

Origin of Papers

- very most paper from Germany, from recognised Universities and recognized Professors
- but also from Ahmadabad, Patna (India), Tokyo (Japan), Bucharest (Romania), Warsaw (Poland), Sao Paulo (Brazil)
- not from the US

Main Topics

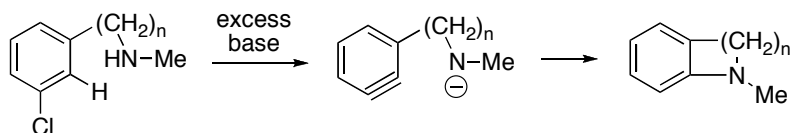
- sugars, lignin
- all kinds of standard heterocycle syntheses with N, S
- steroids (no total syntheses)
- Stetter: Adamantane Chemistry

Miscellaneous

- reactions done on a very big scale (big apparati)
- chiral products are derived from chiral starting material (no total synthesis)
- paper chromatography to purify compounds preparatively

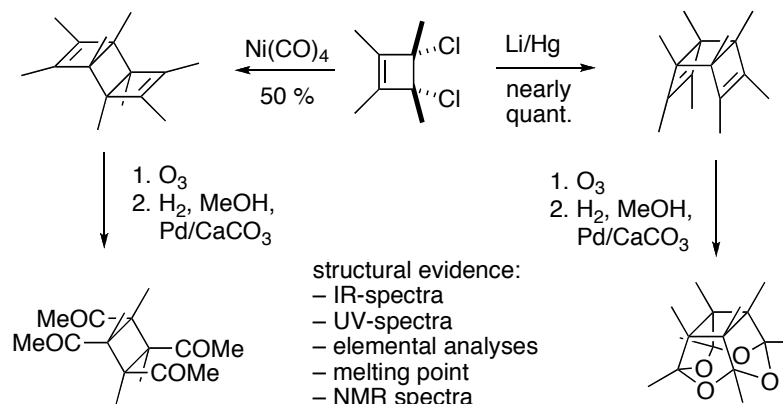
Important Names and their Chemistry

- p. 689: Criegee: First isolation of a primary ozonide
- p. 775: Rosenmund: Contribution to the structure of strychnine
- p. 809: Alder: Diels-Alder-reactions
- p. 909: Hünig: acylation of 1-Morpholino cyclopentene
- p. 1206: Bredereck: amendment of the structure of a purine base
- p. 1374: Treibs: allylic oxidation with $\text{Hg}(\text{OAc})_2$ in AcOH



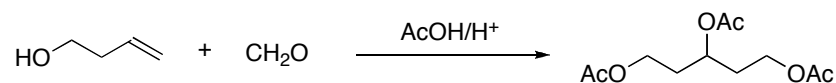
base: PhLi or NaNET_2 or NaNH_2 or NaH
 yield: 88 % ($n=2$), 50 % ($n=3$), 67 % ($n=5$)

Huisgen: Aryne chemistry: *Chem. Ber.* **1960**, *93*, 1496.



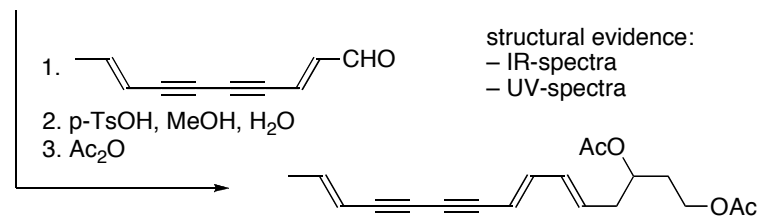
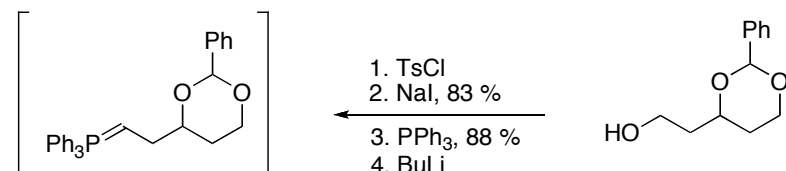
structural evidence:
 - IR-spectra
 - UV-spectra
 - elemental analyses
 - melting point
 - NMR spectra

