

Radicals – Experiments, Existence, Electrons



Microscópico (stuff; wet chemistry, reacciones de identificación)

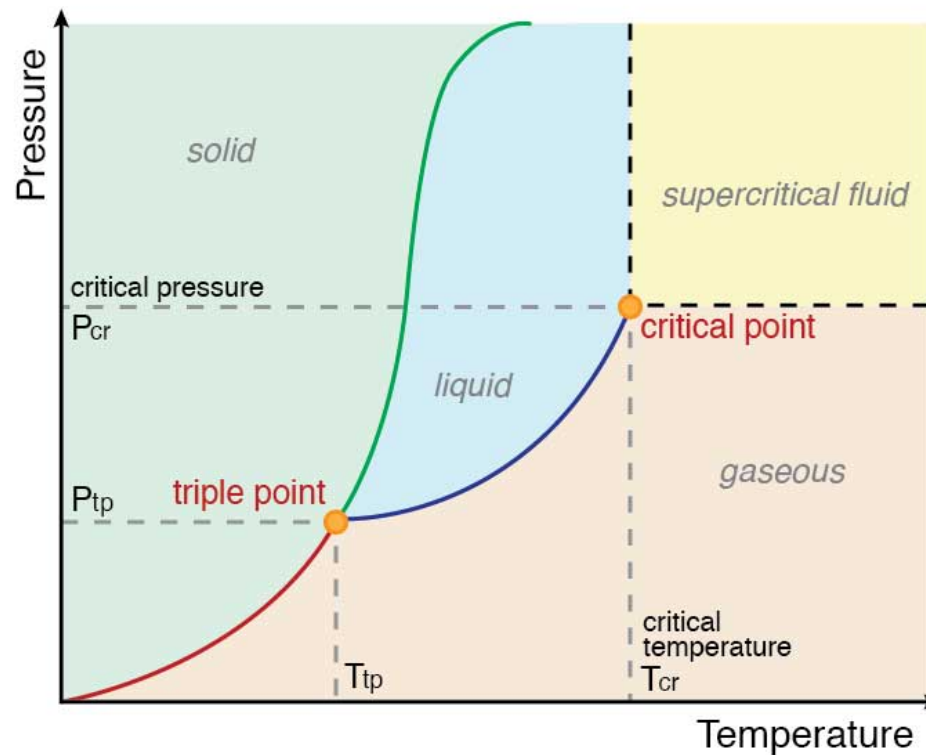
TABLA 11.1 Tipos de reacciones de los alcoholes

$R-OH$	$\xrightarrow{\text{tipo de reacción}}$	Producto
$R-OH$	$\xrightarrow{\text{deshidratación}}$	alquenos
$R-OH$	$\xrightarrow{\text{oxidación}}$	cetonas, aldehídos, ácidos
$R-OH$	$\xrightarrow{\text{sustitución}}$	$R-X$ haluros
$R-OH$	$\xrightarrow{\text{reducción}}$	$R-H$ alcanos
$R-OH$	$\xrightarrow{\text{esterificación}}$	$R-O-\overset{\text{O}}{\parallel}{C}-R'$ ésteres
$R-OH$	$\xrightarrow{\text{tosilación}}$	$R-OTs$ tosيلاتos (buen grupo saliente)
$R-OH$	$\xrightarrow{\begin{matrix} (1) \text{ formación} \\ \text{de alcóxido} \\ (2) R'X \end{matrix}}$	$R-O-R'$ éteres

