

# FRIEDEL-CRAFTS AND RELATED REACTIONS

*Edited by*

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## I

General Aspects

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## Introduction

Part of the importance of this new book derives from the highly important class of book to which it belongs. Much more of its value derives from its unique individual characteristics.

Its class is that of what today might well be called a "source book," strictly speaking a secondary source, but still the practical starting-point, the immediate source of knowledge, for anyone who wishes to understand a major subject in order either to contribute to it or to apply it. Even 20 years ago, such books were not a necessity: one could master a field of organic chemistry on the basis of anything from a week to a month spent with factual compendia and the original papers to which they gave reference. Today, with the increase by an order of magnitude in the rate of growth of chemical literature, no such easy entry into major subjects is possible, and the modern integration of organic chemistry renders the majority of formerly small subjects well-integrated parts of major ones. In these circumstances most recruits to a particular field of research are taught by others already in that field. At a later stage of life, however, such guided entry is less easy to arrange, and the would-be investigator can pass into his desired field only by way of the "source book." From it he can see the whole body of knowledge, together with the details of its frontiers, and thus he can judge where his personal operations ought to start. It is hard to think of any task more important for the maintenance of chemical research than the production of a source book in a field where none exists.

*Friedel-Crafts and Related Reactions* is such a book. Friedel-Crafts reactions embrace all electrophilic organic reactions catalyzed by electron-deficient compounds—Lewis acids—whether these are molecules or cations, and include such reactions as are likewise catalyzed by those proton acids which are strong enough to act somewhat like Lewis acids, perhaps like the proton they donate, if it were free, when it would be a Lewis acid (as proton acids themselves are not). The electrophilic reactions include substitutions, additions, isomerizations, polymerizations, and a number of other general processes. The electron deficiencies on which catalysis depends may, when both neutral and cationic catalysts are taken into account, be provided by any of a very considerable variety of elements. All

these reactions are related, and the field is thus an enormous one, in extreme need of a source book if it is to be satisfactorily developed.

It is a further very good general feature of *Friedel-Crafts and Related Reactions* that it is a *book* rather than what librarians call a "continuing publication." It will comprise four volumes, but as this one appears the others are being printed, and all will appear within a year. To the year of its production this book will be authoritative and complete.

The arrangement of chapters is logical, and the place of each in the complete account is so obvious and natural that one notices very little the discontinuities of style and approach that so often spoil the reading of multi-author books. Each of these authors obviously had as complete or almost as complete an understanding of the context into which his contribution had to fit as if he had written the rest of the book himself. This is, of course, a tribute to the collaborative spirit of these very highly distinguished authors. It is equally a tribute to the organization and leadership of the Editor, Dr. G. A. Olah. Dr. Olah had responsibility not only as Editor, but also as an author, for he has written a not inconsiderable fraction of this long book himself.

The book starts with the history of the Friedel-Crafts reaction, and a consideration of its scope, and of the manner in which this has become widened. The next group of chapters deals with the general chemistry of the reactants themselves. The first of these chapters is one by Dr. R. J. Gillespie on Lewis acids and proton acids which clearly states the principles involved and should dispel any confused thinking that has hitherto clouded this subject. These chapters lead naturally to the next group, which is concerned with the modes of combination, complex formation, or general interaction of the reactants in pairs, and thus finally with a consideration of the intermediates that actually participate in Friedel-Crafts reactions. Chapters follow on spectroscopic and isotopic evidence on intermediates, and hence on mechanism; on constitutional effects on reactivity and selectivity; and then on the thermodynamic and stereochemical aspects of the reaction. All these chapters are excellent, as their authorship would indeed entitle one to expect. They convey a sense of authority and completeness, and, to the reader who has completed his reading of them, a sense of mastery of the field. The chapter by Dr. D. R. Stull on thermodynamic aspects is particularly fundamental and very lucid. When the kinetic aspects of the reaction can be written up in an equally fundamental way we shall indeed be close to a real mastery of this great family of reactions.

