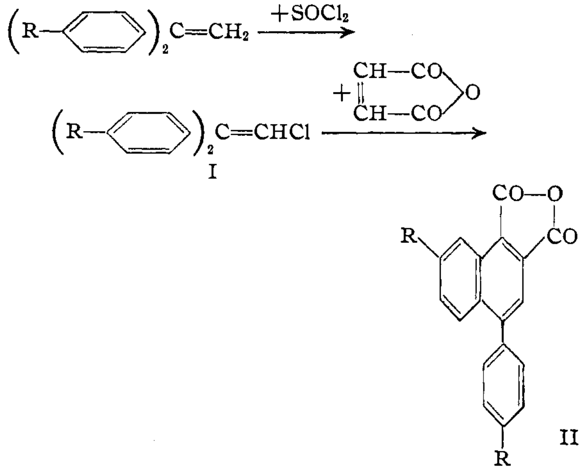


It will be of interest to investigate, whether diarylvinyl fluorides follow the same course of reaction as the bromides and chlorides.

Experimental

As an example the reaction with 1,1-di-(*p*-chlorophenyl)-ethylene is described:

(1) **1,1-Di-(*p*-chlorophenyl)-ethylene and Thionyl Chloride.**—The ethylene (12.5 g.) and thionyl chloride (30 g.) were refluxed for eight hours. Excess thionyl chloride was removed *in vacuo*, the residue dissolved in benzene, washed, dried and fractionated. A clear greenish oil distilled at 158–162° (1.0 mm.), which crystallized upon trituration with methanol. From the same solvent the di-(*p*-chlorophenyl)-vinyl chloride (I, R = Cl) was obtained in long lancets, m. p. 65–66°; yield, 9.5 g. (68%).

Anal. Calcd. for $C_{14}H_9Cl_3$: C, 59.4; H, 3.2. Found: C, 59.1; H, 3.4.

(2) **Condensation with Maleic Anhydride.**—The above vinyl chloride (1.1 g.) and maleic anhydride (4 g., 10 equiv.) were heated first to 180° for three hours, then to 220° for one hour. The reaction mixture was dissolved in acetic acid and left overnight; 600 mg. (46%) of the anhydride (II, R = Cl) was obtained, which after crystallization from benzene–ligroin formed yellow rods of m. p. 196–197°, not depressed by admixture of the same compound described previously.[3]

---

[3] F. Bergmann and Szmuszkowicz, *ibid.*, **70**, 2748 (1948).

WEIZMANN INSTITUTE OF SCIENCE
REHOVOT, ISRAEL
RECEIVED JUNE 9, 1949

The Copolymerization of Some Fluorinated Olefins

BY MAURICE PROBER

The potential availability of some perhalofluorinated olefins prompted a study of their copolymerization behavior. Each of the fluoroölefins: chlorotrifluoroethylene, unsymmetrical dichlorodifluoroethylene, symmetrical dichlorodifluoroethylene, 1,1,2-trichloro-3,3,3-trifluoropropene, 2,3-dichloro-1,1,1,4,4,4-hexafluorobutene-2,1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene and hexafluorocyclobutene was copolymerized with vinyl acetate, styrene, vinyl chloride, methyl methacrylate and acrylonitrile. There are scattered patent references[1,2,3,4] to some of these copolymers and a recent paper by McBee, Bachman and Hill[5] describes the copolymers of unsymmetrical dichlorodifluoroethylene with vinyl acetate, styrene, butadiene and isoprene.

In this study approximately equal molar quantities of the two monomers were polymerized with benzoyl peroxide, and the composition of the polymer established by elementary analysis. A qualitative picture of the relative reactivities of these olefins is given by the ratios of Table I.

In virtually all of the experiments, the fluorine-free comonomer was better than 90% polymerized, and the relative conversions of fluorinated monomer to polymer follow the order in Table I. The degree of polymerization varies with the comonomer and is greatest with vinyl acetate, styrene and vinyl chloride, and is less extensive with methyl methacrylate and acrylonitrile. The results are also illustrative of the lower reactivity of the 1,2-dichloroethylene as compared to the 1,1-dichloroethylene.