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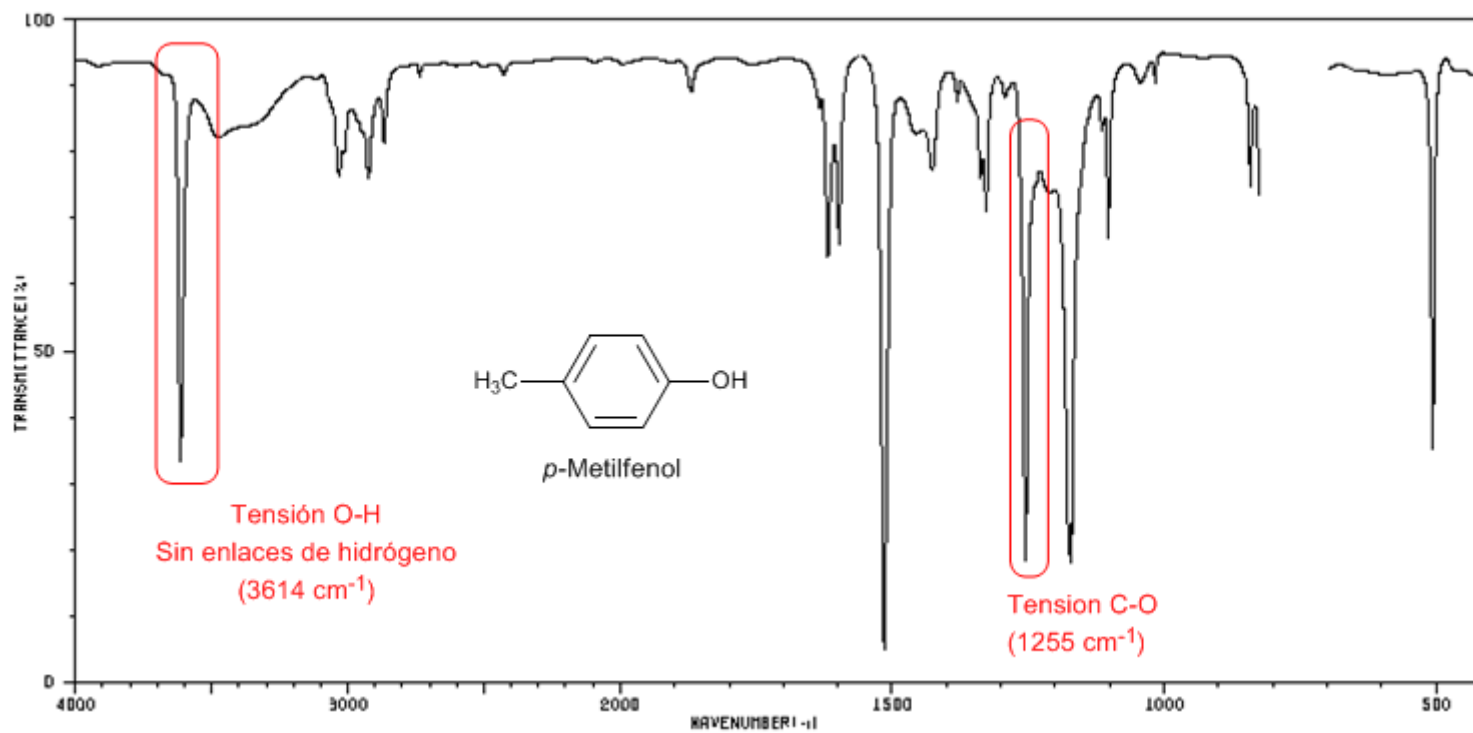
Termodinámico (constantes físicas, calorímetro)



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Espectroscópico (transiciones electrónicas)



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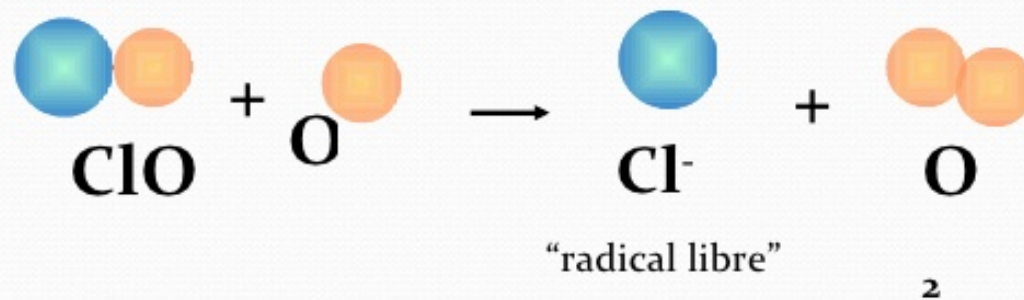
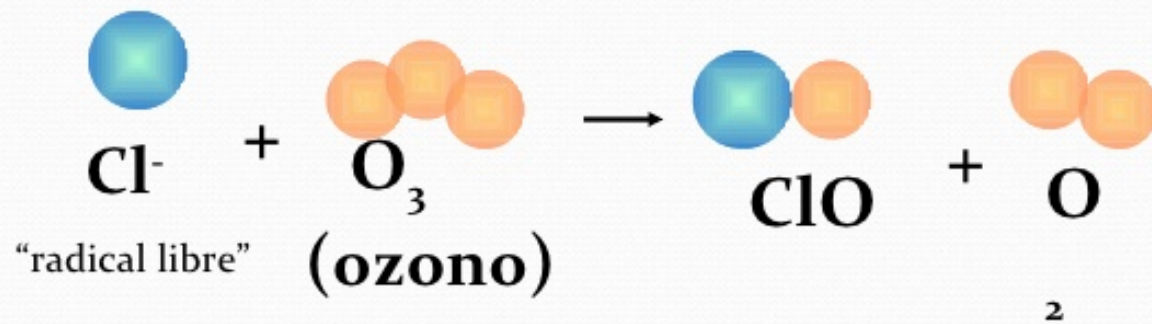
¿Qué es un radical libre?