Criegee: *Chem. Ber.* **1960**, *93*, 1553.



natural product synthesis

1. MeOH/HCl , Δ , 97 %
 2. PhCHO , H^+ , 60 %

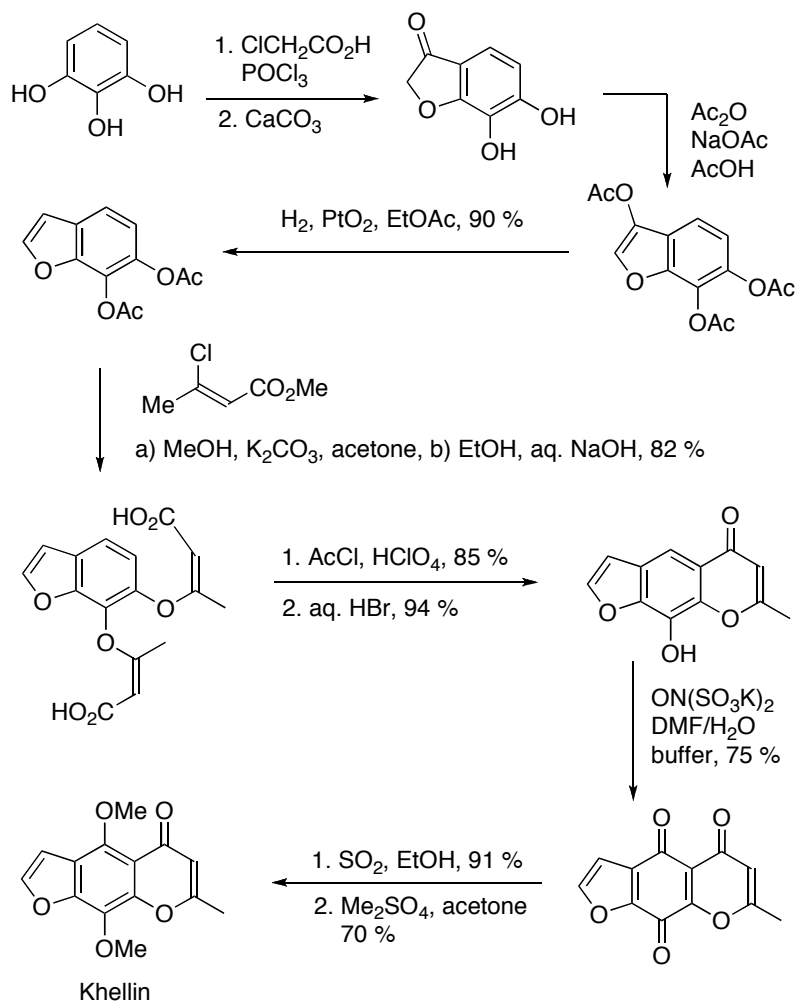


structural evidence:
 - IR-spectra
 - UV-spectra

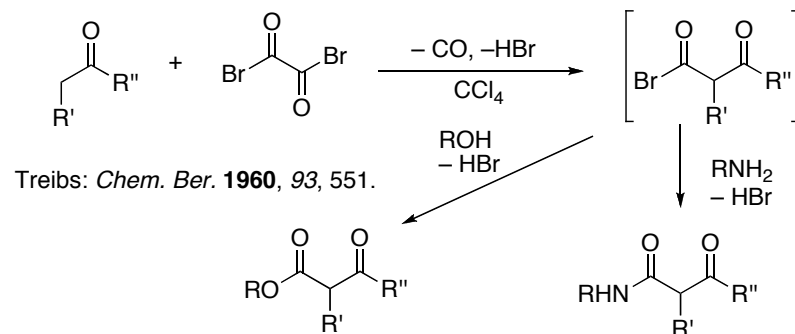
Bohlmann: *Chem. Ber.* **1960**, *93*, 1945.

