TABLE III

Sample	Total time of reaction, hours	First run: *cis*-Dichloro, g.	First run: [α] of *cis*-dichloro	First run: [α] of filtrate	Second run: *cis*-Dichloro, g.	Second run: [α] of *cis*-dichloro	Second run: [α] of filt.
Original				(−0.09)			(−0.09)
A	1	1.92	+0.06	− .13	1.13	+0.01	−0.12
B	5	3.64	+ .05	− .18	4.30	.00	− .19
C	12	0.96	+ .05	− .26	0.75	.00	− .24
D	24	0.88	+ .02	− .34	0.80	.01	− .33
E	48	0.24	+ .04	− .40	0.34	.00	− .40

of [Co en$_2$ (NO$_2$)$_2$]$^+$. The best yield of optically active dinitro product that was ever obtained was 40%. It is apparently possible to convert one form of the [Co en$_2$ *d*-tart]Br to the dinitro salt without affecting the other form. When the reaction is allowed to proceed at room temperature, the precipitation of calcium tartrate goes on slowly but steadily until about half is precipitated; the reaction then stops unless the temperature is raised.

Summary

The presence of two or three optically active chelate groups in an octahedral complex tends to fix a definite configuration upon the complex ion as a whole, and in some cases the number of stereoisomers which can be isolated is limited to a small fraction of those theoretically possible. No such effect has been observed in complex ions containing only one asymmetric chelate group. It is now shown that while both the D and L forms of *dextro*-tartrato-*bis*-ethylenediamine cobaltic ion, [Co en$_2$ *d*-tart]$^+$, form when *dextro*-tartartic acid reacts with [Co en$_2$ CO$_3$]$^+$, they differ greatly in reactivity. When the mixture of the two is shaken with ethylenediamine at room temperature, part of the material reacts within two hours, giving *dextro*-[Co en$_3$]$^{+++}$. The remainder does not react even in twelve hours and can be recovered. At 50°, a 70% yield of *dextro*-[Co en$_3$]$^{+++}$ is obtained, and very little of the original material can be recovered. Evidently the less reactive form changes to the more reactive as the latter is used up. The reaction with hydrochloric acid seems to follow a similar course, and gives a large yield of *dextro*-rotatory *cis*-[Co en$_2$ Cl$_2$] Cl.

Reaction with calcium nitrite gives similar results; at room temperatures or slightly above, about half of the tartrato salt reacts, yielding *dextro*-[Co en$_2$ (NO$_2$)$_2$]$^+$. The remainder will not react at room temperatures. At higher temperatures the product is racemized.

These are evidently the first examples of asymmetric synthesis in the field of inorganic complex ions.

URBANA, ILLINOIS
NEW ORLEANS, LA. RECEIVED JUNE 21, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Hydrofluorination in the Presence of Boron Fluoride

BY ALBERT L. HENNE AND ROBERT C. ARNOLD

The addition of hydrogen fluoride to an olefinic hydrocarbon occurs with great ease[1]; addition also takes place easily with asymmetrically halogenated olefins such as $CH_2=CHX$, $RCH=CX_2$ or $RCX=CH_2$,[2] while the presence of the vinylic halogens on both sides of the double bond impedes or prevents it.[2] We have now observed that when the addition is carried out in the presence of small quantities of boron fluoride the reaction is greatly hastened, and even occurs where it had failed in the absence of boron fluoride.

Besides plain hydrofluorination, an alternation of HF additions and HX removals is observed, so that $RCH=CX_2$ gives not only RCH_2CX_2F, but also $RCH=CFX$, RCH_2CXF_2, $RCH=CF_2$ and RCH_2CF_3 in sequence. The presence of the boron fluoride increases the number of these steps and the extent to which they occur; the net effect is to increase the fluorine content of the final product.

