

# Substitution

A halogenated history of  
“essential” chemistries

ISG Fellows' Meeting  
UCLA Institute for Society & Genetics  
April 18, 2020

Evan Hepler-Smith  
Duke University  
evan.heplersmith@duke.edu  
evanheplersmith.com



## The molecular ideal

The principle that molecular structure (atom-bond topology) is a privileged, default means of defining identities of chemical substances. Embodied in systematic organic chemical nomenclature and machine-oriented chemical identifiers.

*Compound Words (book in progress)*

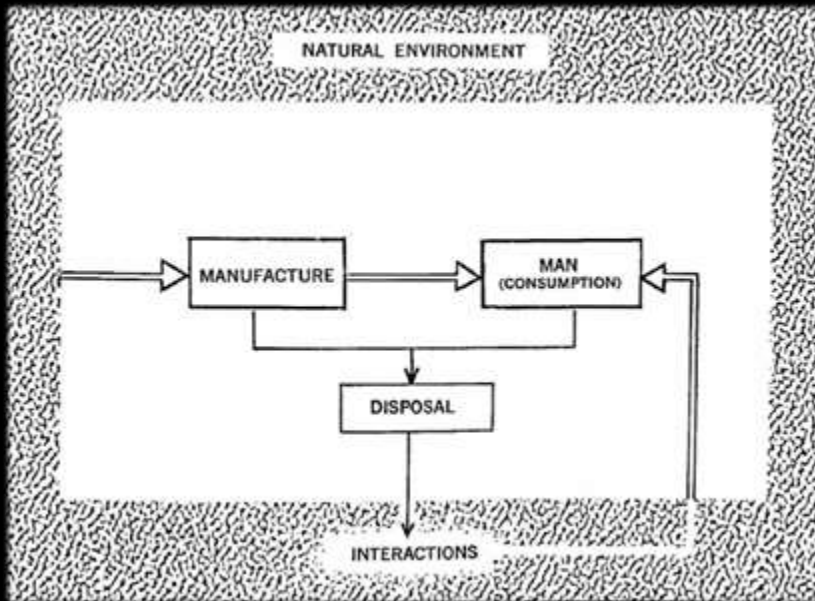
# The molecular ideal & chemistry's information infrastructure

“We must organize and equip ourselves for the scientific and industrial battle to come. And among all the instruments of the chemist, none is more indispensable than good books and good bibliographic literature.” Charles Moureu, founding president of IUPAC, 1919

“The literary activity of the German Chemical Society is one of the cornerstones on which the edifice of our science and industry is based.... It is a condition for the survival of German chemistry.” Festschrift celebrating the 50<sup>th</sup> anniversary of the German Chemical Society, 1918



“A few hours of...  $C_{20}H_{25}N_3O$   $\Delta^2$ -Pyrazoline, 5-(2-furyl)-1-phenyl-3-(1-piperidylethyl)-, -HCl is enough to make us reel...” *Chemical Abstracts* associate editor Janet Scott, 1938



## Chemical holism

“Standard-setting, monitoring, and control can often be done more efficiently and rationally if attention is focused on the particular substance.”

*Toxic Substances* (1971 Nixon admin. report)