Centaur X_2

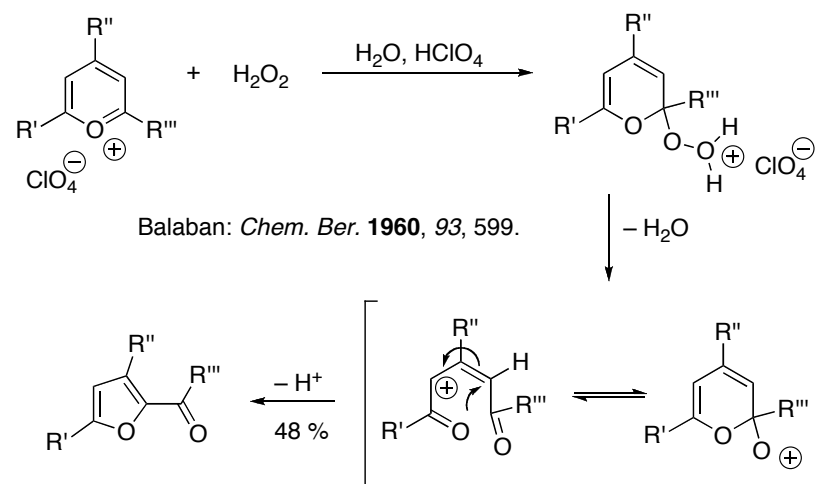
Improvement of the Natural product synthesis of Khellin:

Dann: *Chem. Ber.* **1960**, 93, 2829.

Preparation of 1,3-dicarbonyl compounds:



	$\text{CCl}_4 + \text{N}_2$	Dioxan
acetone	15 %	35 %
methyl ethyl ketone	17 %	—
cyclopentanone	22 %	55 %
cyclohexanone	15 %	42 %
cycloheptanone (suberone)	10 %	—



Origin of Papers

- even fewer papers from outside Germany
- although some e. g. from Budapest (Hungary), Cluj (Romania), Sofia (Bulgaria), Sheffield (England), Rehovot (Israel), Milan (Italy), Brussels (Belgium), Tsu (Japan)
- again no contributions from the USA! :-)

Main Topics

- still sugars, heterocycles, steroids, nucleosids
- still all kinds of aromatic compounds, especially heterocycles
- a little bit more peptide synthesis: activation of carboxylic groups of amino acids, protecting groups, determination of racemization in peptide synthesis
- phenylenes, benzannulenes

