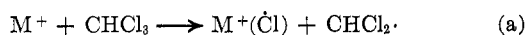
TABLE III

EFFECT OF SOLVENT ON $CF_2BrCFClBr$ + 1-OCTENE REACTION

Solvent	% yield	% conversion
t-Butyl alcohol	95	96
Isopropyl alcohol	98	79
Acetonitrile	85	77

initiation, one observation is discussed here in an attempt to clarify previous mechanistic hypotheses.

Asscher and Vofsi have postulated the following mechanism for their oxidation–reduction-type additions[3,4]

$$M^+ + CHCl_3 \longrightarrow M^+(\dot{C}l) + CHCl_2 \cdot \qquad (a)$$

$$CHCl_2 \cdot + CH_2{=}CHR \longrightarrow CHCl_2CH_2\dot{C}HR \qquad (b)$$

$$CHCl_2CH_2\dot{C}HR + M^+(\dot{C}l) \longrightarrow$$

$$CHCl_2CH_2CHClR + M^+ \qquad (c)$$

where M^+ represented copper(I) or iron(II) ion and M^+ ($\dot{C}l$) represented copper(II) or iron(III) ion with at least one chlorine ligand in the coordination shell. Asscher thus called the oxidation–reduction steps a and c "redox-transfer."[6] The authors comment that in the presence of an amine much less vigorous conditions are necessary to bring about this reaction. The data in Table II lend support to this observation as, with less reactive alkyl polyhalides, no reaction occurred under mild conditions without the presence of added ethanolamine. Thus, as both the amine and the copper salt are indispensable for addition of the less reactive halides, a complex of the amine with copper ion is strongly suggested as the reactive species.

$$Cu^+(ammine) + CCl_4 \longrightarrow Cu^+(ammine)(\dot{C}l) + CCl_3 \cdot$$
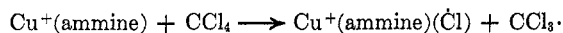
Experimental Section

Boiling points are uncorrected. Elemental analyses were performed by personnel in this laboratory. Infrared spectra were obtained on a Perkin–Elmer Model 21 double-beam recording spectrophotometer. The pmr spectra were recorded on a Varian A-60 instrument with tetramethylsilane as an internal standard. Glpc analyses were obtained with a F & M Model 720 gas chromatograph, and peak areas were used to calculate the yield of addition adducts.

Copper chloride was purified via the method of Keller and Wycoff.[7] Bromoform and bromotrichloromethane were distilled before use. $CF_3CFBrCFBrCF_3$,[8] CCl_2BrCCl_2Br,[9] $CF_2ClCFCFClI$,[10] $CF_2BrCFClBr$,[5] and CF_3CCl_3[11] were prepared by reported methods.

1,1-Dibromo-1-chloro-2,2,2-trifluoroethane.—$CF_2BrCFClBr$ (176 g) and anhydrous aluminum chloride (13 g) were allowed to react at room temperature for 2 hr. The organic product was extracted with ether and distilled to give 146 g of CF_3CClBr_2, bp 91–92°.

1,1,1-Tribromo-2,2,2-trifluoroethane.—CF_2BrCF_2Br (400 g) and anhydrous aluminum chloride (10 g) were refluxed for 22 hr. The organic product was extracted with ether and distilled to give 148 g of CF_3CBr_3, bp 114–115°.

All other materials were best commercial grade used without further purification.

Addition of Perhaloalkanes to Olefins.—The experimental data for these addition reactions are compiled in Table I. A

typical reaction procedure is described in detail. The additions were carried out in a 500-ml flask containing a Teflon-covered stirring bar and fitted with a cold-water condenser, topped by a tube leading to a Dry Ice cooled trap.

Initial reactions were catalyzed by freshly prepared copper(I) chloride. The copper(I) chloride is slowly oxidized by moist air to yield a green compound, $CuCl_2 \cdot 3Cu(OH)_2$. However, it was found that this partially oxidized mixture of Cu(I) and Cu(II) was an effective catalyst for these additions, and the mixture was therefore used to initiate subsequent addition reactions.