The above is a description in outline of this first volume. The remaining three volumes deal with the various Friedel-Crafts reactions, arranged by classes.

The Editor and authors are all distinguished contributors by research to chemical knowledge. To such men, it is always much more enjoyable to contribute oneself to a field of knowledge than to work with the object of displaying the field for the help of other contributors. The Editor and authors have obviously taken much time out of their personal research programmes in order to produce this book. We, at the receiving end, must feel deeply grateful to them for having fulfilled a task of such magnitude and of such vital importance to future research.

C. K. INGOLD

## Editor's Preface

It was eighty-six years ago that Friedel and Crafts published from their Sorbonne Laboratory the first observation on the action of aluminum chloride in organic reactions, a work which led to numerous synthetic methods bearing their names. Friedel-Crafts reactions, as we know them today, have grown with the Grignard methods to perhaps the most versatile and frequently used tools of organic chemistry, covering aromatic and aliphatic systems alike. This latter field has long failed to receive its deserved recognition and many of our textbooks still leave the unjustified impression that the Friedel-Crafts reactions are related only to aromatic systems.

The realization that Friedel-Crafts reactions are general acid-catalyzed processes and by no means limited to anhydrous aluminum chloride as the catalyst, extended substantially the scope and versatility of the reactions. It is indeed somewhat difficult today to define the limitations of what we understand by Friedel-Crafts type reactions and what should differentiate them from general acid-catalyzed electrophilic reactions. Authors contributing to *Friedel-Crafts and Related Reactions* considered this question before defining the scope of their treatment and agreed that the time-honored custom in organic chemistry to name basic reactions from their original investigators should be maintained by naming Friedel-Crafts type reactions those processes which proceed under the general conditions laid down by the pioneering investigators, and which can also be carried out by the later realization of the general acid-catalyzed nature of the reactions. Thus in the present treatise reactions catalyzed by all related acid catalyst systems are incorporated: Lewis acid type halide, Brønsted-Lowry type proton acid and other related acid-catalyzed reactions are treated alike if they are equally capable of effecting the reactions.

Over the years the number of investigators in the Friedel-Crafts field and the amount of material in both the scientific and patent literature have grown tremendously. It is obviously no longer possible for any individual to attempt to survey the field, even if limitations were introduced confining it to one specific catalyst, as was done in the time-honored and excellent books of Thomas and Kränzlein dealing with aluminum chloride catalyzed reactions.

The reason for a collective effort of collaboration by a rather large number of contributing authors is therefore indicated.

It was with considerable reluctance three years ago that I accepted the Publishers' invitation to act as editor of a comprehensive monograph on Friedel-Crafts reactions. My reluctance was due neither to a lack of enthusiasm for the topic nor the conviction that a comprehensive and critical coverage of the field would be untimely; it was entirely due to the realization that the field of Friedel-Crafts reactions had grown to such proportions that an attempt to try to survey it—even in a somewhat limited way—would inevitably put a very substantial and perhaps even prohibiting burden on all the authors participating in the project.

The deepest gratitude is extended to all those who generously agreed to participate in this project. The authors sacrificed time and effort in a way that can only be appreciated by those actually involved, and it was through their efforts that this book was born. The editor can only add that it was a unique pleasure to give his limited services in coordinating this project. His task was greatly facilitated by the splendid cooperation and unselfish help given by all contributors.

The extraordinary convergence of organic and inorganic reagents and catalysts in the Friedel-Crafts field provides an area of mutual interest shared by experimental and theoretical chemists of both fields alike—hence our effort to include a number of chapters emphasizing the inorganic and physical-chemical aspects of the field. It is hoped that discussion of the inorganic catalyst systems, the nature of acid catalysts, the complexes formed between catalysts and reagents or products, as well as the thermochemical, kinetic and mechanistic aspects of the systems, will arouse interest in readers otherwise interested perhaps only in the organic chemical aspects and will add to a better understanding of the problems involved.

