Dow Chemical Company - commonly referred to as Dow, is an American multinational chemical corporation headquartered in Midland, Michigan.

Disclaimer - this group meeting is by no means a comprehensive summary of Dow and everything it did/does (the company is huge). Selected key events and research (with a particular emphasis on organic chemistry) are covered. If you wanna learn more about Dow..read more or do another group meeting on it.

Brief outline of talk:
I. Introduction
   - Quick facts
   - Markets & solutions
   - Things you use from Dow
II. History
   - Early years
   - Key events & acquisitions
III. Medicinal chemistry from Merrell Marion Dow - syntheses
IV. Medicinal chemistry from Merrell Marion Dow - fluorinated compounds
V. Medicinal chemistry from Merrell Marion Dow - miscellaneous methods
VI. Chemistry from DowAgroScience

Quick facts from Wiki:
- 2015, ranked third largest chemical company in the world (after BASF and Sinopec)
- Before merging with Olin, Dow was the largest chlorine producer in world (5.7 billions/y)
- Ranked was ranked as the world's largest plastics manufacturer during 2008
- Ranked the largest manufacturer of polyalkylene glycols in 2013
- >50,000 employees worldwide
- Dow's 2014 sales totaled approximately $58.2 billion
- Dow has been called the "chemical companies' chemical company" in that most of its sales are to other industries rather than end-users, although Dow sells directly to end-users primarily in the human and animal health, agriculture and consumer products markets

Business lines: (sales data from 2014)
- Agrosciences: 12.5%
- Consumer solutions: 8%
- Infrastructure: 14.5%
- Performance chemicals & materials: 26%
- Performance plastics: 39%

Dow products you may or may not know:

- Seeds!!
- Herbicides & Insecticides (see E.Cherney GM)
- 2,4-Dichlorophenoxyacetic acid
- Glyphosate
- Omega-9-oils
- Adhesives
- Coatings
- HDPE
- LDPE
- LLDPE
- MDPE
- Elastomers
- Polyethylene Resins
- Polymers
- Sealants

Dow packaging

Dow coating material

- ACousticryl
- ACRYSOL
- AVANSE
- ECOSURF
- EVOQUE
- FORMASHIELD
Dow - Brief History

1920s
Rapid diversification around WWI - major producer of agro-chemicals, phenol, chlorine dyestuff and magnesium metal. (1918 - 90% of Dow production was towards the war)

Dow Process (second one) - phenol synthesis from benzene

Cl_2 + phenol + NaOH → Cl + H^+ + ONa → OH

BrMe

Br

After the war - still researched Mg for developing efficient automobile pistons. Won Indie500 in 1921 w/ Dow piston

1930s - began producing plastic resins. First ethylcellulose in 1935 and polystyrene in 1937.

Ethylcellulose (ETHOCEL polymers)
- cellulose treated with alkaline solution to produce alkali cellulose. Alkylation with ethyl chloride affords ethylcellulose

Polystyrene

1940s - Dow built its first plant at Freeport, Texas, in order to produce magnesium extracted from seawater rather than underground brine, marking the first time that humans had mined the ocean for metal

Freeport site is still one of biggest manufacturing sites in the world. produced NaOH, chlorine, Mg (84% of whole country's production), and ethylene

1942 - international expansion, produced styrene-butadiene synthetic rubber.

Dow-Corning formed during WWII - produced silicone


Vietnam War: Napalm and Agent Orange
Dow was one of several manufacturers who began producing the napalm B compound under government contract from 1965 at its Torrance, California plant
Napalm: developed in 1942 at Harvard in a secret lab led by Fieser.
Marion-Merrell-Dow

1980s - Acquired Merrell (R&D) in 1980 and Marion (Sales) in 1989. Marion-Merrell-Dow was acquired by Hoechst AG in 1995. 1999 - Aventis then succeeded by Sanofi.

An Acyl-iminium Ion Cyclization Route to a Novel Conformationally Restricted Dipeptide Mimic: Applications to Angiotensin-Converting Enzyme Inhibition. JACS 1987, 7914

Modest Affinity for ACE
$K_M = 1 \times 10^{-5}$ M

Potent Affinity
$K_M = 1.2 \times 10^{-11}$ M

Total Syntheses of Castanospermine and Nojirimycin (potent glycohydrolase inhibitors)
TL 1990, 4321; TL 1990, 2085 (potent anti-diabetic, anti-AIDS, anti-cancer NP's)

Functionalized Pyrazoles from Indazol-4-ols
JOC, 1987, 4384

Synthesis of ZJ9-Bridged Androstenediones
JOC, 1992, 5150
potent, time-dependent inhibitor of human placental aromatase
Chemistry of fluorinated compounds

DAST to convert sulfoxide to fluorothioethers, JACS, 1984, 735

Wittig Equivalent. JCS, 1985, 678

Difluoromethylidiphenylphosphine Oxide, TL 1990, 5571

1-Fluoroethene anion, TL 1994, 1027.

α-α-difluoroaldehydes with [3,3], TL 1985, 2861

α-oxyradical addition to vinylfluoride. JOC 1990, 2973.
Miscellaneous Methods & Transformations for MedChem
Annealation with vinylsulfide/sulfone, JOC 1984, 3134

Z + X + R₂N → Z = PO(OMe) X = Br
Z = CO₂H X = Br
Z = NO₂ X = OAc

S₂,2-Michael

Cl + O → Cl + O
Orgsyn 1990, 8

1) NH₂

2) SPh

3) H₂O
Mechanistic proposal - Pummerer


Cyano-Imidazoles
JMC 1990, 317

JOC, 1986, 3228
5% NH₄OH
87%

Cyanation of imidazole with DMAP-Cyanogen-bromide.
Syn. Comm. 1988, 471

Amination chemistry
Facile synthesis of β-substituted-α-alkenyl primary amines. TL 1987, 2207.

RMgBr + MeO + N(TMS)₂ → NH₂HX

Reductive amination of hindered amines. TL 1990, 5547
DowAgroscience
Process synthesis of Isoclast Active. OPRD 2015, 454.
Discovery route

- Cost/Yield
- Safety
- Ease of operation

Process route

(Amino acid PG. OL 2002, 1249)