Typical Reaction Procedure. Reaction of $CF_2BrCFClBr$ with 1-Octene.—Utilizing the reaction apparatus described above, 55.3 g (0.2 mol) of $CF_2BrCFClBr$, 11.2 g (0.1 mol) of 1-octene, 0.1 g (~0.001 mol) of copper chloride [Cu(I)–Cu(II) mixture], 3 g (0.05 mol) of ethanolamine, and 100 ml of t-butyl alcohol were refluxed, with stirring, for 24 hr. After cooling to room temperature, the reaction mixture was diluted with ether and the organic layer was separated. Glpc analysis on a silicone rubber column indicated a 95% yield of the 1:1 adduct, based on 1-octene. Subsequent fractionation yielded 27.0 g (70%) of pure addition adduct, bp 88° (0.4 mm), $n^{20}D$ 1.4612.

Dehydrohalogenation of $CF_2BrCF_2CH_2CHBr(CH_2)_5CH_3$ (VIII). —A mixture of KOH (3.6 g) in ethanol (150 ml) was dripped slowly into 18.2 g of VIII at 100°. After refluxing for 3 hr the reaction mixture was poured into water and the organic layer separated, washed, and dried. Distillation gave 9.25 g of product, bp 54° (0.9 mm), identified as $CF_2BrCF_2CH{=}CH(CH_2)_5-CH_3$. Anal. Calcd for $C_{10}H_{15}BrF_4$: C, 41.4; H, 5.16. Found: C, 41.6; H, 5.45. The pmr and ir spectra were consistent with the above structure (cf. Table IV).

Dehydrohalogenation of $CF_2BrCFClCH_2CHBr(CH_2)_5CH_3$ (IX).—A mixture of KOH (9.9 g) in ethanol (150 ml) was dripped slowly into 45.9 g of IX at 100°. The reaction mixture was then poured into water and the organic layer separated, washed, and dried. Distillation gave 12.7 g of product, bp 69–70° (1 mm), identified as $CF_2BrCFClCH{=}CH(CH_2)_5CH_3$ (XXI). Anal. Calcd for $C_{10}H_{15}BrClF_3$: C, 39.1; H, 4.88. Found: C, 39.0; H, 5.12. The reported[5] boiling point for XXI was 62° (0.5 mm). The pmr and ir spectra were consistent with the above structure.

Dehydrohalogenation of CF_3CBr_3 + 1-Octene Adduct (XIII).— A mixture of KOH (29 g) in ethanol (200 ml) was dripped slowly into 163.2 g of XIII at 100°. After refluxing for 3 hr the reaction mixture was worked up in the usual manner. Distillation gave two compounds: (a) 17.1 g, bp 79–80° (2 mm); (b) 14.0 g, bp 102–105° (1 mm).

Compound a gave the following analysis. Calcd for $C_{10}F_3-BrH_{14}$: C, 44.3; H, 5.20. Found: C, 44.2; H, 5.21. The ir spectrum of this fraction showed no double-bond absorption; pmr δ 5.4 (m, 1, methine), 2.5 (m, 2, methylene), 0.7–1.9 (m, 11, remaining protons). The pmr spectra, the lack of double-bond absorption in the infrared and the elemental analysis, suggest that this compound is $CF_3CHBrC{\equiv}CCH_2(CH_2)_4CH_3$, formed by the loss of two molecules of HBr from the 1:1 adduct and rearrangement (in the basic reaction media) of the intermediate allene.

Compound b gave the following analysis. Calcd for $C_{10}F_3-Br_2H_{15}$: C, 34.1; H, 4.29. Found: C, 34.0; H, 4.28. The ir spectrum showed double-bond absorption at 6.0 μ; pmr δ 4.5–7.0 (m, 2, methine + vinyl), 0.7–2.4 (m, 13, remaining protons). The structure of this fraction could not be unequivocally determined, but the pmr spectrum suggests that it is a mixture of both possible compounds: $CF_3CBr{=}CHCHBr(CH_2)_5CH_3$ and $CF_3-CBr_2CH{=}CH(CH_2)_5CH_3$.

Dehydrohalogenation of $CHClBrCH_2CHBr(CH_2)_5CH_3$ (III).— The attempted dehydrohalogenation of III gave a mixture of products, none of which were identified.