In all fields undergoing rapid expansion, and Friedel-Crafts type reactions are in a state of continuous growth of extreme proportions, the problem of merely reporting significant advances is difficult enough. To attempt a critical evaluation of data and results in a permanent reference text is next to impossible. On the other hand as the volume of published information in a field becomes larger, the greater is the need for the average chemist to be informed of new lines of progress having significance, and one hopes, major scientific merit. It is therefore highly desirable to provide not only a more or less complete summary of data—which could today perhaps be achieved much better by electronic rather than human brains—but



also to attempt to achieve some evaluation of the data and to formulate a general picture of a specific field from both a theoretical and preparative chemical point of view. This latter consideration is emphasized throughout the book.

We cannot claim to have achieved a really complete coverage of such an immense field, but perhaps this would have been too much to expect. The individual authors have used their own judgment in limitation, critical evaluation and discussion of their topics. Whenever comprehensive surveys on any field were available (like those available in monographs, chapters of *Organic Reactions*, articles of *Chemical Reviews*, etc.) no repetition was attempted—besides the essentials needed for the general discussion up to the time of the previous survey. In general the authors have provided comprehensive data, frequently in tabular form, to cover the literature to the end of 1960, and in most essential novel developments making use of additions during proofreading up to late 1962.

Limitation was impressed on the treatment of rearrangements (with the exceptions of typical Friedel-Crafts isomerizations) as an extensive monograph on "Molecular Rearrangements" (edited by de Mayo) is currently being published covering many of these.

Short indexes at the end of the individual volumes and a comprehensive author and subject index at the end of Volume IV are provided.

No attempt has been made to equate styles of presentation of different chapters besides a combined effort by the authors and editor to coordinate topics in order to achieve a suitable unity of the general project and to eliminate unnecessary overlapping. It is believed that each of the authors—who are actively engaged in research in their own specific field of interest—knows best how to present his own subject. Indeed it is hoped that each chapter will reflect to a certain degree the character and personality of its author.

It was realized from the beginning of this project that owing to the scope and volume of the material to be covered we would inevitably be dealing with a multi-volume publication. Lest the first volumes should be outdated when the last was published, it was decided from the beginning to plan the book as a whole and to proceed with all volumes simultaneously. As the first volume is published, Volumes II-III are being printed and it is hoped that publication of the whole project will be completed by the end of the year. Considering the inevitable delays in a technical publication of this size where, owing to the substantial number of contributing authors, we are dealing with a "chain process" determined by the

slowest member of the series—frequently the editor himself—this is considered a fair, although by no means a spotless record.

It is not possible to thank all who contributed so greatly to the realization of this project. The editor personally would like to thank the Dow Chemical Company for its generous understanding and substantial help given to this project, without which he would have been unable to cope with his task. Particular gratitude is expressed to the staff of the Midland and Sarnia Technical Libraries of Dow Chemical in connection with their help in providing literature. My wife, Judith, gave most valuable assistance throughout the whole editing and preparation of the manuscript. Mr. R. E. A. Dear helped in the editorial work and prepared the indexes. Dr. C. G. Carlson shared in the task of proofreading. Mrs. Bernice Robb and Mrs. Fran Cadwallader are thanked for typing the manuscript. Nearly all of the contributing authors and many other colleagues and friends, too numerous to be thanked here individually, read parts or all of the different chapters and helped with their useful suggestions and criticism to improve the manuscript.

The publishers and the printer are thanked for their excellent job.

Sarnia, Ontario  
January, 1963

GEORGE A. OLAH

Action de  $\text{H}_2$  unpendide sur  $\text{C}_2\text{H}_2\text{Cl}_3$   
 Réaction très vive, beaucoup de  $\text{HCl}$ , peu  
 de gaz; résidu brun-rouge, gris avec l'eau  
 dans une matière brune fragile et  
 de l'aluminium et soluble de la benzine.

Ours avec zinc et iode.

Fig. 1. The first experiment of the Friedel-Crafts type, recorded in Friedel's laboratory notebook. The page is not dated but three pages later the date April 3 (1877) (in Crafts' handwriting) is recorded (see Fig. 3). (All the illustrations are reproduced in the same chronological order as the original entries in Friedel's records.)