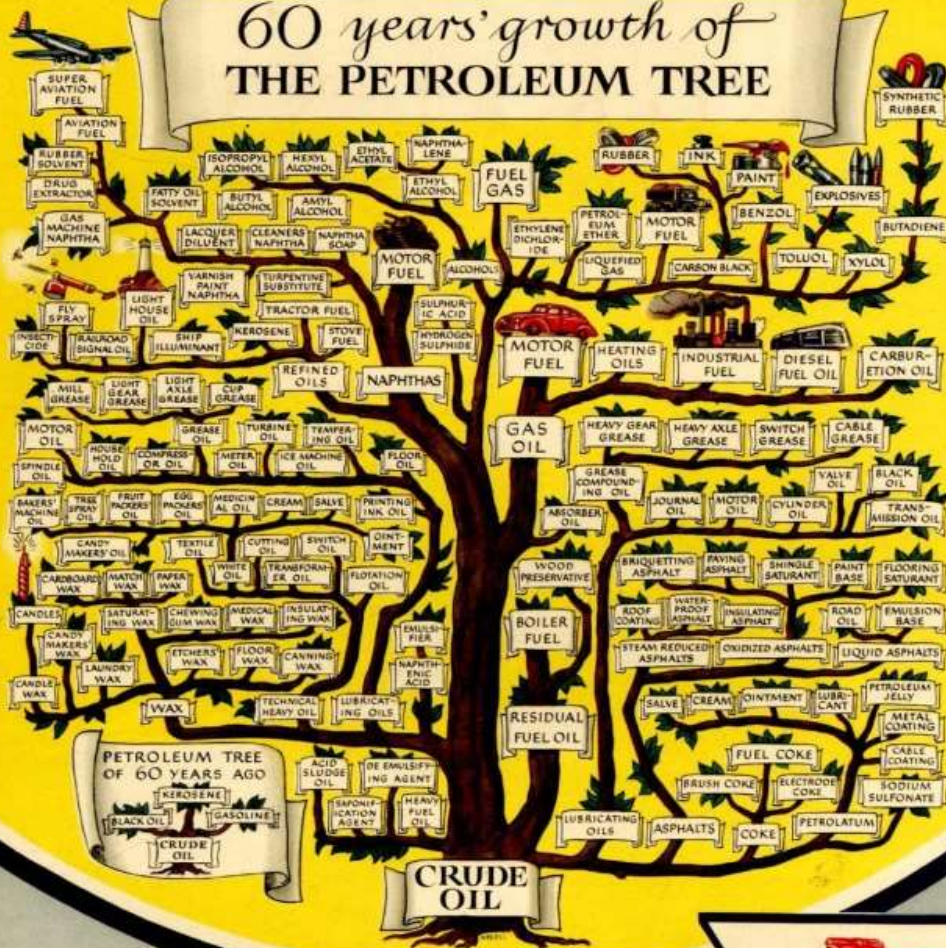
## Molecular bureaucracy

The complex of information systems, nomenclature conventions, legal structures, administrative procedures, and regulatory lists that render chemical environments tractable to regulatory politics on a molecule-by-molecule basis.

(EHS, “Molecular Bureaucracy,” 2019)



# 60 years' growth of THE PETROLEUM TREE



“Are you doing post-war planning? Be sure you make use of petroleum’s new miracles.”



**Process  
Products**

SOCONY-VACUUM

**Socony-Vacuum  
ad, 1943**

SEE THAT LITTLE “TREE” in the lower left-hand corner above? It shows that only sixty years ago the oil industry was making just three products!

Look at that tree today—and realize it may be growing right into your business—with uses for you that you never expected.

Today petroleum is more than a source of lubricants and fuels. It is

the U.S.A.’s richest source of organic material for every major industry!

In pioneering this field, Socony-Vacuum has created new kinds of waxes and processing oils and agents which have virtually revolutionized other businesses.

We call them Socony-Vacuum Process Products. They have helped develop new products... new uses for old products. They have helped

improve quality. There are hundreds of them—and we’ve begun!

Are you doing post-war planning? Be sure you make use of petroleum’s new miracles. We offer you counsel from 77 years of petroleum experience—the world’s greatest.

SOCONY-VACUUM OIL CO., INC.  
26 Broadway, N. Y. C., and Affiliates  
Magnolia Petroleum Company, General Petroleum Corporation of California.

FROM U.S.A.’S RICHEST  
SOURCE OF  
ORGANIC MATERIAL



come hundreds of Socony-Vacuum Process Products used in making Shoes, Textiles, Paper, Plastics, Rubber, Pottery, Paint, Tree Sprays, Cardage and Fabric Preservatives, Moisture-proofing Agents

and Anti-rust Compounds. These products include Carcase Waxes, Paraffin Oils, Wax Emulsions, Water Soluble Processing Oils and Naphthenates. Product availability is subject to war restrictions.