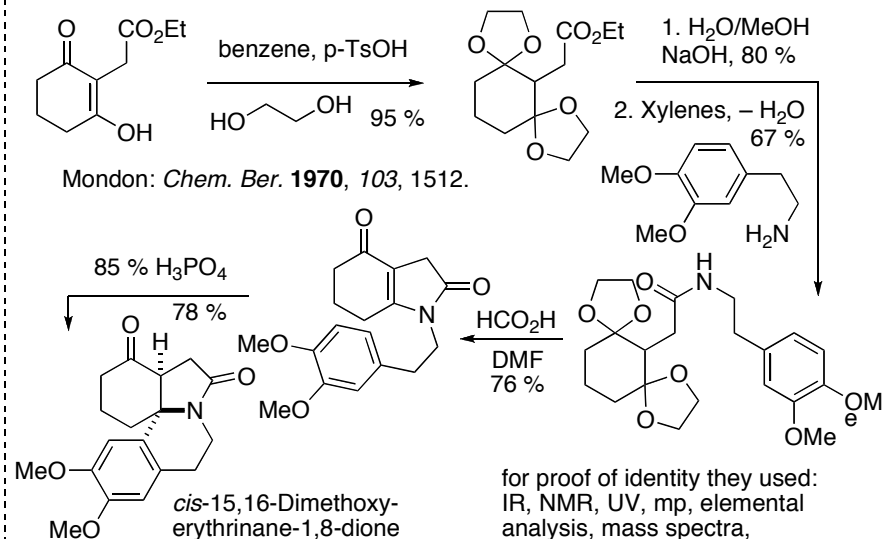
Miscellaneous

- Bohlmann still isolates and synthesizes only natural products with the same unsaturated side chains, isolated for example from *bellis perennis* L. (daisy), also Criegee and Stetter still do the same as well
- less interesting papers, less fun to get through
- still no enantioselective or metal catalyzed reactions
- one paper was only about a crystal structure to figure out the structure and relative configuration of a really boring molecule

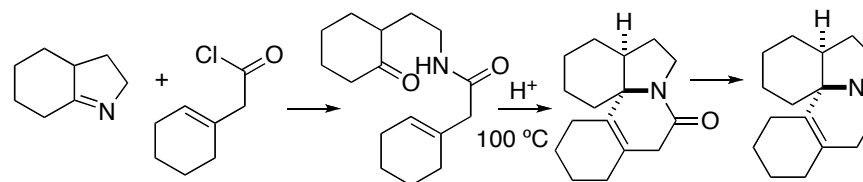
Important Names and their Chemistry

- p. 339: Eicher: Reaction of Cyclopropenes with Diazoalkanes
- p. 369: Dürr: Photochemistry with Small Rings
- p. 389: Simchen: A New Pyridine Synthesis
- p. 426: Roth: Stereochemistry of Sigmatropic 1,5-H Shifts
- p. 573: Viehe: Ynamine Addition to Imines: Ring Expansion of Heterocycles by Two Carbon Atoms
- p. 1463: Regitz: Kinetic Study on the Mechanism of the Wolff rearrangement
- p. 2598: Huisgen: Contributions to the Mechanism of the Dakin-West Reaction

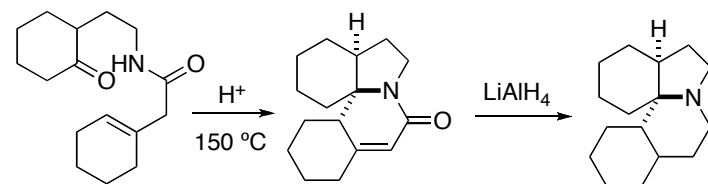
Synthesis of Aromatic Erythrina Alkaloids:



Clarification of results from Belleu and from Boekelheide by Mondon:



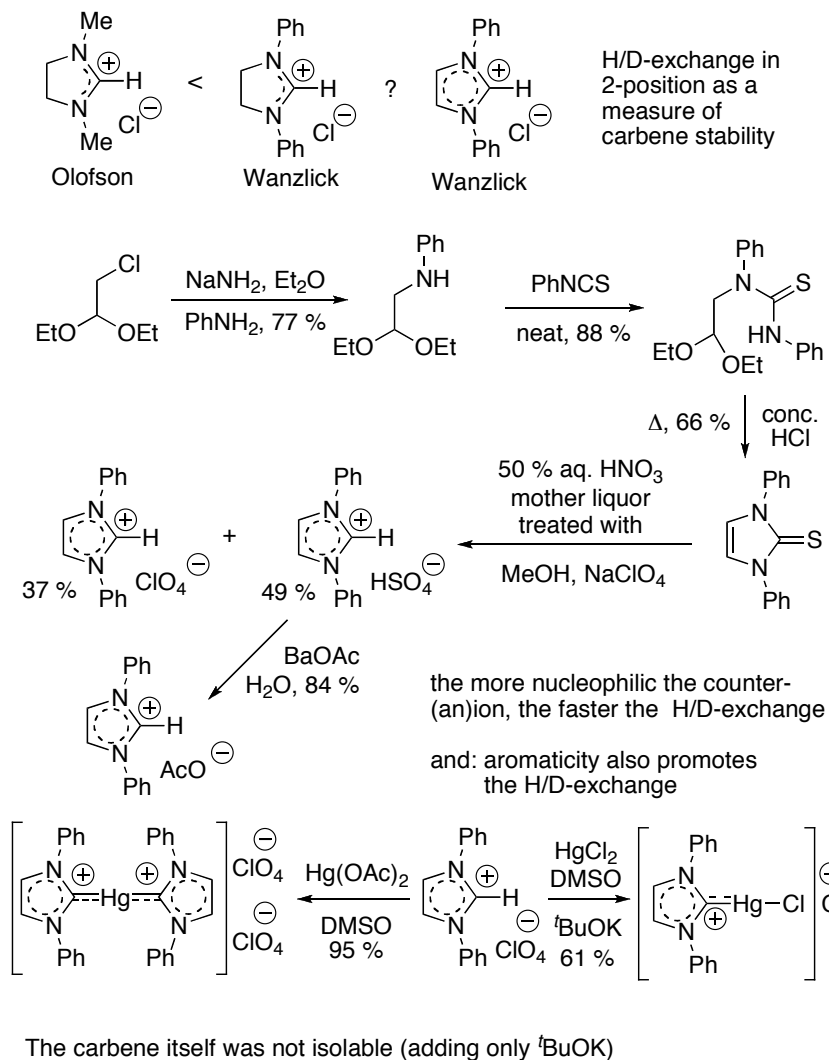
Why is the product not consistent with the one obtained by Mondons route?
Mondon repeated Belleus route and found the following:



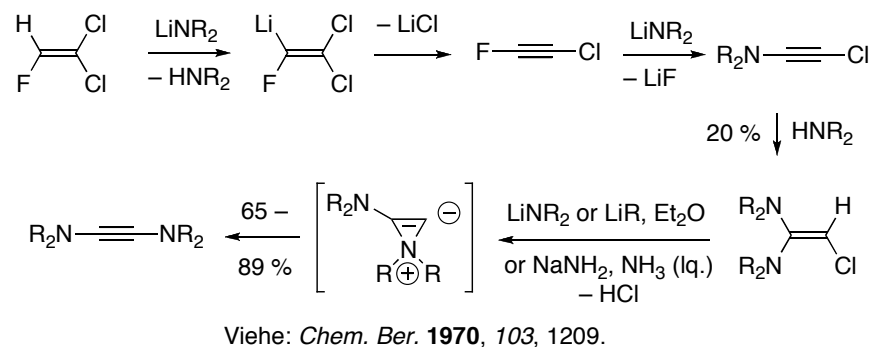
Mondon: *Chem. Ber.* **1970**, *103*, 3050.

mass difference determined
by mass spectra

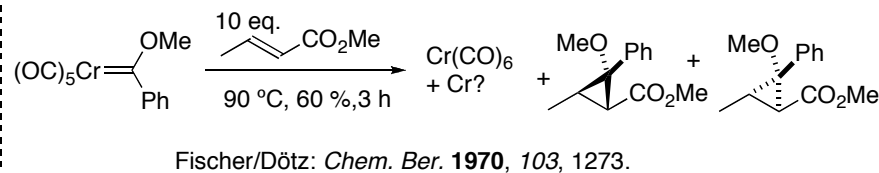
Chemistry of nucleophilic carbenes:

Wanzlick: *Chem. Ber.* **1970**, 103, 1037.

