



81. Latvijas Universitātes
starptautiskā zinātniskā
konference 2023

Valdena apgriezenība – pavērsiens zinātnieku domāšanā

RTU Zinātniskā bibliotēka Ķīmijas filiāle
vec. bibliotekāre Maija Piekuse

Pauls Valdens – izcilākais un pasaules mērogā pazīstamākais latviešu zinātnieks

1963 – 1957



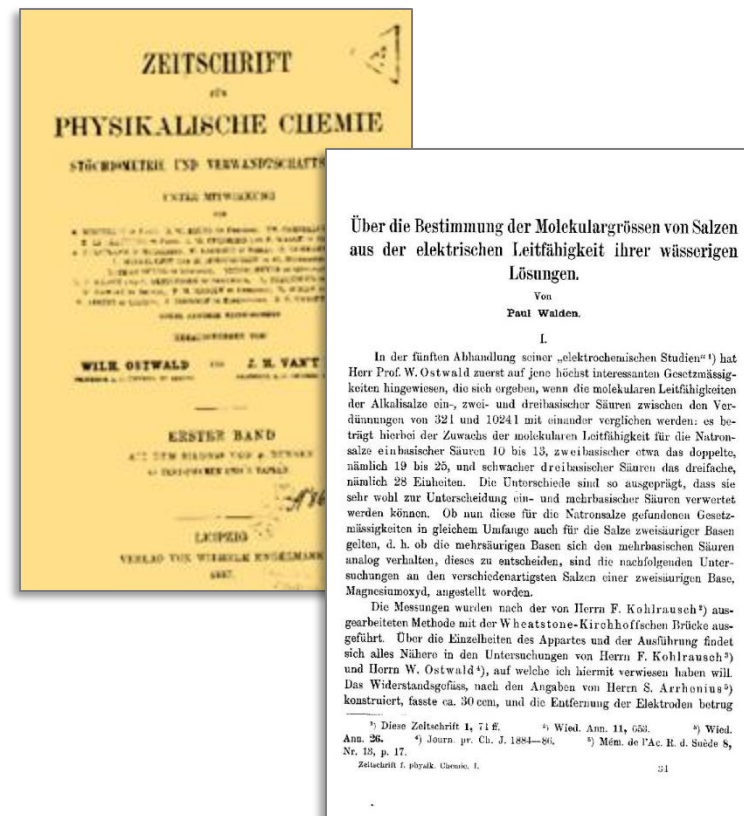
Karjera Rīgas Politehnikumā

- Studijas Rīgas Politehnikuma Ķīmijas tehnoloģijas nodaļā (1882-1889)
- Fizikas asistents (1885-1887)
- Ķīmijas asistents (1887-1892)
- Docents fizikālajā ķīmijā (1892-1894)
- Analītiskās un fizikālās ķīmijas profesors (no 1894)
- RPI Ķīmijas nodaļas dekāns (1906-1916)
- RPI direktors, rektors (1902-1905; 1917-1918)



Fizikālā ķīmija

- Pirmie pētnieciskie darbi fizikālajā ķīmijā prof. V. Ostvalda vadībā
- Publikācija žurnālā «*Zeitschrift für physikalische Chemie*» (1887)
- **Ostvalda-Valdena likumība** ļauj «.. noteikt skābes anjona vai bāzes katjona vērtību pēc to šķīdumu molārajām elektrovadītspējām»