Los radicales libres son moléculas o átomos que contienen por lo menos un electrón sin aparear, es decir que no se encuentra formando un par electrónico en un orbital atómico o molecular.

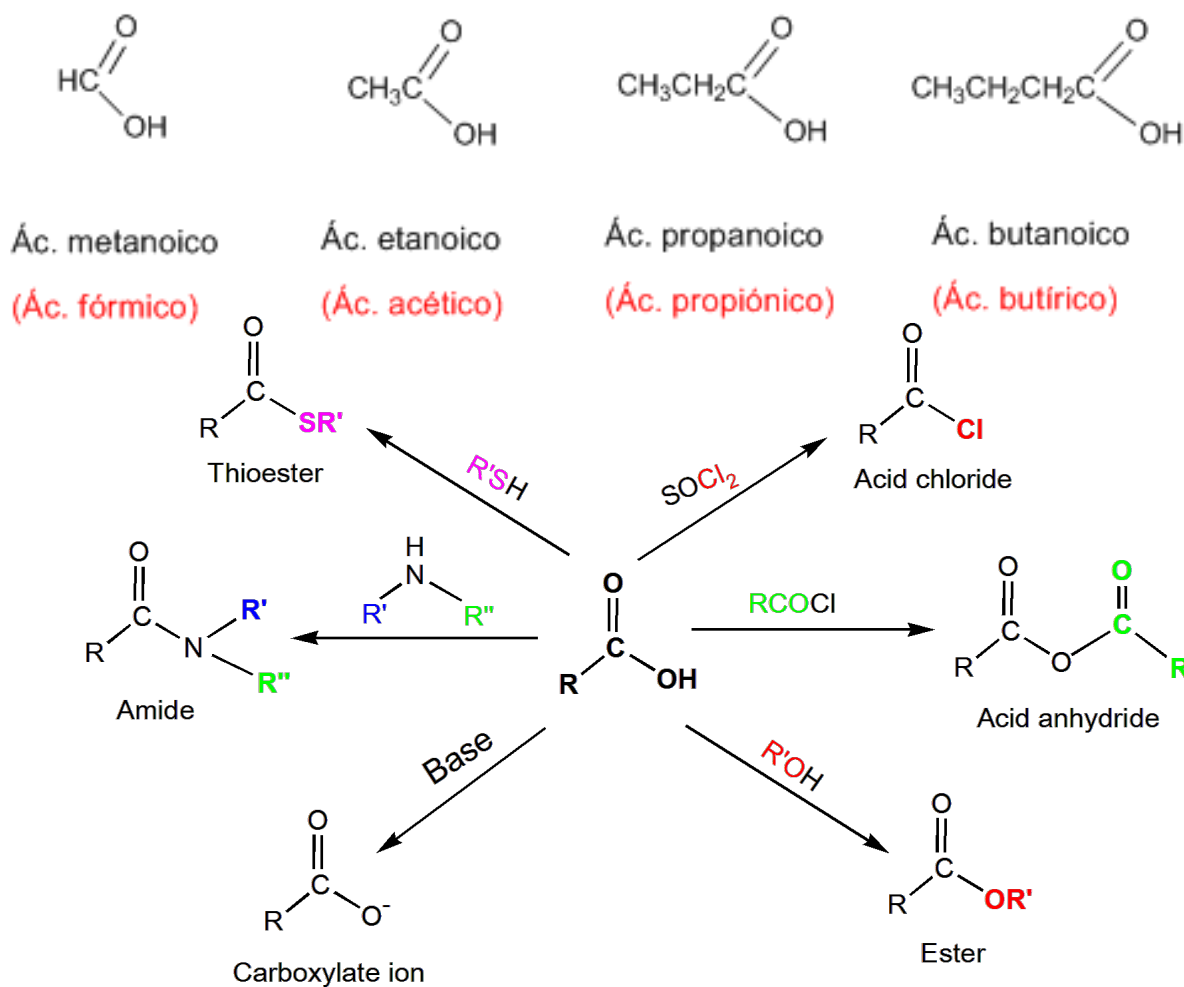
Esta es una estructura muy inestable, por lo cual los radicales libres reaccionan muy rápidamente con otras sustancias y tienen una vida media muy corta, tal como una **millonésima de segundo**.