Auxiliary experiments with the fluorinated olefins alone demonstrated that only chlorotrifluoroethylene polymerizes with benzoyl peroxide, indicating that the other polymers are true copolymers. Solubility tests on the chlorotrifluoroethylene polymers indicated that this fluorinated olefin also forms a copolymer.

Experimental

The unsymmetrical dichlorodifluoroethylene, symmetrical dichlorodifluoroethylene, 1,1,2-trichloro-3,3,3-trifluoropropene, 2,3-dichloro-1,1,1,4,4,4-hexafluorobutene-2, and 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene were made available for this study through the courtesy of Dr. B. H. Wojcik and Mr. L. S. Bovier of the Hooker Electrochemical Company. The chlorotrifluoroethylene was purchased from E. I. du Pont de Nemours and Company, and the hexafluorocyclobutene was synthesized according to the procedure of Henne and Ruh.[6]

The fluorinated olefins were washed with concentrated sulfuric acid, water, dried and fractionally distilled. Middle cuts of narrow boiling range were taken for the polymerization runs. The other monomers were purified by rectification of the commercially available pure compounds. The non-volatile monomers and two weight per cent. (based on the total monomer charged) of recrystallized benzoyl peroxide were placed in heavy-walled Pyrex tubes and the volatile monomers distilled in under vacuum. The sample was thawed, refrozen, and sealed under vacuum. Approximately equal molar quantities were selected. The tubes were heated at 60–65° for seventy-two hours. The polymer was then pulverized, and the excess monomer removed by heating in a vacuum. (Some samples were purified by precipitation from solvents, but the analytical results were substantially the same as for vacuum treated samples.) The polymer composition was determined by chlorine analysis (Parr bomb) or by carbon analysis when the former method was not feasible. The experimental error in Table I is approximately ±0.03.

---

[1] I. G. Farben, French Patent 796,026 (March 27, 1936).

[2] F. G. Pearson (to American Viscose Corp.), British Patent 584,742 (Jan. 22, 1947).

[3] Imperial Chemical Industries, British Patent 590,390 (July 16, 1947).

[4] E. I. du Pont de Nemours & Co., British Patent 596,943 (Jan. 14, 1948).

[5] McBee, Bachman and Hill, *Ind. Eng. Chem.*, **41**, 70 (1949).

[6] Henne and Ruh, THIS JOURNAL, **69**, 279 (1947).

TABLE I

RATIO OF THE MOLE FRACTION OF FLUORINATED MONOMER IN POLYMER TO THE MOLE FRACTION OF FLUORINATED MONOMER IN MONOMER MIXTURE

	Vinyl acetate	Vinyl chloride	Styrene	Methyl methacrylate	Acrylonitrile
Chlorotrifluoroethylene	0.73	0.71	0.42	0.29	0.10
Unsymmetrical dichlorodifluoroethylene	.82	.65	.56	.26	.14
Symmetrical dichlorodifluoroethylene	.60	.29	.22	.06	< .05
1,1,2-Trichloro-3,3,3-trifluoropropene	.54	.10	< .05	< .05	< .05
2,3-Dichloro-1,1,1,4,4,4-hexafluorobutene-2	.55	.10	< .05	< .05	< .05
Hexafluorocyclobutene	.11	< .05	< .05	< .05	< .05
1,2-Dichloro-3,3,4,4,5,5-hexafluorocyclopentene	.18	< .05	< .05	< .05	< .05

The chlorotrifluoroethylene–vinyl acetate and methyl methacrylate copolymers were completely soluble in ethyl acetate. The vinyl chloride copolymer was completely soluble in ethylene dichloride. Nearly all of the styrene copolymer was soluble in benzene, but 10% was polymeric chlorotrifluoroethylene, which was insoluble in benzene as well as in the previously mentioned solvents.

RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENECTADY, N. Y.