The use of boron fluoride is particularly advantageous with heavily halogenated olefins, or with olefins bearing a CF_3 group which slows down the reactivity of their double bond. For more reactive olefins, boron fluoride may not be so desirable because it hastens resinification as well as addition; the economy of each case should be individually considered. The literature statement[1] that BF_3 is of no help should be restricted to non-halogenated olefins, where addition is so easy that it does not need any help.

Eleven different olefins were treated with hydrogen fluoride in the molar ratio of 1/2; when BF_3 was added, it was in the concentration shown in grams per mole of olefin in the table of experimental results.

The observed improvements can be explained by the formation of a coördinated complex $HF \rightarrow BF_3$, which enhances the percentage of ionic character of the H–F bond; this facilitates the separation of hydrogen as a proton, and makes it more available for addition to the more negative of the

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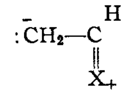
(1) Grosse and Lind, *J. Org. Chem.*, **3**, 26 (1938).

(2) Henne and Plueddeman, THIS JOURNAL, **65**, 1271 (1943), also Renoll, *ibid.*, **64**, 1115 (1942).

EXPERIMENTAL RESULTS

°C.	Hours	BF_3, g./mole	mole % A	mole % B	mole % recovery
$CHCl=CCl_2 + HF \rightarrow CH_2ClCCl_2F$ (A) + $CH_2ClCClF_2$ (B)					
60	24	12	18	0	88
95	12	3	16	3	92
95	3	6	19	2	90
95	12	6	35	9	82
95	1	12	16	2	93
95	3	12	20	3	90
95	12	12	45	10	84
95	24	12	60	9	86
95	3	24	38	2	87
120	20	20	35	22	57
160	12	0	0	0	95
$CHCl=CHCl + HF \rightarrow CH_2ClCHClF$ (A) + polymer (B)					
25	21	12	3	10	83
60	21	6	17	17	80
60	11	12	26	25	82
60	21	12	26	33	68
95	3	3	10	9	82
95	3	6	21	17	80
95	11	6	20	29	54
95	1	12	19	26	79
95	3	12	24	29	63
160	11	0	0	0	60
$CF_2=CCl_2 + HF \rightarrow CF_3CHCl_2$ (A) + polymer (B)					
95	10	24	0	0	97
150	12	24	42	traces	87
150	12	0	0	traces	80
$CFCl=CFCl + HF \rightarrow CF_2ClCHClF$ (A) + polymer (B)					
95	18	24	0	0	89
150	12	24	trace	trace	96
180	17	24	43	trace	87
180	17	0	0	trace	95
$CFCl=CCl_2 + HF \rightarrow CF_2ClCHCl_2$ (A) + $CF_2=CCl_2$ (B)					
180	17	24	33	17	82
180	17	0	0	0	89
$CCl_2=CCl_2 + HF \rightarrow CCl_2FCHCl_2$ (A) + $CFCl=CCl_2$ (B)					
95	13	30	0	0	82
140	7	24	7	trace	82
160	14	24	15	3	77
180	17	24	trace	20	87
180	17	0	0	0	97
$CHCl=CF_2 + HF \rightarrow CH_2ClCF_3$ (A)					
25	0.5	3	90	0	90
95	3	0	70	0	90
$CF_3CCl=CCl_2 + HF \rightarrow CF_3CHClCCl_2F$ (A) + $CF_3CCl=CClF$ (B)					
95	18	14	0	0	88
150	12	24	9	trace	91
180	17	24	22	7	90
180	17	30	21	10	91
180	17	0	0	0	92
$CF_3CH=CClF + HF \rightarrow CF_3CH_2CClF_2$ (A)					
95	24	5	65	0	85
120	24	0	0	0	85
$CH_3CH=CHCl + HF \rightarrow CH_3CH_2CHClF$ (A) + CH_3CHFCH_2Cl (B)					
60	6	2	12	20	56
100	4	0	10	20	60
$CH_3CCl=CHCl + HF \rightarrow CH_3CClFCH_2Cl$ (A) + $CH_3CF_2CH_2Cl$ (B)					
25	5	2	35	4	76
95	4	0	5	10	92

doubly bonded carbons. In support of this interpretation is the opposite fact that hydrogen fluoride addition to alkynes is *slowed down* by an oxygenated solvent such as ether or acetone[3]; in this case, complex formation with the solvent involves hydrogen bonding to the unshared electrons of the oxygen atom and obstructs separation as a proton for the first stage of addition to the triple bond.