Destrucción del ozono



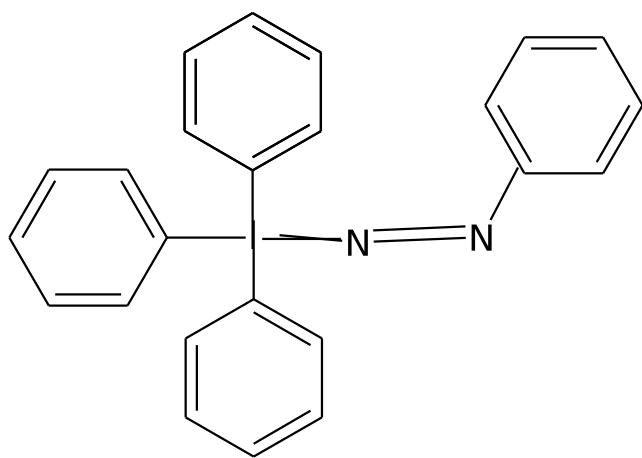
- 1815–1835 Radicals were agencies for classifying the increasing number of organic substances
- 1835–1850 It became apparent that the analogy between radicals and elements was merely formal
- 1848–1858 The type theory came into being
- 1860–1900 Valency theory and the quadrivalency doctrine for carbon emerged.



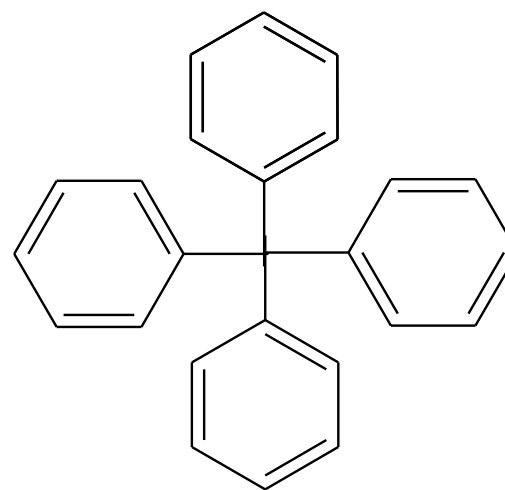
Periodo especulativo
 Periodo sintético
 Periodo electrónico

Síntesis de Gomberg

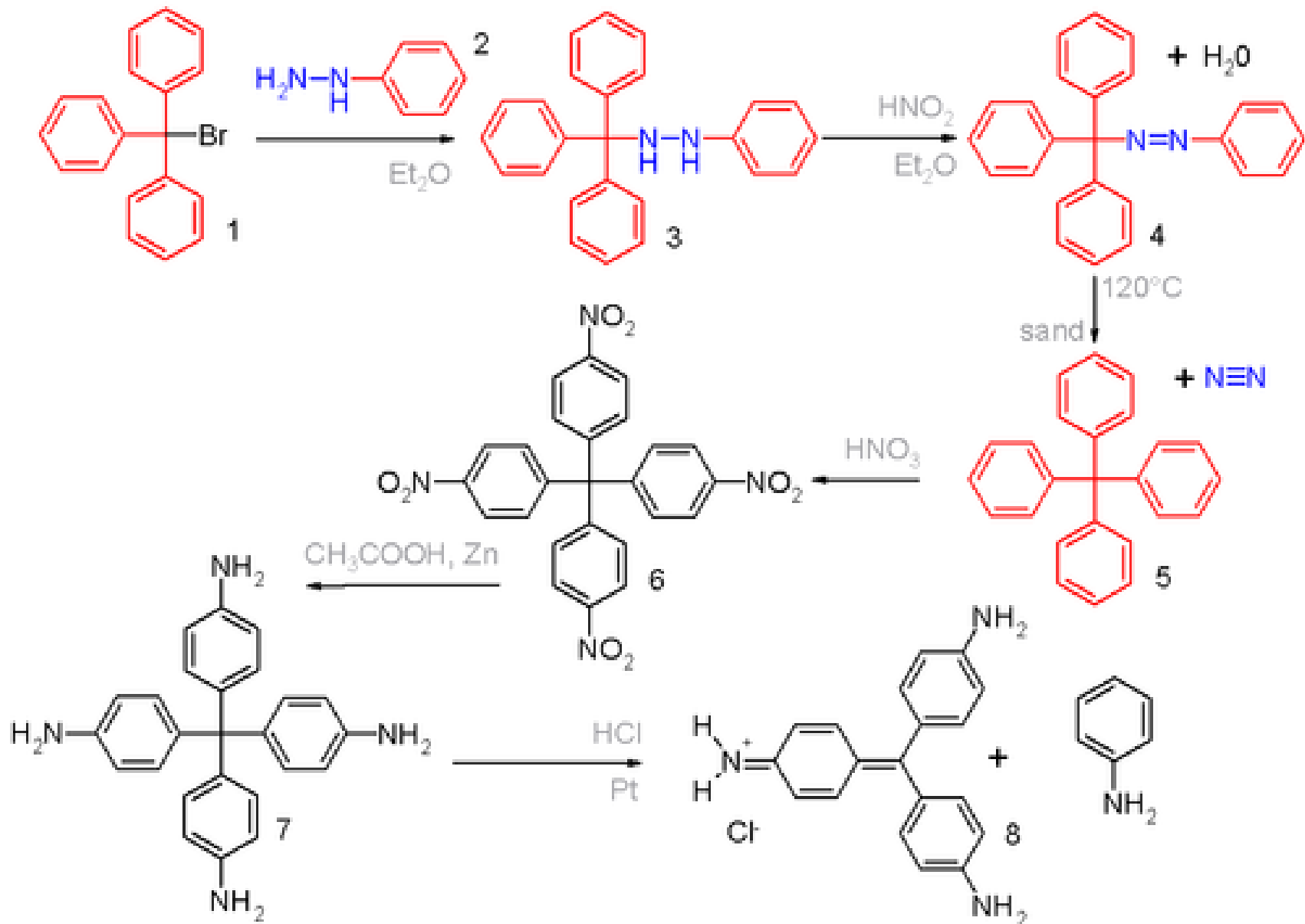
The chemical world was moving into the twentieth century quite happily with the quadrivalency of the carbon atom and was inclined to look upon free radicals as speculative inventions. It was in this environment that Moses Gomberg's paper ›Triphenylmethyl, ein Fall von Dreiwertigen [sic] Kohlenstoff‹ made its appearance.