Zeitschrift für physikalische Chemie,
1887, 1, 529-549

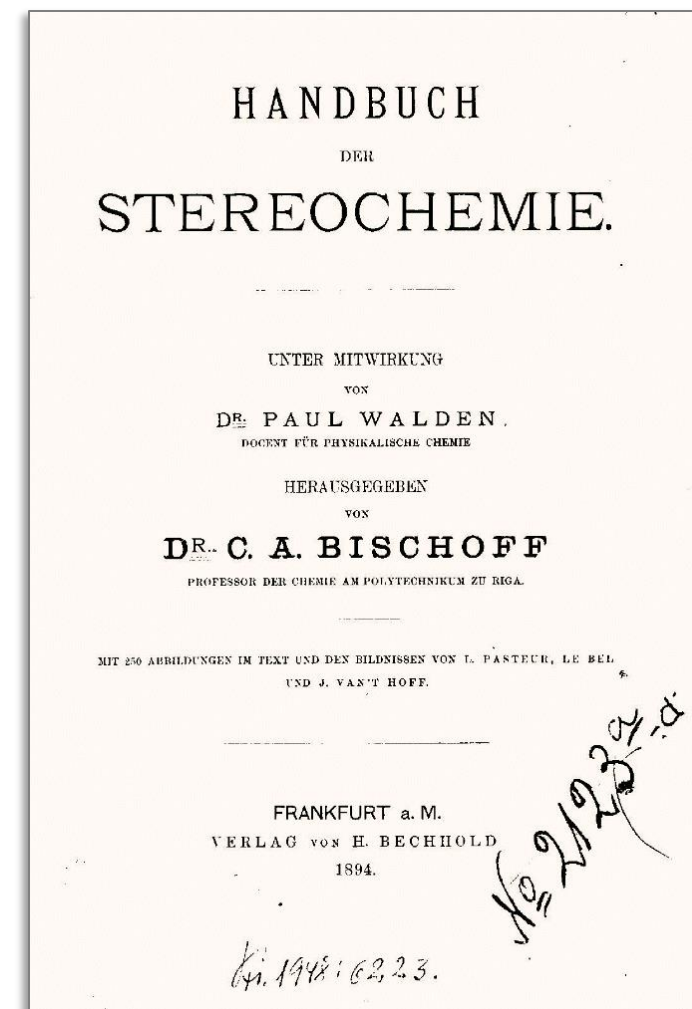
Über die Bestimmung der Molekulargrößen von Salzen aus der elektrischen Leitfähigkeit ihrer wässrigen Lösungen



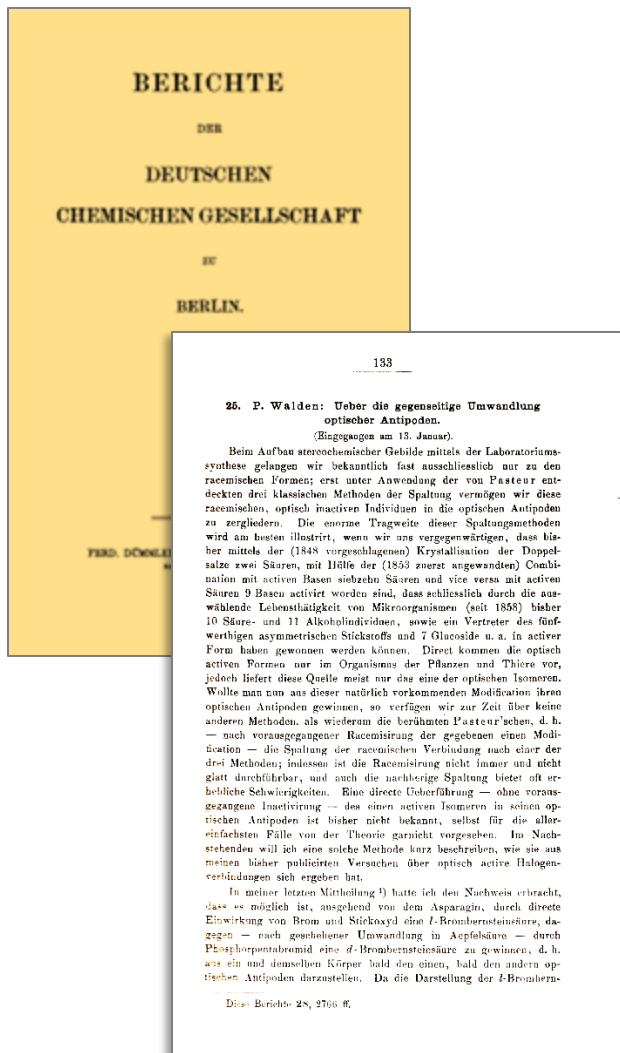
Stereoķīmija

- RPI organiskās ķīmijas profesora K. Bišofa asistents
- Ķīmiskās sintēzes un publikācijas žurnālos (57)
- Rokasgrāmata «Handbuch der Stereochemie», 1894

