

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

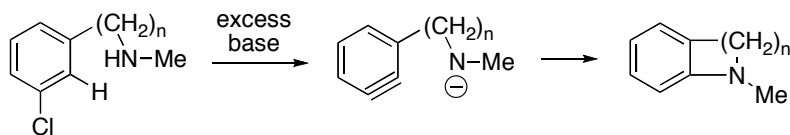
- sugars, lignin
- all kinds of standard heterocycle syntheses with N, S
- steroids (no total syntheses)
- Stetter: Adamantane Chemistry

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

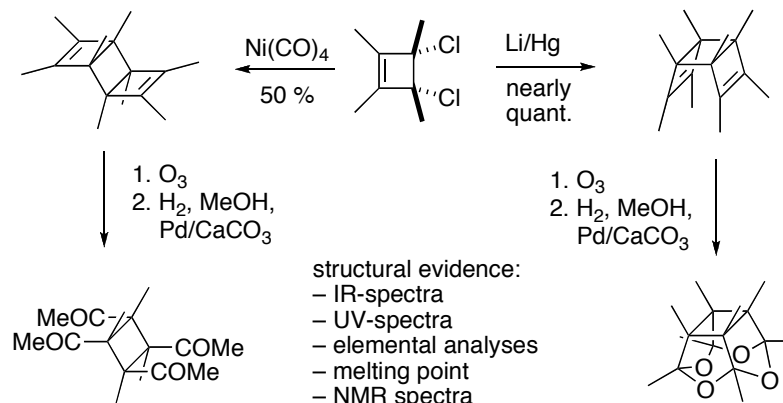
Important Names and their Chemistry

- 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

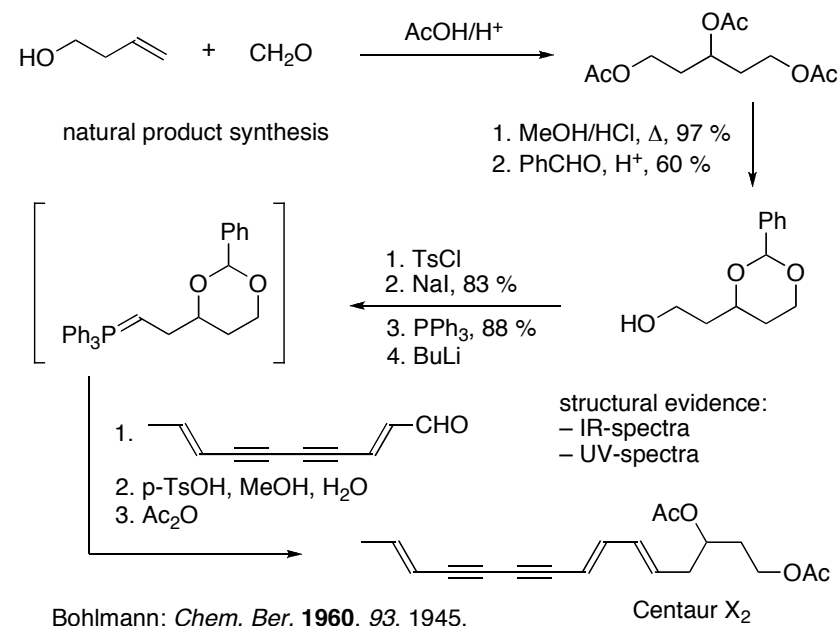


base: PhLi or NaNET_2 or NaNH_2 or NaH
 yield: 88 % (n=2), 50 % (n=3), 67 % (n=5)