LET SOCONY-VACUUM HELP YOU IN PROCESS PRODUCTS RESEARCH

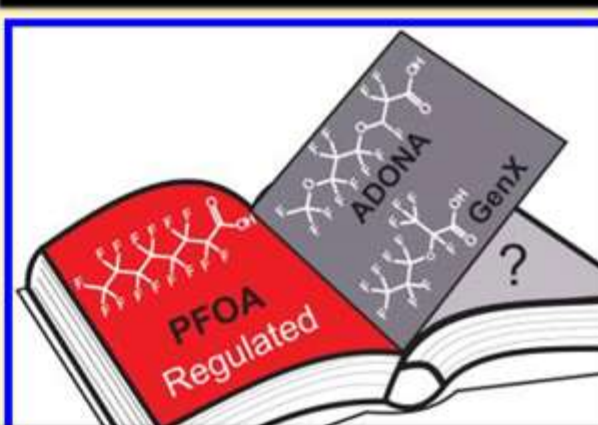


## Regrettable Substitution

### A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)?

(Wang  
et al.  
2017)

**ABSTRACT:** More than 3000 per- and polyfluoroalkyl substances (PFASs) are, or have been, on the global market, yet most research and regulation continues to focus on a limited selection of rather well-known long-chain PFASs, particularly perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA) and their precursors. Continuing to overlook the vast majority of other PFASs is a major concern for society. We provide recommendations for how to proceed with research and cooperation to tackle the vast number of PFASs on the market and in the environment.



Opinions

### Stop playing whack-a-mole with hazardous chemicals



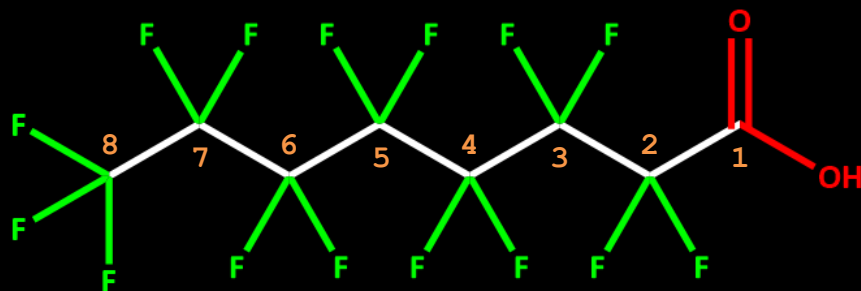
(Allen 2016)

### Fluorotechnology Is Critical to Modern Life: The FluoroCouncil Counterpoint to the Madrid Statement

“Fluorotechnology is essential technology for many aspects of modern life, a critical consideration for adoption of any social policy on PFASs.” (FluoroCouncil 2015)

“Fluorotechnology is essential technology for many aspects of modern life, a critical consideration for adoption of any social policy on PFASs.” (FluoroCouncil 2015)

## Three possible explanations: Capitalism, Carbon, Complexity



2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-  
pentadecafluorooctanoic acid

## Substitution

In chemistry, term for the replacement of one atom/group by another within an organic compound. A central theory, approach to experimental design, and method for making novel materials in 19<sup>th</sup>-21<sup>st</sup> century organic chemistry.

# Chemical whack-a-mole: four canonical cases

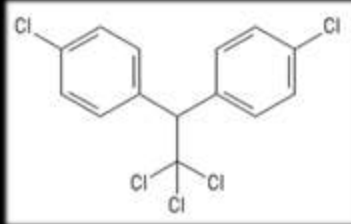
<u>Use</u>	<u>Phased out</u> (why)	<u>Substitute</u> (regret)
Pesticides	<u>DDT</u> (chronic hazard, esp bad for birds)	<u>parathion</u> (acute haz.); <u>↑ toxaphene</u> (esp bad for fish & fishing lifeways)
Plastics	<u>BPA</u> (endocrine disrupting estrogen mimic)	<u>BPS</u> (ditto)
Refrigerants	<u>CFCs</u> (ozone depleters & greenhouse gases)	<u>HFCs</u> (greenhouse gases)
“Many aspects of modern life”	<u>PFOA</u> & <u>“long-chain” PFASs</u> (associations w/ cancer + kidney, liver, immune problems)	<u>Perfluoro ethers</u> & <u>“short-chain” PFASs</u> (less persistent in human bodies, otherwise ?)