Handbuch der Stereochemie / unter Mitwirkung Paul Walden; herausgegeben von C. A. Bischoff; mit 250 Abbildungen im Text und Bildnissen. Frankfurt a. M.: H. Bechhold, 1894. 1060 lpp.



Nozīmīgākais & slavenākais atklājums 1895/1896



Publikācija žurnālā «Berichte der Deutschen Chemischen Gesellschaft» (1896) par optisko antipodu savstarpējo pārvēršanos

Ueber die gegenseitige Umwandlung optischer Antipoden von P. Walden

Ber. Deutsch. Chem. Gesell. 1896, 29, 133 - 138



Nozīmīgākais & slavenākais atklājums 1897

Publikāciju turpinājumi žurnālā «Berichte der Deutschen Chemischen Gesellschaft» (1897)



2795

467. P. Walden und O. Lutz: Ueber die gegenseitige Umwandlung optischer Antipoden.
[II. Mittheilung].
(Eingegangen am 16. November.)

Vor einiger Zeit habe ich der Eine von uns über eine eigenartige optische Inversion berichtet, die es ermöglichte, direct von einem Antipoden zum entgegengesetzt drehenden Uebergang, somit einem optischen Kreisproceß durchzuführen. Zum Schluss wurde die Ansicht ausgesprochen, dass es gelingen werde, nach mit Hilfe anderer Agentien den gleichen Vorgang zu verwirklichen.

In Verfolgung dieser Frage haben wir das Studium der Einwirkung von Ammoniak auf die activen Chlor- und Brom-Bromstoffsäuren¹⁾ wieder aufgenommen, was der Eine von uns früher nur orientirend durchgeführt hatte. Die nacheinander zeitlich und quantitativ erfolgten Versuche ergaben das ausstehende merkwürdige Resultat.

Lässt man auf die *D*-Brom- (oder Chlor-) Bromstoffsäure in methylalkoholischer Lösung Ammoniak einwirken und verfolgt die Reaction mit Zuhilfenahme des Polarisationsapparates, so sieht man allmählich die Linksdrehung abnehmen und durch Null in eine erhebliche Rechtsdrehung übergehen. Am besten verfährt man in der Weise, dass man 50 g *D*-Bromstoffsäure in wenig Methylalkohol löst und 200 g einer ca. 12-proc. Lösung von Ammoniakgas in Methylalkohol vorsichtig hinzutägt; das verkorkte Gefäß wird nun, zur Beschleunigung der Reaction, in ein auf 40–45° erwärmtes Wasserbad gesteckt und durch Einleitung der Drehungsänderung an herausgenommenen Proben der allmählichen Fortgang der Reaction verfolgt; ist eine Vernehrung der Rechtsdrehung nicht mehr zu constatiren, was im Allgemeinen nach 10–12 Stunden eintritt, so entfernt man das Gefäß aus dem Wasserbad. Nach einiger Zeit scheiden sich aus der Reactionsmasse tropfenförmige, strahlig krystallinisch erscheinende Gebilde aus, die den Boden mit einer dicken Kruste bedecken; sie wiegen 20 g und lassen sich durch Lösen in wenig Wasser und Fällen mit ammoniakalischem Methylalkohol von geringen bromhaltigen Beimengungen trennen. Aus beiden Mutterlauge lässt sich leicht durch Eindampfen im Vacuumexsiccator eine weitere Menge — etwa 4 g — desselben Productes isoliren, demnach insgesamt 80 pCt.