Dehalogenation of $CF_3BrCFClCH_2CHBr(CH_2)_5CH_3$ (IX).— IX (38.8 g) in isopropyl alcohol (50 ml) was added slowly to a slurry of granulated zinc (6.5 g) in isopropyl alcohol (100 ml) at 100°. After refluxing for 3 hr the reaction mixture was poured into water and the organic layer separated, washed, and dried. Distillation gave 12.3 g of product, bp 57–58° (0.4 mm), identified at $CF_2{=}CFCH_2CHBr(CH_2)_5CH_3$. Anal. Calcd for $C_{10}H_{16}BrF_3$: C, 44.0; H, 5.87. Found: C, 44.4; H, 5.91. The pmr and ir spectra were consistent with the above structure.

Dehalogenation of $CF_2ClCFClCH_2CHCl(CH_2)_5CH_3$ (X).—X (11.0 g) in isopropyl alcohol (50 ml) was added slowly to a slurry of granulated zinc (2.6 g) in isopropyl alcohol (100 ml) at 100°. After refluxing for 24 hr the reaction mixture was worked up in

(6) This same redox reaction has been called "ligand-transfer" by Kochi and coworkers: J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).

(7) R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, **2**, 1 (1946).

(8) T. J. Brice, J. D. Lazerte, and W. H. Pearlson, *J. Amer. Chem. Soc.*, **75**, 2698 (1953).

(9) E. Malaguti, *Ann.*, **56**, 276 (1845).

(10) M. Hauptschein, M. Braid, and A. Fainberg, *J. Amer. Chem. Soc.*, **83**, 2495 (1961).

(11) W. T. Miller, E. Fager, and P. Griswald, *ibid.*, **72**, 705 (1950).

TABLE IV

PROTON MAGNETIC RESONANCE DATA[a]

Adduct	CH₃(CH₂)₅	Chemical shifts, δ (ppm) Isolated –CH₂–	–CHX	Rel intensities
II	0.8–2.0 (m)	3.0 (m)	4.2 (5), J_{HH} = 6	13:2:1
III	0.8–2.0 (m)	2.7 (m)	4.1 (5), J_{HH} = 6.5	13:2:1:1
			6.0 (3), J_{HH} = 6.5	
IV	0.8–2.0 (m)	2.8 (4), J_{HH} = 6.0, $J_{HH'}$ = 8.0	4.2 (m) 6.0 (m)	13:2:1:1
V	0.8–2.0 (m)	4.0 (m)	5.9 (3), J_{HH} = 6.5	13:2:1
VI	0.7–2.1 (m)	3.2 (4), J_{HH} = 5.5, $J_{HH'}$ = 5.0	4.2 (m)	13:2:1
VII	0.8–2.2 (m)	3.3 (3), J_{HH} = 5.5	4.4 (m)	13:2:1
VIII	0.8–2.2 (m)	2.7 (6), J_{HH} = 6.5, J_{HF} = 18	4.2 (5), J_{HH} = 6.0	13:2:1
IX	0.7–2.2 (m)	2.2–3.2 (m)	4.4 (m)	13:2:1
X	0.7–2.2 (m)	2.2–3.0 (m)	4.3 (m)	13:2:1
XI	0.7–2.7 (m)		4.0–4.8 (m)	15:1
XII	0.8–2.2 (m)	2.9 (m)	4.4 (m)	13:2:1
XIII	0.7–3.1 (m)		4.3 (m)	15:1
XIV	0.8–2.1 (m)	2.8 (4), J_{HH} = 5.5, $J_{HH'}$ = 5.0	4.2 (5), J_{HH} = 5.5	13:2:1
XVII	0.7–2.1 (m)	2.5–3.3 (m)	4.4 (m)	13:2:1
XVIII	0.7–2.1 (m)	2.4–3.3 (m)	4.4 (5), J_{HH} = 6.5	13:2:1
XIX	0.7–2.1 (m)	2.6–3.2 (m)	4.4 (m)	13:2:1

[a] In parentheses is given the multiplicity of the peak; the coupling constants are in cycles per second.

the usual manner and the organic layer distilled to give 2.4 g of product, bp 54–55° (0.8 mm), identified as CF_2=$CFCH_2CHCl$-$(CH_2)_5CH_3$. The pmr and ir spectra were consistent with the above structure.