The **direction** of addition was always that expected from the ionic character of the olefin. The vinylic halides acted as if entirely in their resonating form  $:\overset{-}{C}H_2-\overset{H}{\underset{\underset{X_+}{\|}}{C}}$, so that $RR'C=CR''X$ lead exclusively to $HRR'C=CR''XF$. By induction, a CF_3 group attached to a doubly bonded carbon caused a polarization opposed to that created by a CH_3 group, so that the polarization of propene and trifluoropropene could be represented as $CH_3\underset{+}{CH}=\underset{-}{CH_2}$ and $CF_3\underset{+}{CH}=\underset{-}{CH_2}$, respectively.

The **ease** of addition was not determined solely by the extent of polarization of the double bond. $CH_2=CCl_2$ accepted hydrogen fluoride more readily than $CHCl=CHCl$ and $CCl_2=CF_2$ more than $CClF=CClF$; $CH_3CCl=CClH$ was more easily hydrofluorinated than $CF_3CH=CClF$, yet the latter compound should be much more polarized than the former due to the combination of the eletronegative character of the CF_3 group and the vinylic character of the $=CFCl$ group. It is proposed that the *absolute* electron density around the double bond should also be taken into account; if this is done, it is to be expected that all ethylenes bearing a CF_3 group should be slowed down by the electron drainage away from the double bond; in agreement, $HCCl=CCl_2$ was found more easily hydrofluorinated than $CF_3CCl=CCl_2$. This explanation would be similar to that used for the meta-directing effect of an electronegative group on a benzene ring, and its retarding influence.

Experimental Details

Reaction Equipment.—For relatively low pressure, an 800-ml. steel vessel fitted as previously described[4] was used; for the higher pressures prevailing with more boron fluoride, a 200 cc. Aminco bomb was used, with superpressure fittings. Heating was done by immerging in a hot water-bath, or by strapping to the electrically heated mantle of a mechanical rocking devise.

Reagents.—Commercial grades.

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[3] Henne and Plueddeman, THIS JOURNAL, **65**, 587 (1943).

[4] Henne and Flannagan, *ibid.*, **65**, 2362 (1943).

Loading Procedure.—As previously described.[5,6]

Metering of Boron Fluoride.—A steel cylinder of known capacity was connected to a commercial tank of boron fluoride; the gas was admitted and the pressure created was noted. Next, this loaded steel cylinder was connected to the reaction vessel and the amount of boron fluoride delivered was computed from the observed drop in pressure. For very small additions of boron fluoride, a stream of the gas was passed through weighed liquefied hydrogen fluoride cooled to $-70°$.

Treatment of Reaction Products.—Gaseous products were released through a washing train and collected in a Dry Ice cooled receiver. Liquids were poured on cracked ice, neutralized, steam distilled, dried and separated by fractional distillation. In the few cases where the olefin and its addition product boiled practically at the same temperature, the composition of the distillate was estimated from the index of refraction, but this procedure was avoided as much as possible by using efficient dephlegmators.

Summary

The addition of hydrogen fluoride to halogenated olefins is accelerated or made possible by using small amounts of boron fluoride as a catalyst. The action is attributed to the formation of a coördinate compound $HF \rightarrow BF_3$, in which the H to F bond is weakened; this favors the supply of protons for the first step of the addition to the double bond. The direction and ease of addition are discussed. Eleven olefins have been tried and the results are tabulated.