10 gr  $\text{C}_2\text{H}_2\text{Cl}_3$ .  
 10 gr benzine  
 1 gr aluminium. réaction très vive  
 et dég. environ 2 lode  
 obtenu.  $\text{HCl}$  (condensé de l'eau) environ 4 gr.  
 un peu de gaz brûlant avec  $\text{C}_2\text{H}_2$ ,  
 une matière résineuse soluble de la benzine  
 et dans la benzine, non dans l'alcool.  
 présence d'une impureté

au. les opérations  
 15 gr  $\text{C}_2\text{H}_2\text{Cl}_3$   
 40 gr benzine  
 1 gr aluminium  
 L'alcool de l'eau  
 $\text{HCl}$  dégagé = 5 gr

Fig. 2. Condensation of 1,1,1-trichloroethane with benzene in the presence of aluminum and iodine. The amount of  $\text{HCl}$  evolved is recorded by Crafts.

Apr 3<sup>rd</sup>

Aluminium + Cl Amyl

50 = 60  
114 11  
35.5 35  
106

$$\frac{Al}{3} = 9$$

Cl Amyl = 26 gms

Al - 2.5 gms

lavi à l'air sulfuré

Apr 5 Cl Amyl inactif, distillé

Cl Amyl 100

+ 2 gms Al (sans Iod)

HCl = 4 gms

+ 2 ~ ~

~ = 6 1/2

+ 2 gms ~

~ = 4

Fig. 3. The first experiments with amyl chloride. Both are entries by Crafts.



flacon à eau. 17.5 gr

$Cl^{-} + H^{+} = 15 gr$   $Al^{2+}$  en 2 fois 2 gr

voir réaction.

La part de HCl environ

il y a 3.5 de HCl dans le

liquide

$$\begin{array}{r} 60 \\ 11 \\ 35.5 \\ \hline 106.5 \\ 36.5 \\ \hline 143 \\ 182.5 \\ 365 \\ \hline 547.5 \\ 150 \end{array} \quad \begin{array}{r} 106.5 \\ 5.1 \end{array}$$

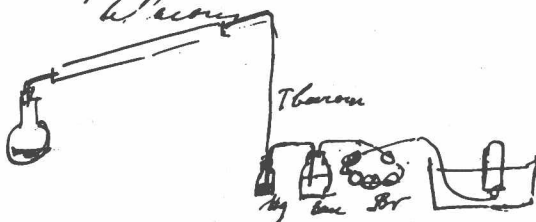


Fig. 4. The first recorded use of aluminum chloride in such experiments. The calculation shows that 5.1 g. HCl should be evolved, whereas 3.5 g. were collected during the experiment.

Al<sub>2</sub>Cl<sub>6</sub>  
C<sub>5</sub>H<sub>8</sub>Cl

app. - amersan sans tubes en cavithone terminale  
pne 2389.5 gr

M<sup>1</sup>Cl<sup>6</sup> 11 gr en 2 fois.

J'ai bord 5 gr puis 11 de chlorure et une dose de 11 gr  
à une légère réaction qui lors qu'on chauffe  
pour ôter le chlorure à 60° puis à 160°  
On a obtenu dit alors et on a obtenu encore 8 gr.  
More très violente réaction.

Fig. 5. A repeat with a larger quantity (11 g.) of aluminum chloride.

Mai 3

Amalg Cl. 100.

Al<sub>2</sub>Cl<sub>6</sub> 18 grms added at once to  
Am Cl in flask that had already served violent reaction

App in Al 348.8

lost

Fig. 6. Another entry by Crafts where aluminum chloride was added to a previous reaction mixture. A "violent reaction" was noted followed by the terse comment "lost"!

7 Mai. Benzine crist. 10 gr  
Al<sup>1</sup>Cl<sup>6</sup> 5 gr  
sans réaction

(La benzine avec Al<sup>1</sup>Cl<sup>6</sup> semblait réagir lentement à  
l'ébullition, mais on obtient peu à peu le 2.  
plus haut que la benzine)

Un peu de gaz et des produits distillés à de  
température moins haute, bien au-dessus de 80°.