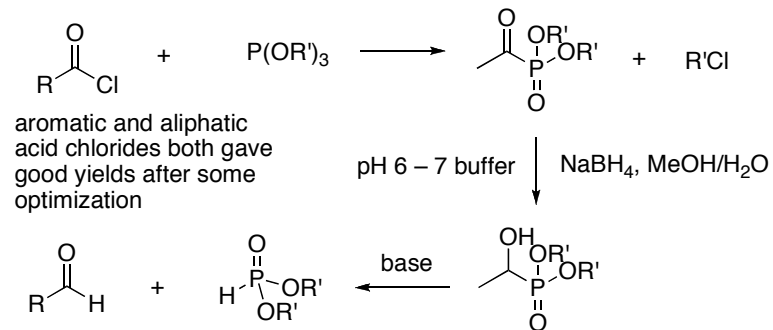
Synthesis of Yndiamines via "onium" rearrangement:



Application of Fischer Carbenes in a non-Dötz reaction



Reduction of Carboxylic acid chlorides to aldehydes:



Origin of Papers

- nearly no papers from outside Germany anymore
- although a few from e. g. Budapest, Szeged (Hungary), Bucharest (Romania), Lodz (Poland)
- Leo A. Paquette (Columbus, Ohio, USA) published together with Armin de Meijere :-)

Main Topics

- still sugars, heterocycles (easy ones), steroids, nucleosids, peptides
- more and more papers on kinetic and reaction mechanisms
- for the first time a quantum chemical study
- Electrochemistry
- in the few synthesis papers the authors write about pharmacologically interesting properties of their molecules for the first time

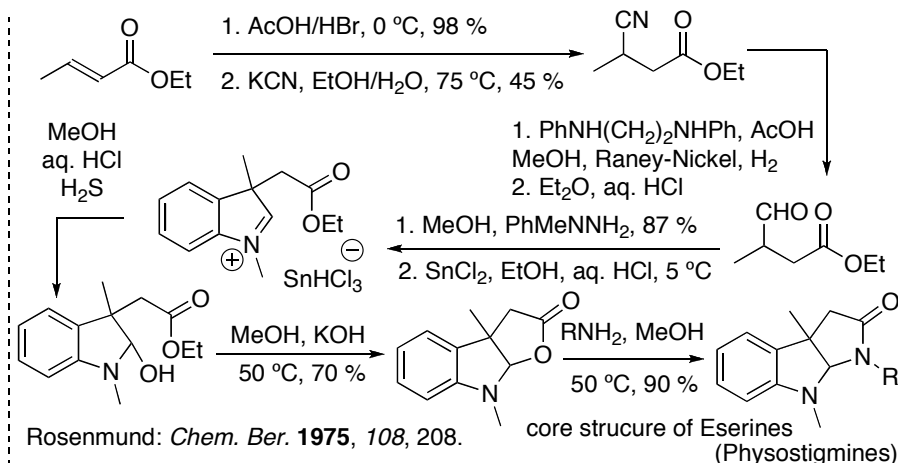
Miscellaneous

- Bohlmann does something new!! New molecules out of new plants! But still publishes the most papers about the chemistry he makes since 20 years. And he published a lot in 1975
- once I saw $\text{Ät}_3\text{N}$ instead of Et_3N - a very German paper!