COLUMBUS, OHIO RECEIVED SEPTEMBER 22, 1947

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[5] Henne and Haeckl, THIS JOURNAL, **63**, 2692 (1941).

[6] Henne and Whaley, *ibid.*, **64**, 1157 (1942).

[CONTRIBUTION FROM GENERAL MILLS, INC., RESEARCH DEPARTMENT]

Polyamide Resins from Dilinoleic Acid and Ethylenediamine. Molecular Weight–Viscosity Relationships[1a]

BY R. H. ANDERSON AND D. H. WHEELER

Introduction

In 1941, Bradley and Johnston[1b] isolated dilinoleic acid in a pure state as the methyl ester by fractional molecular distillation of the heat-polymerized methyl esters of the acids from dehydrated castor oil. They prepared polyesters of triethylene glycol with molecular weights of about 4300. Cowan and Wheeler[2] prepared polyesters with various glycols having molecular weights up to 20,000 to 30,000.

Polyamides have been prepared by Falkenburg, Teeter, Skell and Cowan[3] from various diamines and the residual polymeric fatty acids or esters (mixtures of dimer and trimers of linoleic and linolenic acids). The polyamide from ethylenediamine and these mixed polymeric fatty acids was proposed as a new synthetic coating material[4] under the name *Norelac*. The molecular weights of these resins were 3,000 to 5,000, determined by the method of end-groups. The same type of polyamide has been commercially prepared on a pilot plant scale,[5] and is apparently finding some use as a coating for heat-sealing and laminating paper.

No description has appeared of polyamides from pure dilinoleic acid and ethylenediamine. The present investigation describes the preparation and some properties of such linear polyamides having molecular weights from 2,000 to 15,000.

Viscosities were determined on solutions in 1:1 butanol-toluene solvent at concentrations from 0.2 to 9.8 g. per 100 cc. and intrinsic viscosities were calculated. The intrinsic viscosity was found to be related to molecular weight by the formula

$$[\eta] = KM^a \qquad (1)$$

Flory and Stickney[6] have pointed out the fact that a relationship such as equation (1) really relates to *viscosity* average (M_v) rather than *number* average (M_n) molecular weights of non-homogeneous polymers, and that M_v is greater than M_n, but less than M_w, the weight average molecular weight.

Now, the molecular weights, as determined by end-group titration in the present study, are actually *number* average molecular weights. The fact that the determined molecular weights and viscosities of these polyamides agree with equation (1) is interpreted to mean that these polymers, as prepared, have essentially a constant ratio of M_v to M_n. Flory[7] has shown on theoretical grounds that for bifunctional condensation polymers, M_w/M_n approaches 2 for higher polymers. Taylor[8] has shown that the ratio is very nearly 2 for 66-nylon polyamide, and that the value of M_v is close to that of M_w. The weight average can therefore be used interchangeably with M_v without introducing serious error.

When mixtures of condensation polyesters or polyamides are considered, the importance of considering a weight average rather than a number average in calculating viscosity is apparent. The viscosity in the molten state of a mixture of polyesters was shown by Flory[7] to agree with the M_w,

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[1a] Paper No. 79, Journal Series, General Mills, Inc., Research Department.

[1b] Bradley and Johnston, *Ind. Eng. Chem.*, **33**, 86 (1941).

[2] Cowan and Wheeler, THIS JOURNAL, **66**, 84 (1944).

[3] Falkenburg, Teeter, Skell and Cowan, *Oil and Soap*, **22**, 143 (1945).

[4] Cowan, Lewis and Falkenburg, *ibid.*, **21**, 101 (1944).

[5] Cowan, Schwab and Falkenburg, *Modern Packaging*, [9] **17**, 103 (1944).

[6] Flory and Stickney, THIS JOURNAL, **65**, 372 (1943).

[7] Flory, *ibid.*, **62**, 1057, 3032 (1940).

[8] Taylor, *ibid.*, **69**, 635, 638 (1947).