RECEIVED AUGUST 10, 1949

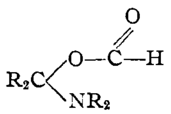
Preparation of Tertiary Amines by the Leuckart Reaction

BY PETER A. S. SMITH AND A. JOHN MACDONALD

We had recently begun investigating the preparation of tertiary amines by the reaction under Leuckart conditions of ketones with secondary amine formates, when the publication by Bunnett and Marks[1] on the same subject appeared. Because of their considerable priority, we are abandoning further work on this subject, but wish to record our work to date insofar as it differs from their results.

We have investigated the preparation of tertiary amines from three ketones, all of which were also investigated by Bunnett and Marks. Our experimental conditions were different in that we used amine formates directly instead of first dehydrating them to formamides, and a mole ratio of amine formate to ketone of only 2:1 instead of 4:1. Furthermore, we did not use excess formic acid, or other catalyst, such as magnesium chloride. Our results are presented in the accompanying table along with those of Bunnett and Marks for comparison. The success of the reactions reported here as compared with the failure of the uncatalyzed reactions reported by Bunnett and Marks can be attributed to the greater reactivity of ammonium formates compared to formamides in the Leuckart reaction.[2,3]

Certain proposals regarding the mechanism of the Leuckart reaction have embodied the intermediate formation of N-alkyl imines, $R_2C{=}N{-}R$, recently shown capable of being reduced by formates.[3] The success of the Leuckart reaction with secondary amines, which cannot proceed by such intermediates (unless they are charged, as $(R_2C{=}NR_2)^+$), suggests that the path through N-alkyl imine formation may not be a necessary one, although it may very well function as a concurrent reaction path in cases where such intermediates can be formed. We have been considering favorably the intermediate occurrence of formate esters of carbinol amines



which might rearrange to a tertiary amine and carbon dioxide by a 1,3-hydride shift of the type which seems probable in the Cannizzaro reaction[4] and which was foreshadowed by Webers and Bruce.[5] Such a compound might arise either by a conventional esterification of the carbinol amine, or by the addition of formic acid to the imine. These considerations can also be applied to a synthesis of tertiary amines by a Leuckart-like reaction reported in the patent literature,[6] which appears to have been overlooked in previous discussions. The reactions are carried out by heating mixtures of secondary amines, aldehydes or ketones, and methyl formate at 260–270°, and

TABLE I

TERTIARY AMINES FROM KETONES AND PIPERIDINE

Ketone	Moles of reagents: pip. formate +	Amine yield, % Conv.[b]	Adj.[c]	Bunnett and Marks' results[a] Conv.[b]	Adj.[c]
Cyclohexanone	2	62	65	54	54
Heptanone-2	2	14	29	54	54
Heptanone-2	8 + 1 HCOOH	8	19		
Acetophenone	2	14	26	29	49

[a] The reagents used in each case were 2 moles N-formylpiperidine, 1 mole formic acid and 0.15 mole $MgCl_2 \cdot 6\,H_2O$ per mole ketone. [b] Conversion; yield of amine based on ketone used. [c] Adjusted yield, corrected for recovered ketone.

---

(1) J. F. Bunnett and J. L. Marks, THIS JOURNAL, **71**, 1587 (1949). A comprehensive article on this subject by E. Staple and E. C. Wagner (*J. Org. Chem.*, **14**, 559 (1949)) appeared a month after this note was submitted.

(2) F. S. Crosley and M. D. Moore, *J. Org. Chem.*, **9**, 529 (1944).

(3) E. R. Alexander and R. B. Wildman, THIS JOURNAL, **70**, 1187 (1948).

(4) E. R. Alexander, *ibid.*, **69**, 289 (1947); T. A. Geissman, in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 96.

(5) V. J. Webers and W. F. Bruce, *ibid.*, **70**, 1422 (1948).

(6) W. Speer, German Patent 620,510 (to I. G. Farbenind A. G.), *C. A.*, **30**, 732[6] (1936); I. G. Farbenind A. G., French Patent 751,286, *ibid.*, **29**, 3687[9] (1935).