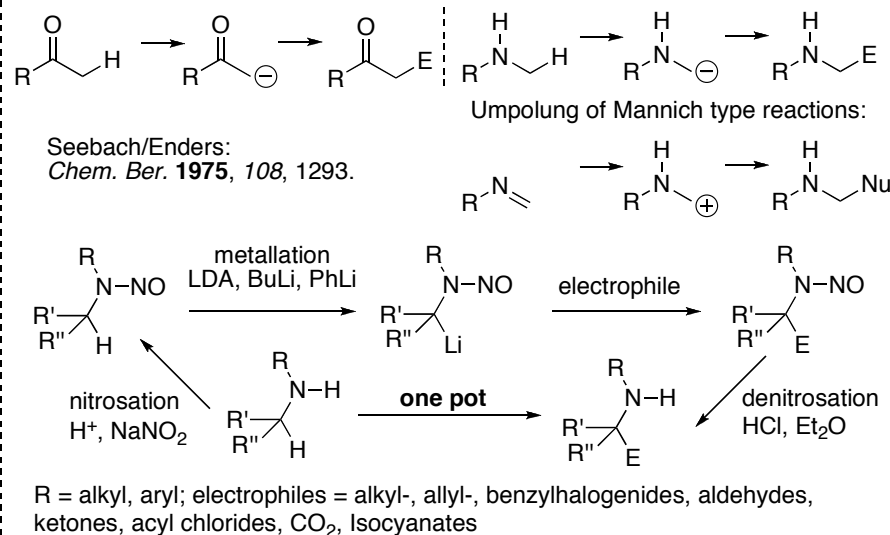
Important Names and their Chemistry

- p. 88: Severin: 1,4-Dicarbonyl Compounds from ketones and 2-Phenylhydrazonopropanal
- p. 640: Günther/Vogel: Bridged [14]Annulenes with Anthracene Perimeter (NMR-Spectroscopy)
- p. 1093: Spiteller: 16,17-Dihydroxy-9(11)-kauren-18-oic acid - A Compound of Roasted Coffee
- p. 1182: Heesing: On the Mechanism of Friedel-Crafts Alkylation with allyl alcohol
- p. 1321: Schmidbaur: Gold(I) Compounds of Simple Phosphorus Ylides
- p. 2176: Conformation of protected Amino Acids: NMR and IR Investigations of Boc-L- α -Amino Acids
- p. 2598: Huisgen: Contributions to the Mechanism of the Dakin-West Reaction
- p. 3141: Günther: The Cope rearrangement of 3,4-Homotropylidene

A New Synthesis of the Eserin Skeleton

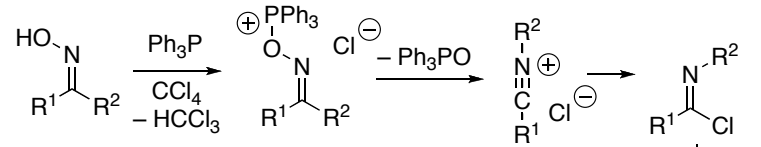
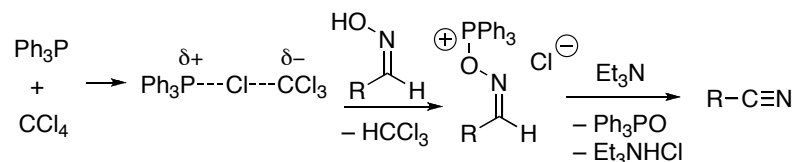


One Pot Procedure for a Nucleophilic Aminomethylation



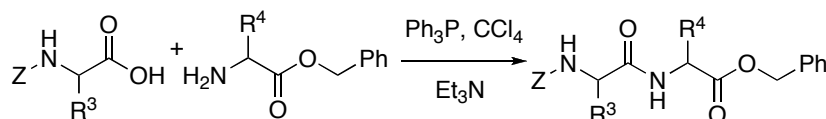
For example: With CO_2 the products are amino acid derivatives

Transformation of oximes into nitriles: Appel: *Chem. Ber.* **1975**, *108*, 1437.

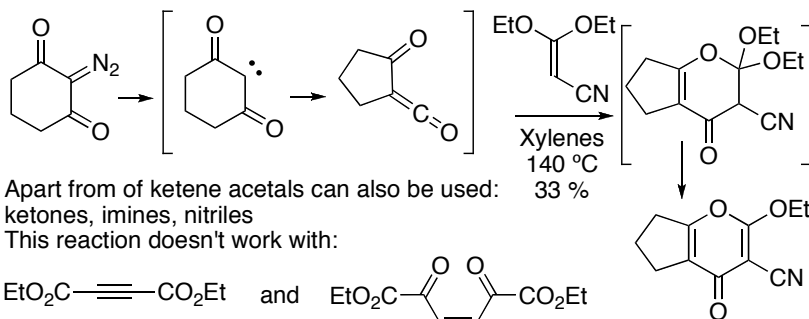


20 % more PPh₃ should be used because of side reactions.
Name of the reaction? Migratory Aptitude?