Fig. 7. Action of aluminum chloride on benzene in a sealed tube. Little or no reaction appears to have occurred.

$\text{H}_2\text{N}$ . Benzine, Chlorobenzol,  $\text{AlCl}_3$ .  
 $\text{H}_2\text{N}$   $\text{H}_2\text{N}$   $\text{H}_2\text{N}$   
 $\frac{12}{78}$   $\frac{60}{106.5}$   $\frac{55}{268}$

benzine 50 gr  
 $\text{AlCl}_3$  25 gr  
 $\text{H}_2\text{N} = 79$  (Tube +  $\text{H}_2\text{N}$  20 gr)

réaction avec = 48 gr.  
 ajoutée au pur de  $\text{H}_2\text{N}$  et de  $\text{AlCl}_3$ , et la benzine  
 purifiée après de l'acide de l'acide, à froid.  
 réaction négative, qui devient plus vive  
 sous un poir que l'on ajoute  $\text{H}_2\text{N}$ . Il  
 se forme bientôt deux cristaux.

Fig. 8. The classic reaction of benzene with amyl chloride in the presence of aluminum chloride. This has often been quoted as the first Friedel-Crafts reaction when in fact it is recorded 14 pages after the first experiment (Fig. 1).

Benzine 70 gr  
 Benzol 20 gr  
 $\text{AlCl}_3$  10 gr.

App. à  $\text{H}_2\text{N}$  wt. = 291.0 grms

Rien

Fig. 9. An attempt at the condensation of benzene with chlorobenzene. Friedel's emphatic "Rien" appears after a line written in Crafts' hand.

May 13.

70 gms  $\text{AlCl}_3$  + 18  $\text{Al}_2\text{Cl}_6$  added gradually

The reaction was too active and about (1/4?) ligand escaped.

18 gms  $\text{Al}_2\text{Cl}_6$  seemed to be an excess i.e. the last portion did not wholly dissolve and the chloroaluminum of HCl was nearly ended

much gas was given off when the product was treated with  $\text{Ag}$ .

The prodn. distilled. entirely up to and a very high temp

Fig. 10. One of the few pages entirely in English. Again the work of Crafts, it is dated May 13 yet appears four pages after the experiment dated May 14 (Fig. 8).

19

Amylbenzene 185-190°

190° =  $\text{Benzene} + 0.7158$

$$\begin{array}{r} 0.5158 \\ \hline 0.200 \end{array}$$

0.45° =  $\text{Benzene} + 0.8858$

$$\begin{array}{r} 0.1978 \quad 191 \\ 118 \quad 0.02094 \quad 200 \\ \hline 110 \quad 10.97 \end{array} \quad \begin{array}{r} 0.688 \\ \hline 0.1985 \end{array}$$

90° =  $\text{Benzene} + 4.869$

$$\begin{array}{r} 4.160 \\ \hline 0.658 \end{array}$$

$$\begin{array}{r} 1.9755 \quad 11 \\ 105 \quad 0.17959 \quad 2 \\ \hline 65 \quad 19.79 \\ 100 \end{array}$$

$$\begin{array}{r} \text{C}^6\text{H}^5\text{C}^5\text{H}^{11} = \\ = \text{C}^{11}\text{H}^{16} \\ \hline 132 \\ 16 \\ \hline 148 \\ \hline 13200 \quad 148 \\ 1360 \quad 89.18 \\ 280 \\ 132 \\ \hline 1600 \quad 148 \\ 1200 \quad 10.81 \\ 86 \end{array}$$

Fig. 11. Analysis of the amylbenzene prepared in the experiment of May 14, 1877. Theoretical percentages are calculated at the right: C, 89.18; H, 10.81. The results obtained were C, 89.79; H, 10.97.