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



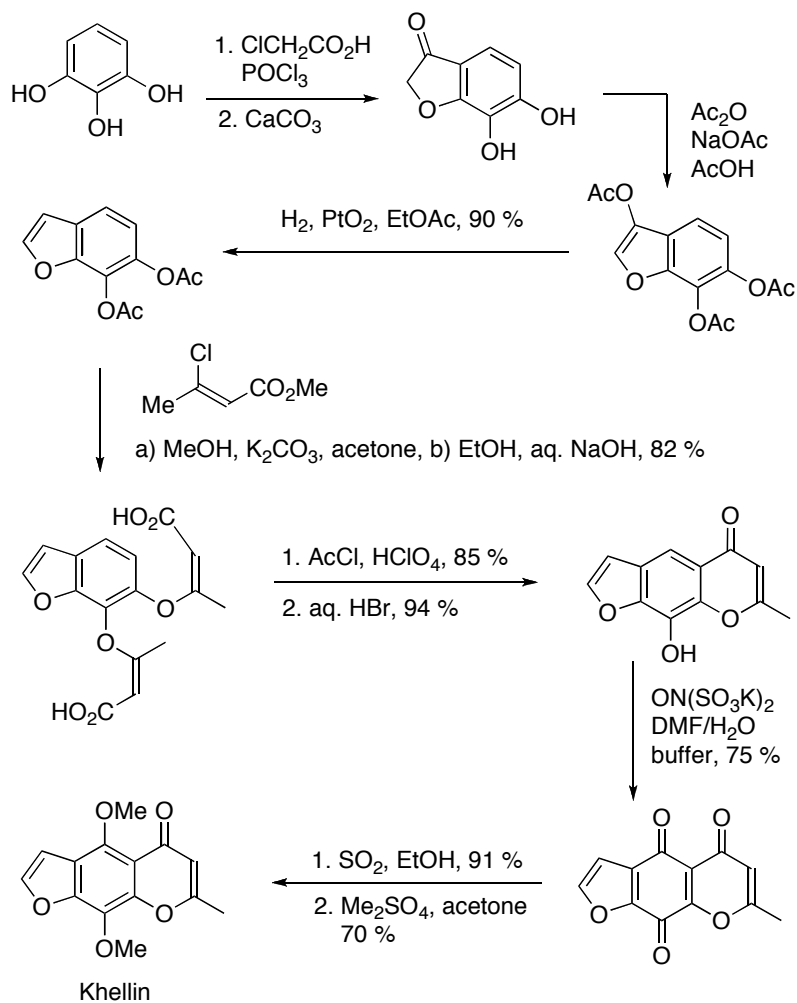
Criegee: *Chem. Ber.* **1960**, *93*, 1553.



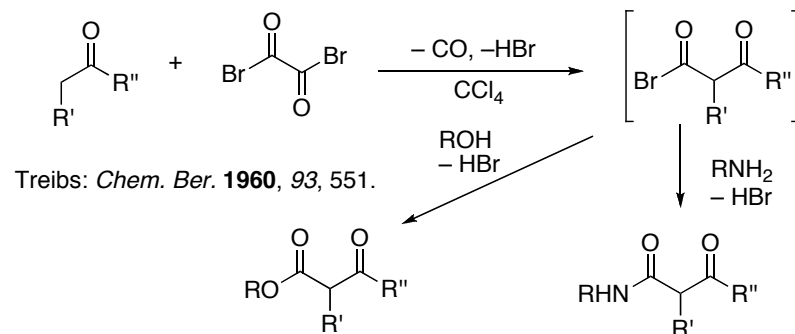
Bohlmann: *Chem. Ber.* **1960**, *93*, 1945.

Centaur X₂

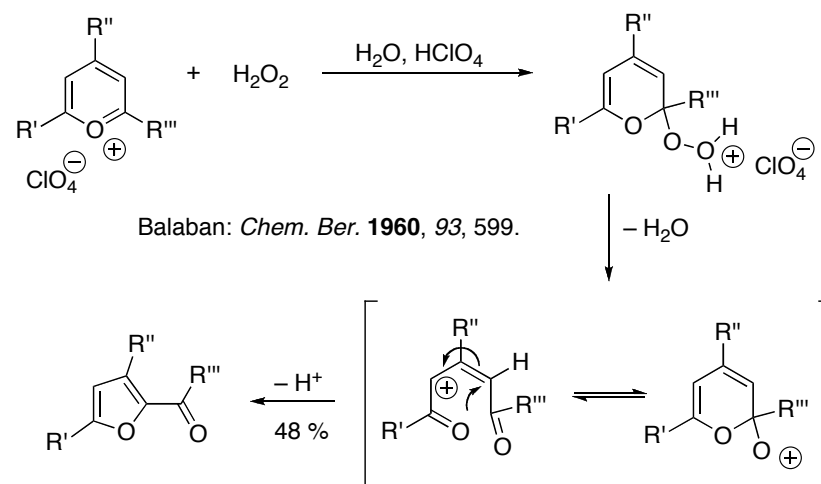
Improvement of the Natural product synthesis of Khellin:

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

- most paper again from Germany
- but also from Budapest (Hungary), Cluj (Romania), Sofia (Bulgaria), Helsinki (Finland), Sao Paulo (Brazil), Rajasthan (India), Brussels (Belgium), Strasbourg (France), Tempe (Arizona, USA!!!), Stanford (California, USA!!!), but both articles from German postdocs! :-)

Main Topics

- a little more inorganic chemistry: metal carbonyls, sandwich complexes
- still all kinds of aromatic compounds, especially heterocycles
- still sugars and steroids (no total synthesis)
- dyes
- Isolation of natural products and evidence of structure
- Synthesis of peptides (with special protecting groups) and nucleotides