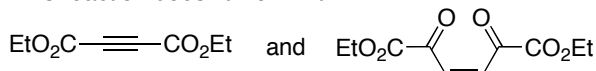
And peptide synthesis: Appel: *Chem. Ber.* **1975**, *108*, 2680.



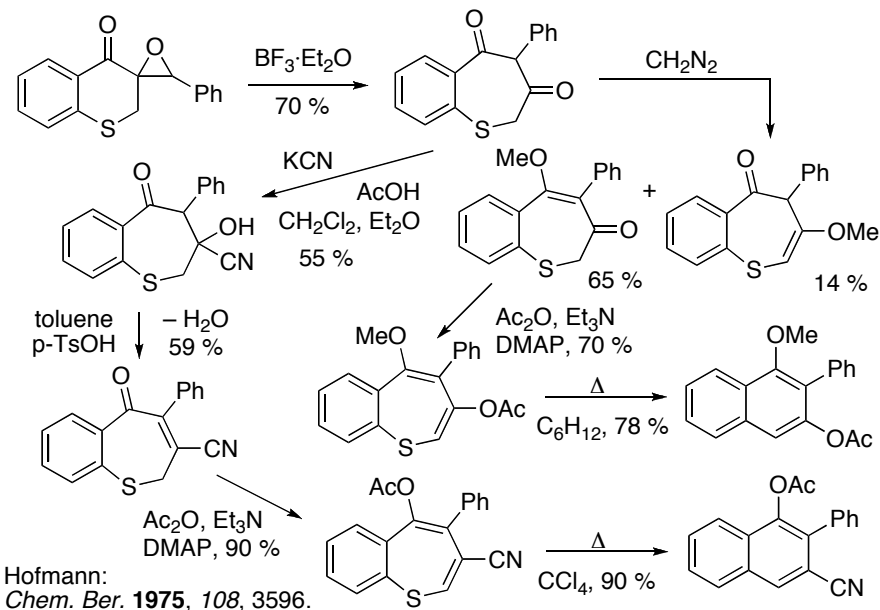
The Challenge in this time was to avoid racemisation: Good results with these protecting groups, also good yields, but Ph₃PO has to be removed. Also amino acids with functional groups in the side chain can be used without protecting these. Yields usually 80 to 90 %.
I don't want to bother you with their determination of the mechanism...



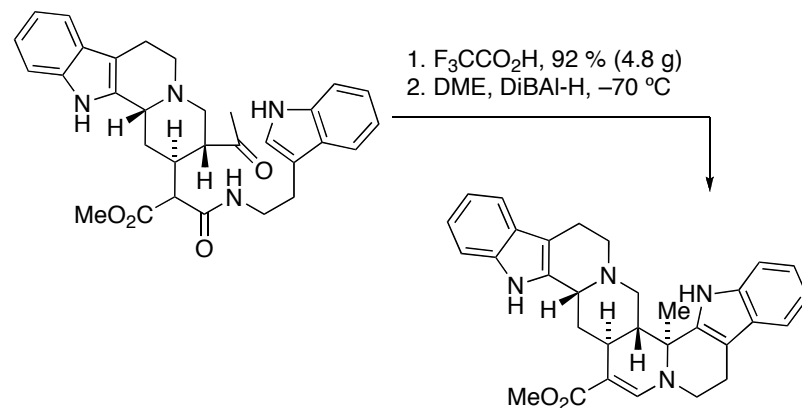
Apart from of ketene acetals can also be used: ketones, imines, nitriles
This reaction doesn't work with:



Stetter: *Chem. Ber.* **1975**, *108*, 3314.



The Stereoselective Total Synthesis of Roxburghin D: All stereogenic centres were assigned, only C-19 had to be clarified by synthesis.



Winterfeld: *Chem. Ber.* **1975**, *108*, 248.