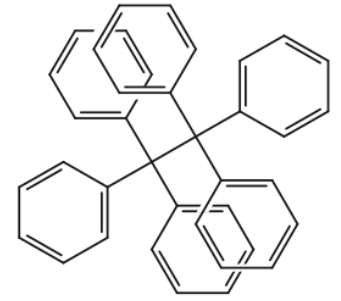
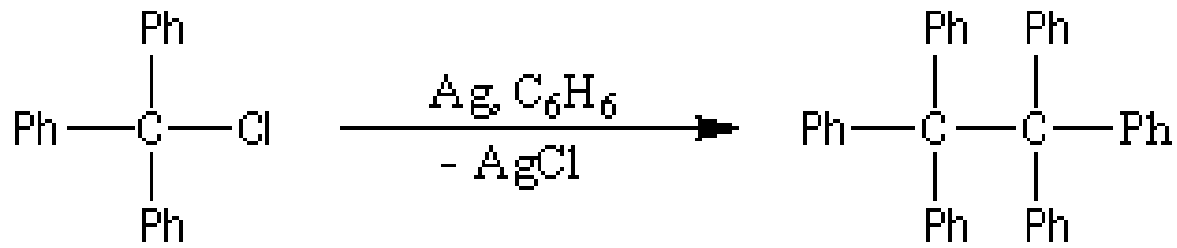
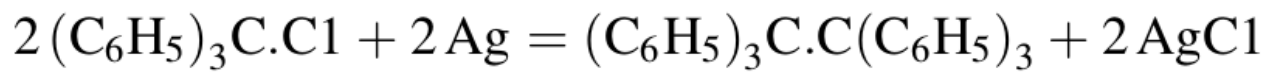