**What do we learn by putting these histories together?**



# DDT

Othmar Zeidler, 1874:  
dimonochlorophenyltrichloroethane



1938: Geigy chemist Paul Müller: chlorine-substituted methyldiphenyls as insecticides → DDT (& others) → *War: urgency, resources, investment*

1950s-60s: massive DDT use in agriculture and global health

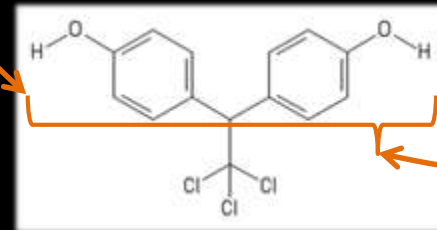
*Dependencies (trees)  
+ problems (moles)*

1970s: ID'ing substitutes becomes condition of pesticide phaseouts

# BPA

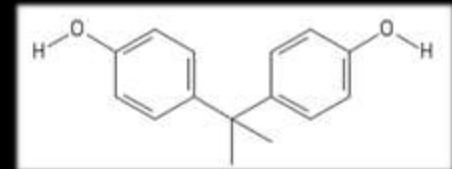
Edmund ter Meer, 1874:

dioxyphenyltrichloroethane



“bisphenol”

BPA: 1891



*War: urgency,  
resources,  
investment*

1950s: Bayer & Monsanto chemists:  
bisphenol-based polycarbonates as  
“engineering plastics” for missiles &  
fighter jets

*Cheap petrochem BPA  
(acetone+phenol): tree*

↓  
BPA-based consumer polycarbonates

↘ *Endocrine disruption: mole*

↘ “BPA-free” substitutes, including BPS

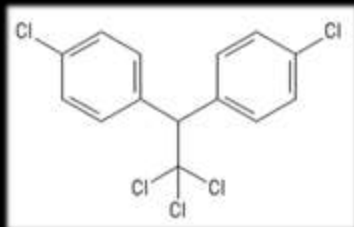
**Coal-tar derived; Lister's "carbolic acid" disinfectant** ↗

1874, Strasbourg: Adolf von Baeyer has students react phenol + chloral.

Goal: 1) advance chemical theory, 2) investigate phthalein dyes for BASF, **chemical**

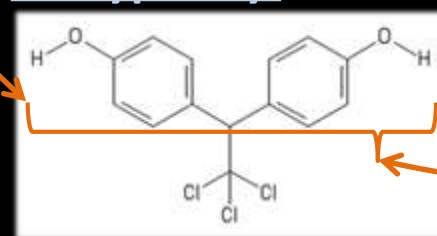
Othmar Zeidler, 1874: **synthetic indigo guy**

dimonochlorophenyltrichloroethane



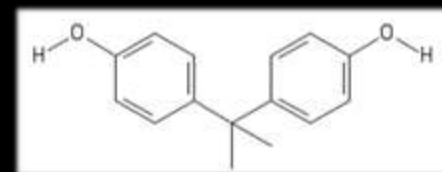
Edmund ter Meer, 1874:

**dioxyphenyltrichloroethane**



**"bisphenol"**

**BPA: 1891**



1938: Geigy chemist Paul Müller: chlorine-substituted methyldiphenyls as insecticides → DDT (& others)

War: urgency, resources, investment

**BPA+phosgene (industrial chem. / poison gas)**

1950s-60s: massive DDT use in agriculture and global health

**Dependencies (trees) + problems (moles)**

1970s: ID'ing substitutes becomes condition of pesticide phaseouts

1950s: Bayer & Monsanto chemists: bisphenol-based polycarbonates as "engineering plastics" for missiles & fighter jets

**Cheap petrochem BPA (acetone+phenol): tree**

BPA-based consumer polycarbonates

**Endocrine disruption: mole**

"BPA-free" substitutes, including BPS

**Déjà vu**

**The substitution Swindle**

**“Essentialism”**

**Chemistries of concern**



**“Chemistries”**: shop talk in 20<sup>th</sup>-21<sup>st</sup> century industrial chemistry; an imprecise term encompassing clusters of useful chemical behaviors as well as the substances and processes (nano to industrial scale) that enact them.

Thank you!

Evan Hepler-Smith  
Duke University  
[evan.heplersmith@duke.edu](mailto:evan.heplersmith@duke.edu)  
[evanheplersmith.com](http://evanheplersmith.com)