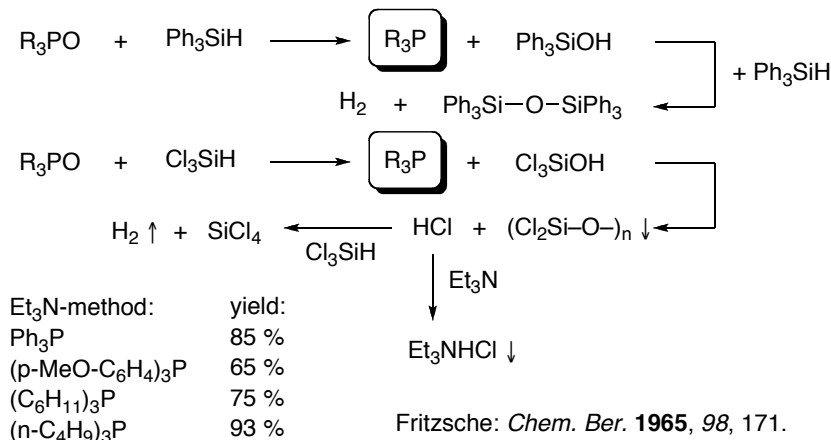
Miscellaneous

- once tlc plates were printed for the control of a column chromatography
- in some cases still the same names and the same chemistry as in 1960

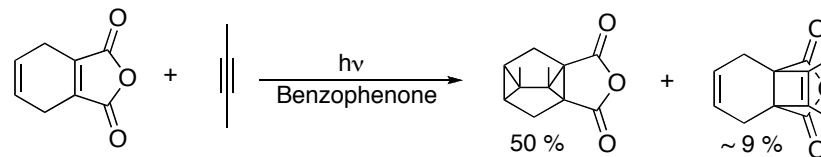
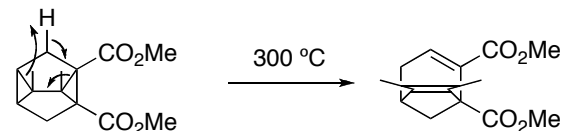
Important Names and their Chemistry

- p. 451: Wittig: Question of Intermediary Appearance of Cyclobutylene
- p. 516: Beckmann: A New Ring Opening Reaction in the Bicyclo-[2.2.1] heptane series
- p. 650: Eistert: Convenient Synthesis of Cycloundecanon
- p. 1081: Bredereck/Effenberger: Heterocycle synthesis
- p. 1138: Huisgen: Click-Chemistry
- p. 1246: Horner: New Mono- and Dihydronaphthochinones
- p. 2221: Schöllkopf: Synthesis of Alkoxypropylenes
- p. 2339: Criegee/Seebach: Valence Isomerizations of Cyclobutenes
- p. 2701: Vögtle: Valence Isomerizations of double Schiff bases of 1,2-diamines
- p. 2906: Schill: synthesis of catena compounds
- p. 3170: Wanzlick: formation and reactivity of Bis[1,3-diphenyl-imidazolidin-2-ylidenes]
- p. 3854: Schenk: four-membered ring synthesis through photo cyclo addition of maleinic anhydride and halogenated olefins

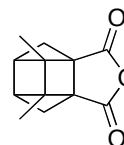
Recovering tertiary Phosphines from their Oxides with Silanes:



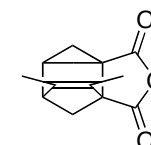
A Very Special Cycloaddition:

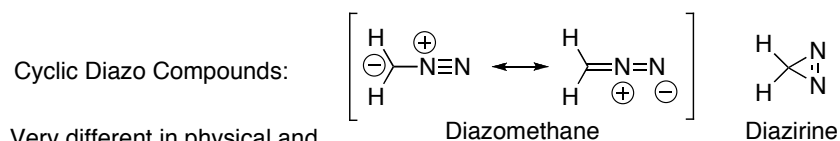
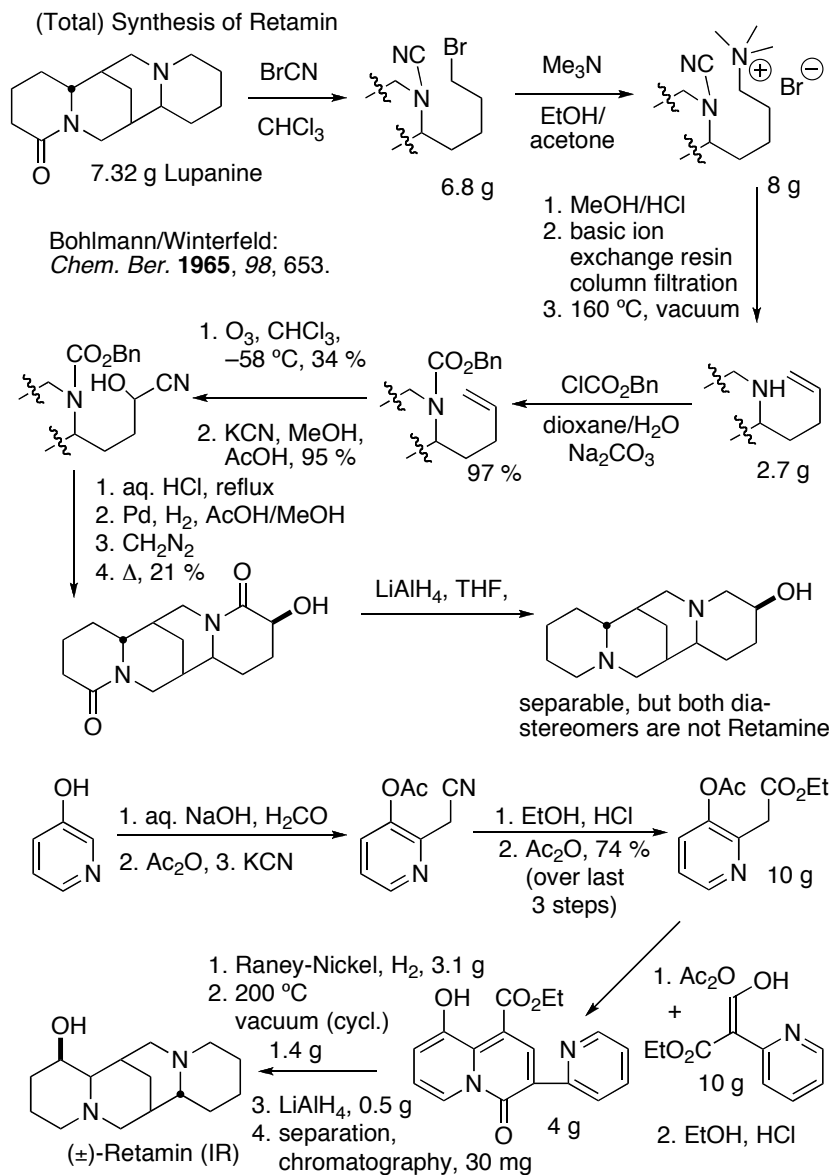
Tetracyclooctane is not reacting with O₃ or OsO₄.

The following structure was not found as shown by spectral data:

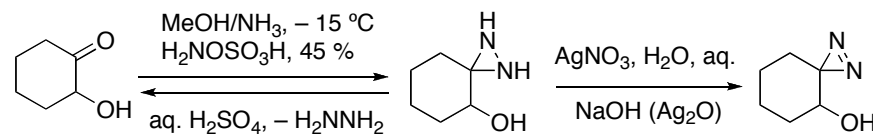
Askani: *Chem. Ber.* **1965**, *98*, 3618.

Probably NOT a stepwise cycloaddition, because the author didn't find intermediates like:

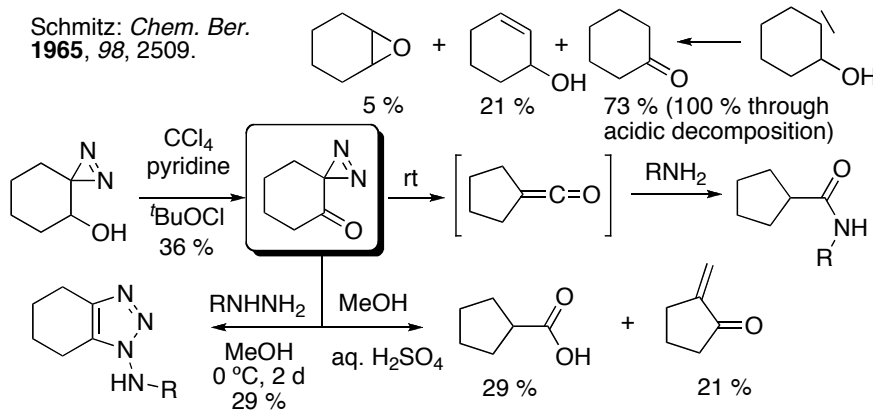




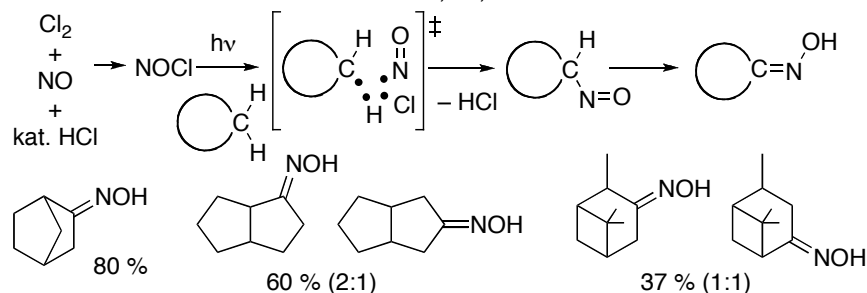
Very different in physical and often in chemical properties, but: both want to get rid of N₂. Maybe with the loss of N₂ the linear diazo compound is formed transiently.



Schmitz: *Chem. Ber.* **1965**, *98*, 2509.



C-H-activation: Müller: *Chem. Ber.* **1965**, *98*, 3493.



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

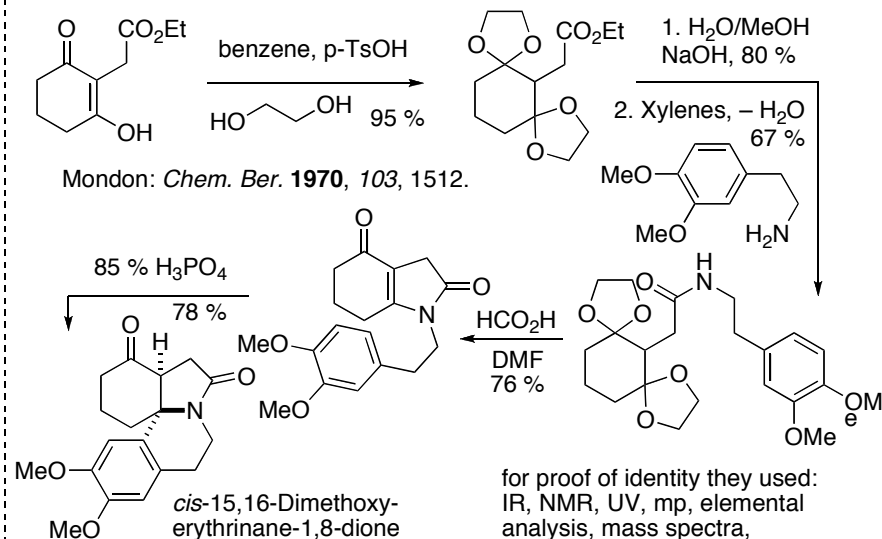
Miscellaneous

- 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

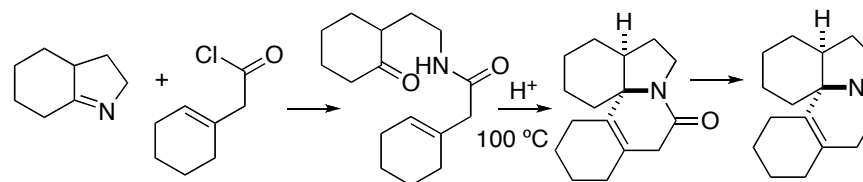
Important Names and their Chemistry

- 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

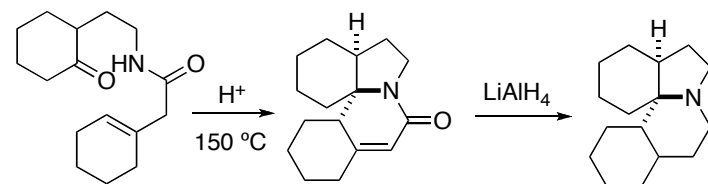
Synthesis of Aromatic Erythrina Alkaloids:



Clarification of results from Belleu and from Boekelheide by Mondon:



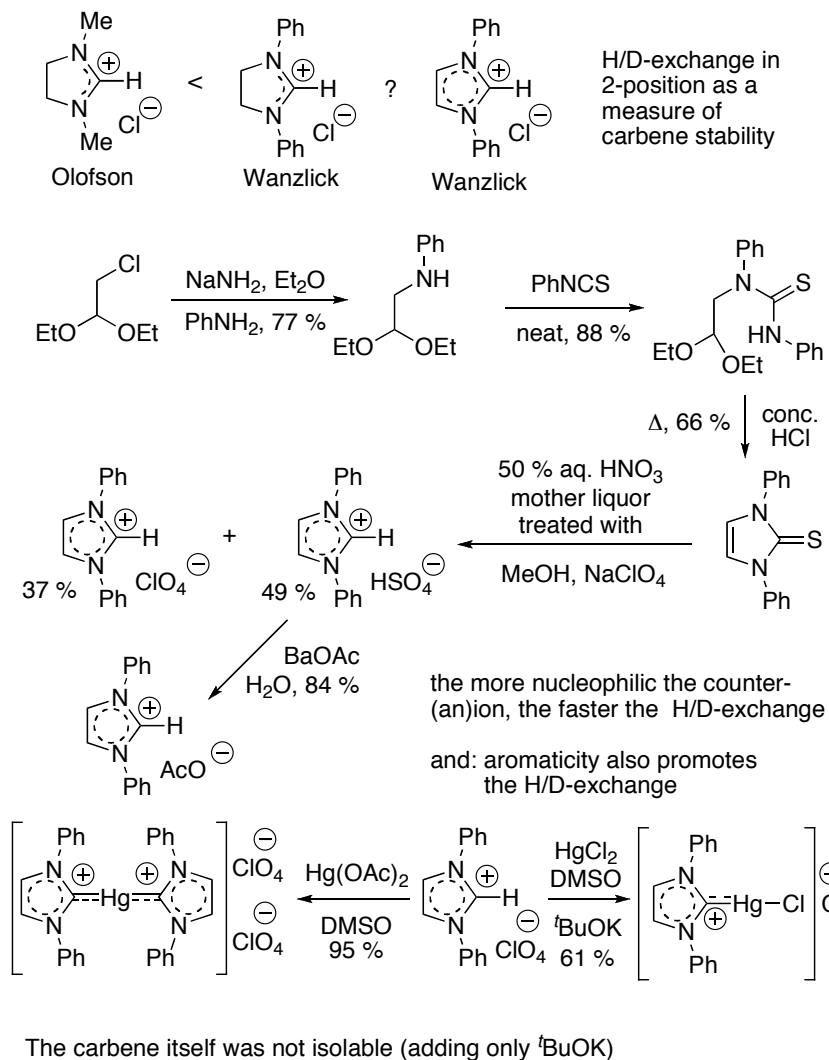
Why is the product not consistent with the one obtained by Mondons route?
Mondon repeated Belleus route and found the following:



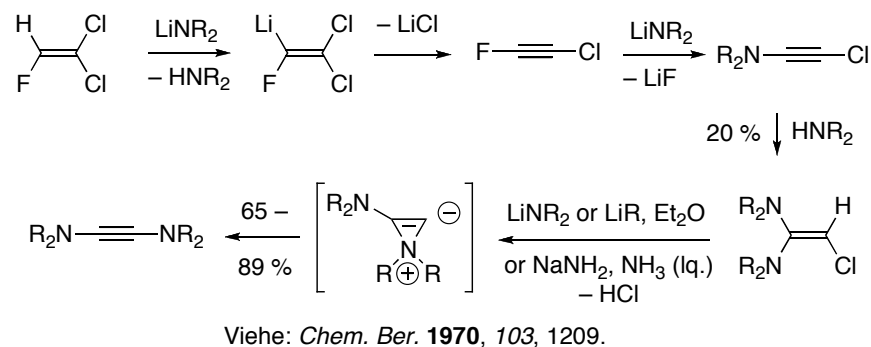
Mondon: *Chem. Ber.* **1970**, *103*, 3050.

mass difference determined
by mass spectra

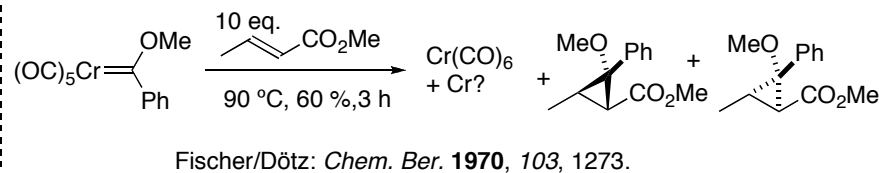
Chemistry of nucleophilic carbenes:



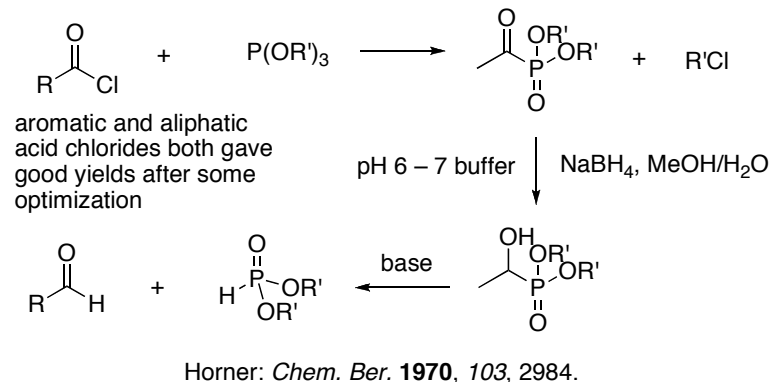
Synthesis of Yndiamines via "onium" rearrangement:



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

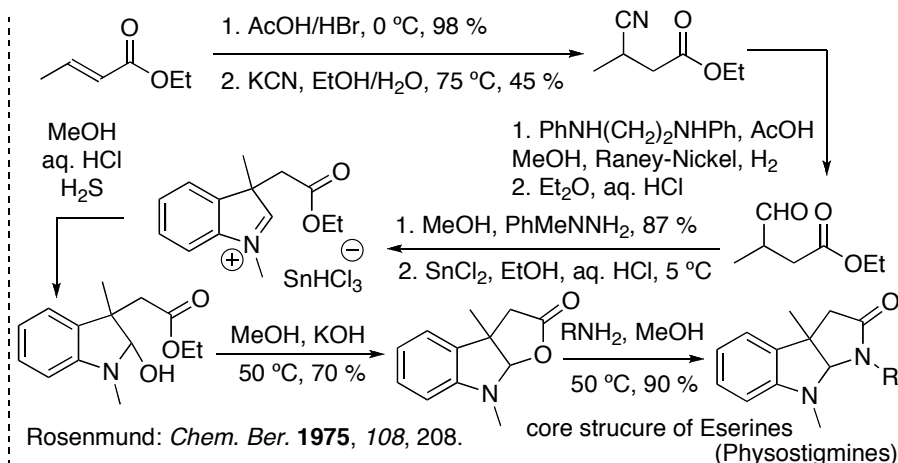
Miscellaneous

- 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!

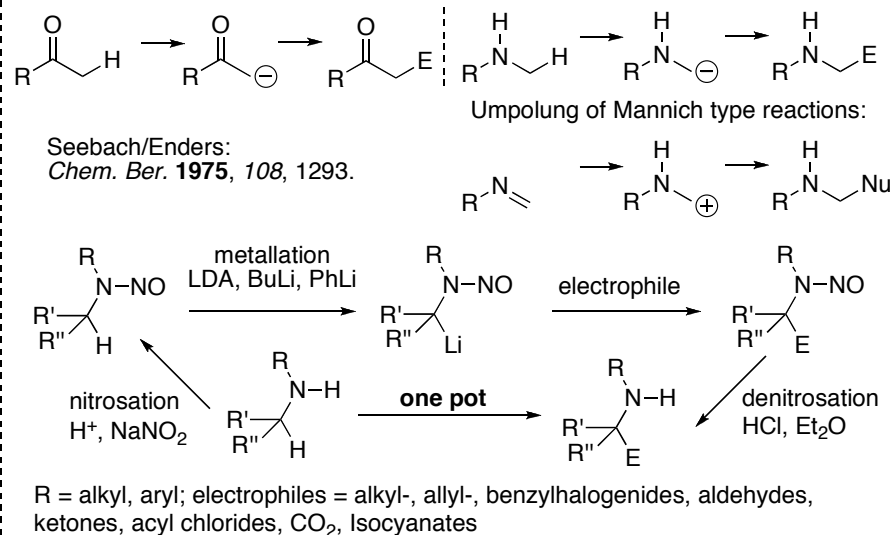
Important Names and their Chemistry

- 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

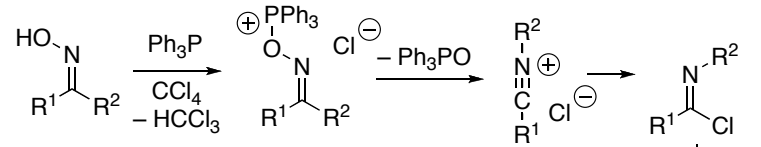
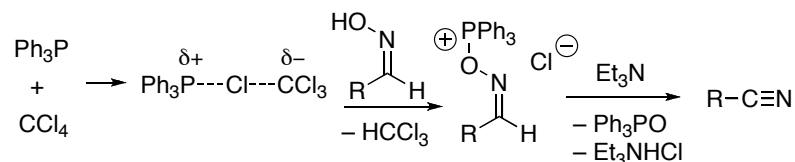


One Pot Procedure for a Nucleophilic Aminomethylation



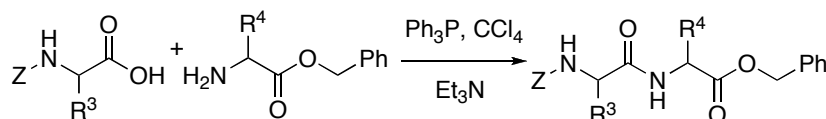
For example: With CO_2 the products are amino acid derivatives