Registry No.—II, 459-78-9; III, 23885-03-2; IV, 1071-51-8; V, 10575-86-7; VI, 1070-27-5; VII, 1070-26-4; VIII, 23885-08-7; IX, 461-01-8; X, 23885-10-1; XI, 23885-11-2; XII, 23885-12-3; XIII, 23885-13-4;

XIV, 23885-14-5; XVII, 23885-15-6; XVIII, 23885-16-7; XIX, 23885-17-8; CF_2BrCF_2CH=$CH(CH_2)_5$-CH_3, 23885-18-9; $CF_2BrCFClCH$=$CH(CH_2)_5CH_3$, 310-63-4; CF_3CHBrC≡$CCH_2(CH_2)_4CH_3$, 23885-20-3; CF_3CBr=$CHCHBr(CH_2)_5CH_3$, 23885-21-4; CF_3-CBr_2CH=$CH(CH_2)_5CH_3$, 23885-22-5; CF_2=$CFCH_2$-$CHBr(CH_2)_5CH_3$, 23942-63-4; CF_2=$CFCH_2CHCl$-$(CH_2)_5CH_3$, 23885-23-6; copper chloride, 7447-39-4; ethanolamine, 141-43-5.

Aluminum Chloride Catalyzed Diene Condensation. V.[1,2]
Selectivity–Reactivity Relationship of Dienophiles toward Butadiene, Isoprene, and 2-Trifluoromethylbutadiene

TAKESHI KOJIMA AND TAKASHI INUKAI

The Central Research Laboratories, Chisso Corporation, Kamariya, Kanazawa-ku, Yokohama, Japan

The relative rates of reactions of isoprene and butadiene, k^i/k^b, with tetracyanoethylene, methyl acrylate–aluminum chloride complex, fumaryl chloride, vinylidene cyanide, maleic anhydride, dimethyl fumarate, dimethyl acetylenedicarboxylate, methyl acrylate, acrylonitrile, and dimethyl maleate were determined and plotted against the *reactivities* (the second-order rate constants with cyclopentadiene in dioxane at 20°) of the dienophiles. The k^i/k^b value increases with the increasing reactivity of the dienophile, in contrast to the accepted selectivity–reactivity relationship. Corresponding data for the 2-trifluoromethylbutadiene–butadiene pair of substrates are reported. The selectivity, based on the relative rate of the *s-cis* species, increases with the increasing reactivity of the dienophiles, here the selectivity being in favor of butadiene. The mechanistic implications of these results are discussed in connection with the selectivity–reactivity relationship and varying electrophilic character of the dienophiles. From the normal position taken by the methyl acrylate–aluminum chloride complex in the correlation line, the mechanism of the aluminum chloride catalyzed diene condensation is assumed to be one of the variety of the Diels–Alder reactions.

It was shown in previous papers that the methyl acrylate–aluminum chloride complex (MA–AlCl₃)[1] is a more discriminating dienophile than uncomplexed methyl acrylate in reactions with isoprene–butadiene[3]

or *trans*-piperylene–butadiene[4] pairs of diene substrates, whereas the former dienophile is more reactive than the latter.[1] The higher selectivity was also found in stereochemical (*endo–exo*)[4–6] and orientational (*meta–para* or *ortho–meta*)[3,4] phenomena. These ob-

(1) Part IV: T. Inukai and T. Kojima, *J. Org. Chem.*, **32**, 872 (1967).

(2) Presented in part: Abstracts, 18th Symposium on Organic Reaction Mechanism of the Chemical Society of Japan, Kyoto, Japan, Oct 1967, p 122; Abstracts, 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, Japan, April 1969, p 1658.

(3) T. Inukai and T. Kojima, *J. Org. Chem.*, **31**, 1121 (1966).

(4) T. Inukai and T. Kojima, *ibid.*, **32**, 869 (1967).

(5) T. Inukai and T. Kojima, *ibid.*, **31**, 2032 (1966).

(6) J. Sauer and J. Kredel, *Tetrahedron Lett.*, 731 (1966).