Et Mat. Benzine 90 gr  
 ICH<sub>3</sub> 20 gr  
 H<sub>2</sub>CCl<sub>6</sub> 10 gr

No action cold nor on boiling at ord. temp.  
 heated under pressure of 45 cc. bz in ag bath

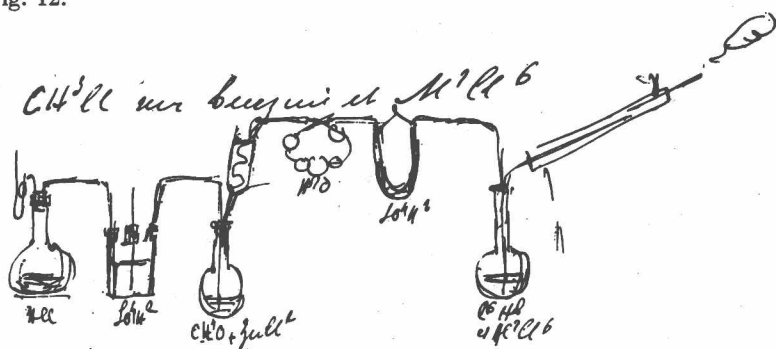
Action begins about 80° with disengagement, y  
~~the~~ #5 and the disengagement  
 was well sustained at 80° - 90°. (NB the  
 temperature was taken in the ag bath)

The product was treated w. ag. (much was lost by  
 violent reaction and the liquid was distilled)

1<sup>st</sup> distil Mast. = 85° - 90° residue 90° - 105° little 105° - 130°  
 about equal quant + 130° I appeared 105° - 130° in small quant  
 2<sup>nd</sup> distil 78° - 87° - 87° - 105° - 105° - 130°  
 and still considerable above 130° The prod was about in same  
 proportion as before.

There was too little to purify —

Fig. 12.



Heat-chamber ben benzine et H<sub>2</sub>CCl<sub>6</sub> à 60°  
 benzine chloroforme et un ballon à alcool  
 de 100.

Benzine 200 gr

H<sub>2</sub>CCl<sub>6</sub> 20 gr

L'apport de la benzine et de l'alcool  
 dans le traitement par le chloroforme.

Fig. 13.



Br-Methyl 40  
Benzine 35.  
Al<sub>2</sub>Cl<sub>6</sub> 12 grms

The Al<sub>2</sub>Cl<sub>6</sub> was added at once & after a few moments reaction became violent. Disengagement of HBr? or H<sub>2</sub> & distillation of Br<sub>2</sub> took place with ice and allowed to set under a pressure about 50 cm Hg. at ord. temp. The reaction went on for a long time and was finally stimulated by heating in a bath up to 60° between 30° - 40°. The reaction was H was necessary to continuously heat higher to produce the same apparent reaction.

The product was added in small portions to Ag but no pains were taken to avoid a certain heating so that most of the remaining CH<sub>3</sub>Br was probably some Benzol.

Results after 4 distill. The two layers were distilled separately for 1<sup>st</sup> distill. the lower gave more highly purified.

74-90 = 1.27 grms	95-98 = 1.2 grms	+ 195° = ?
90-92 14.5 " 20.1	98-115 = 0.9 "	
92-94 4.4 "	115-125 1. "	
94-98 2.3 "	125-135 1.2 "	( 2.4 grms
98-95 2.7 "	135-138 2.4 "	+ 195° = 1.5° dist.
(95-98) (1.2) was distilled with H <sub>2</sub> SO <sub>4</sub> + CuO & gave no Benzol as 1.1 grms.	138-145 1.7 "	+ 200° not dist. but
<u>Total 39.9 grms -</u>		all for upper

Fig. 14.

Fig. 12. The reaction of benzene with methyl iodide in the presence of aluminum chloride. Again a too vigorous reaction has led to extensive losses so that after two distillations further purification was impractical.

Fig. 13. The action of methyl chloride on benzene in the presence of aluminum chloride. Note the complexity of the apparatus.

Fig. 14. One of the more completely documented experiments, the reaction of benzene with methyl bromide in the presence of aluminum chloride.