fenilazotriphenilmetano

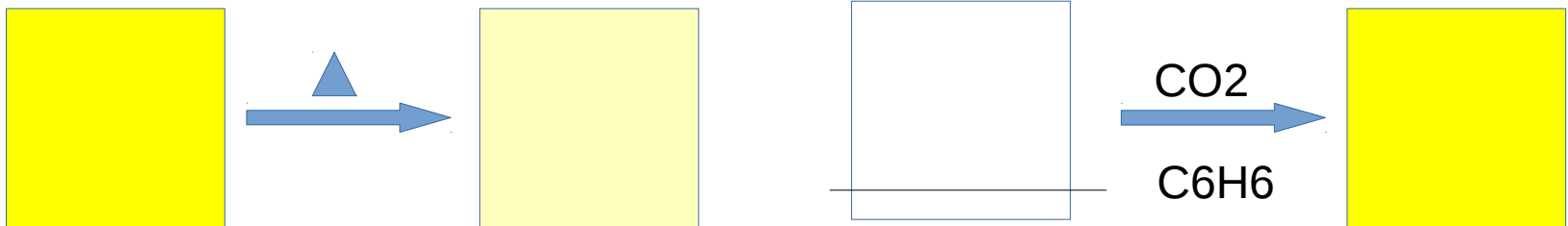


Tetrafenilmetano

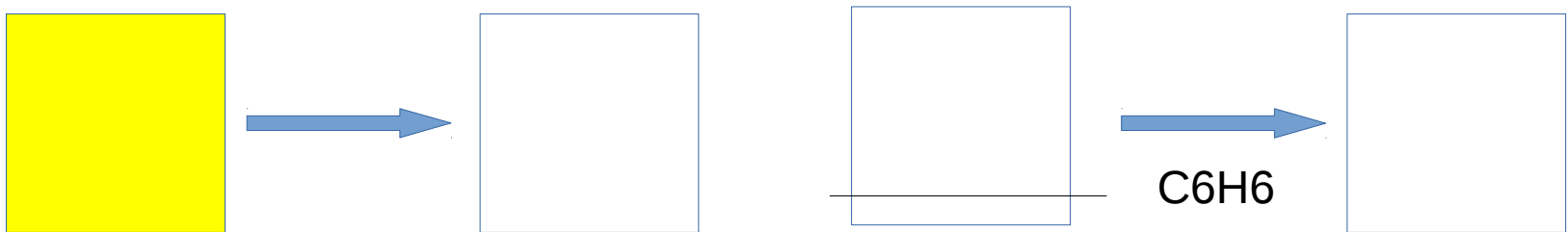


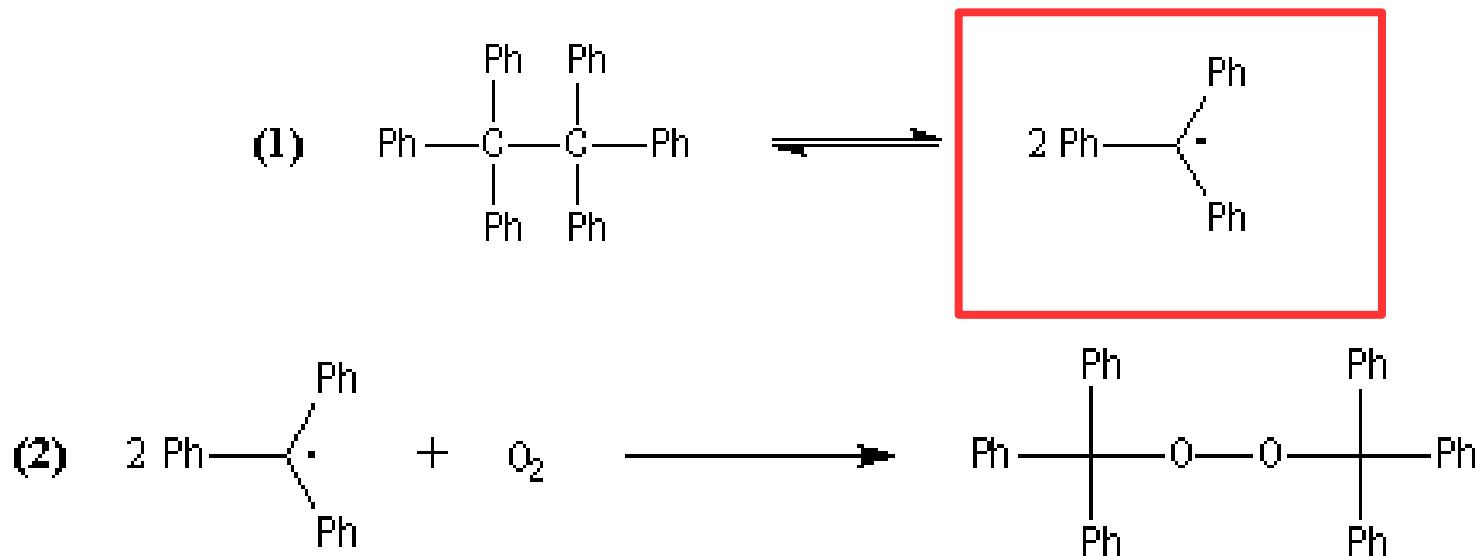


CO2



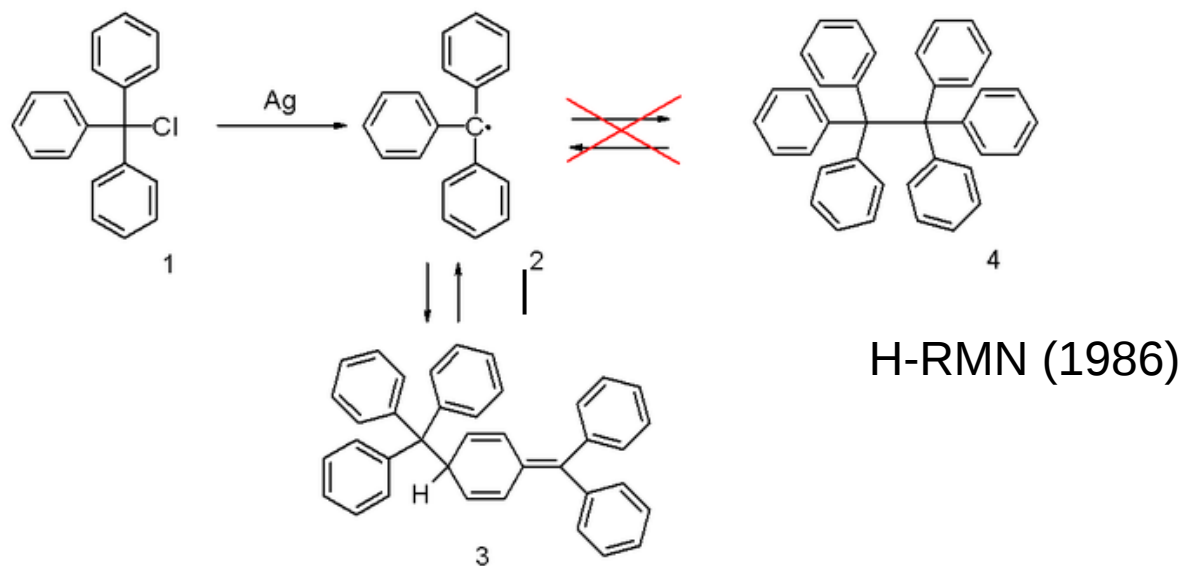
O2





Sustancia química de carbono trivalente, Gomberg sin embargo no aisló esta sustancia (?)

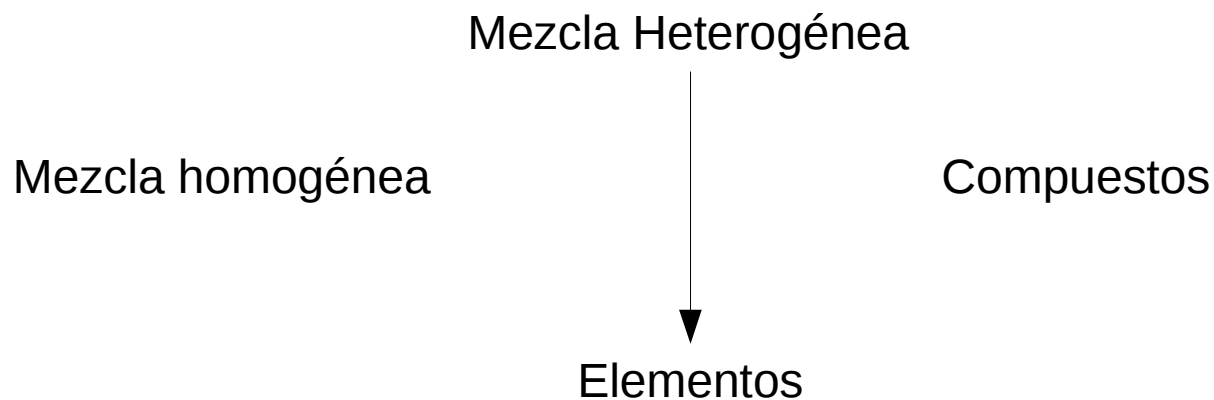
For Gomberg and his contemporaries the break of the quadrivalence doctrine was the main criterion for a substance to be classified as a radical.



The hexa-arylethanes, aside from the irreversible processes of intramolecular rearrangement and autoxidation to which they are subject and which we shall not further consider, exist in a state of tautomeric equilibrium between quinoid forms and the benzoid form which represents the simple substituted ethane. (Lewis 1916)

“Hitherto, the definitely recognized units in chemistry have been: atoms, molecules, ions, and electrons. And now, in addition to these four, chemistry, it seems, has to take into account a fifth entity – free radicals” (Gomberg 1928).

“experimental stuff hierarchy” (Schummer 2008, 13)



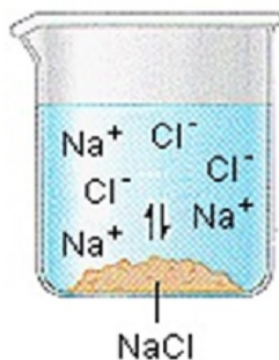
(1) How may a given physical-chemical system be defined without ambiguity?
This is the problem of chemical species;
(2) How may such a system be realized? This is the problem of pure materials;
(3) How may its constants be measured with precision and exactitude?; (4)
How may the best method of purification and the most probable value of the constants of pure materials be found in the literature?” (Timmermans 1940)