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

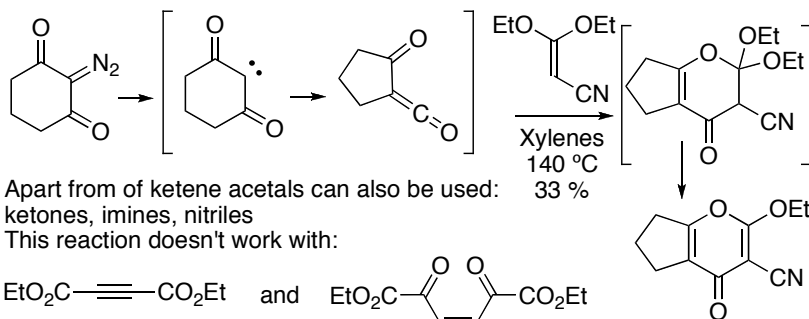


20 % more PPh₃ should be used because of side reactions.
Name of the reaction? Migratory Aptitude?

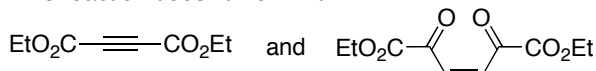
And peptide synthesis: Appel: *Chem. Ber.* **1975**, *108*, 2680.



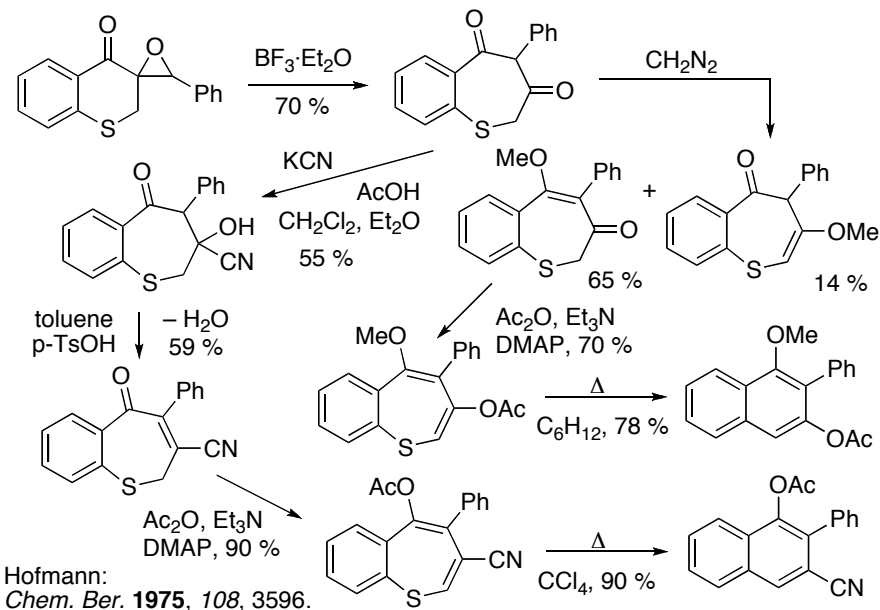
The Challenge in this time was to avoid racemisation: Good results with these protecting groups, also good yields, but Ph₃PO has to be removed. Also amino acids with functional groups in the side chain can be used without protecting these. Yields usually 80 to 90 %.
I don't want to bother you with their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



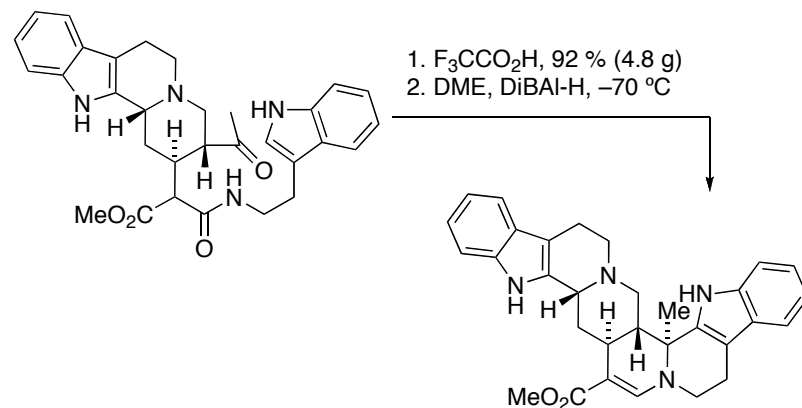
Apart from of ketene acetals can also be used:
ketones, imines, nitriles
This reaction doesn't work with:



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.