- (a) triphenylmethyl is unsaturated which is confirmed by the reactions with oxygen (yielding the peroxide) and iodine (yielding the iodide)
- (b) despite its extremely unsaturated character triphenylmethyl seems to have a double formula in solution (with respect to osmotic molecular mass determinations)
- (c) with compounds containing oxygen like ethers triphenylmethyl builds additive structures (Walden 1924, 50: *Molekülverbindungen*)
- (d) similarly, it yields addition products with nitriles (R-CN)
- (e) with “indifferent” solvents (chloroform, carbon disulfide, benzene, toluene) addition products were built, too
- (f) the “free” triphenylmethyl can be considered a basic radical (*basisches Radikal*) because it has a good electric conductivity in SO₂ solutions
- (g) particularly remarkable is the formation of addition products even with totally saturated hydrocarbons like hexane, heptane, octane, decane, cyclohexane
- (h) similar results are obtained with triarylmethyls other than triphenylmethyl
- (i) triphenylmethyl is reasonably resistant against hydrogen and water
- (j) hydrogen chloride (HCl, in dry benzene) causes a rearrangement to p-benzhydryltetraphenyl methane

The Empiricist or operationalist attitude:

Wilhelm Ostwald (1853– 1932) was among those who were skeptical of metaphysical assumptions in general and with speculative atomism in particular. He claimed that a recognized chemical substance must be capable of being isolated as a stuff sample:

It took a long time before it was finally recognized that the very nature of the organic radicals is, inherently, such as to preclude the possibility of isolating them. And now it is becoming evident that the same holds true of ions (1896).



Another example of an empiricist and operationalist approach to chemistry is the theory of František Wald (1861–1930).

In his article “Was ist ein chemisches Individuum?”, Wald said: Chemical individuals are phases that occur in a phase system with at least one independent variation, and retain evidently consistent for all variations associated with the conditions of the phase system. Phases are characterized by Wald, for example, as follows:

“In brief, with the word phase we denote any part in a mixture in equilibrium that is perceived by the senses, and that is a homogeneous part, distinguishable from another part.”

As to triphenylmethyl, the preparation and comparison of different aggregate states is extremely restricted. The dissolving, for example, leads to higher extinctions in calorimetric measurements if no shielding gas is applied because the reaction with oxygen is very quick. That means, because triphenylmethyl cannot be obtained consistently for all variations of the observed phase system (that is the variations through the states of aggregation) and because it cannot be perceived easily by the senses and because for Gomberg it was not clear whether or not the obtained substance was in equilibrium, it cannot be considered a chemical individual proper according to Wald.

Chemical species which cannot be put into bottles, cannot be subjected to any reversible phase transition, occur only in solutions or other special environments, have an extremely short half-life, only “exist” in excited stages, etc., may have a full claim to being a chemical species and may even claim to be a separate phase, but may or may not claim to be substances. If the species only exist in equilibrium with other species “inside” pure substances or solutions, it seems plausible to admit them as species, but not as substances. This includes radicals, reactive fragments, activated complexes, ligand-receptor complexes, etc. Whether (different kinds of) tautomers should be classified as separate substances or species is less obvious. (van Brakel 2012, 222)

the classical (or phenomenological or thermodynamical) approach of stuff characterization appears not to come to terms with the chemical species radical in general.

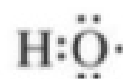
Only few exceptions are stable enough under normal conditions and can be observed, analyzed, characterized or represented along the lines of the methodology of the stuff (or phase) concept.

“Chemistry is the science of stuff and its changes” still hold when applied to radicals, if the emphasis is laid on the last word: what in fact is registered or detected during chemical experiments are stuff changes.

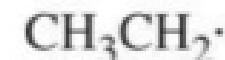
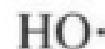
What seems to be peculiar for chemistry is the priority of entity-realism over theory-realism: long before an appropriate theoretical representation was developed chemists denoted their scientific objects as radicals. To put it in other words: the discovery of “triphenylmethyl” has not been the result of theory-driven activities.

Lewis Structures of Free Radicals

Lewis structures



Written



chlorine atom

bromine atom

hydroxyl radical

methyl radical

ethyl radical

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- Free radicals are unpaired electrons.
- Halogens have 7 valence electrons so one of them will be unpaired (radical). We refer to the halides as atoms not radicals.

Thus sodium in the state of vapor has 1, monatomic iodine has 7, NO₂ has 17, ClO₂ has 19, (C₆H₅)₃ has 91, (C₆H₅)₂N has 63, and (C₆H₅)₂NO has 69. *old molecules*

Since an unpaired electron is always held in the molecule by weak constraints, it is usually capable of oscillating with so low a characteristic frequency as to absorb visible light. This absorption, moreover, involving only a single electron, might be expected to be of the simplest possible character.

Con la teoría electrónica del enlace químico (1916) el requisito fundamental para ser un radical es contener un electrón libre.

¿que es una especie química?