Analysen: Ber. für $C_2H_5O_2N$.
Procente: C 32.00, H 6.56,
Nef. » 21.60, » 6.52.

¹⁾ Vergl. diese Berichte 28, 133 ff. (1895).
²⁾ L. c. sowie diese Berichte 28, 1595 ff., 2766 ff.

P. Walden und O. Lutz: Ueber die gegenseitige Umwandlung optischer Antipoden. II. Mittheilung

354. P. Walden: Ueber die gegenseitige Umwandlung optischer Antipoden.
[III. Mittheilung].
(Eingegangen am 24. December.)

Nachdem ich in meiner ersten Mittheilung¹⁾ die umwandelnde Wirkung des Phosphorpestachlorids (und -bromids) constatirt hatte, alsdann in der zweiten Abhandlung²⁾ die Inversion mit Hilfe des Ammoniak (und der Amine) bei weiteren Alkoholen des Zweichlorproductes nachgewiesen worden ist, soll durch die gegenwärtige Arbeit eine weitere und, wie mir scheint, die einfachste Methode mitgetheilt werden, durch welche es gelingt, aus ein und demselben, activen Halogenderivat, durch den gleichen Substitutionsvorgang (directer Ersatz des Halogens durch die Hydroxylgruppe) und durch ganz analog gebaute Agentien (Silber-Oxyd und -Carbonat, sowie Kalhydrat), ohne die Bildung von Zwischenproducten sowohl das rechts-, als auch das links-drehende Hydroxyderivat zu gewinnen.

¹⁾ Diese Berichte 29, 123. ²⁾ Diese Berichte 30, 2755.

P. Walden : Ueber die gegenseitige Umwandlung optischer Antipoden III. Mittheilung

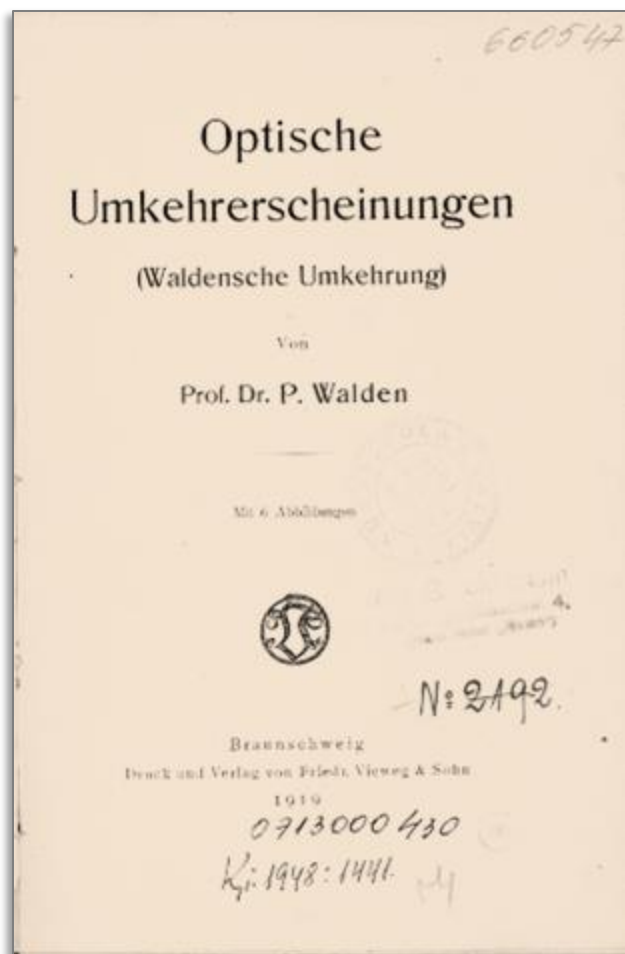
Ber. Deutsch. Chem. Gesell. 1897, 30, 2795 – 2801

Ber. Deutsch. Chem. Gesell. 1897, 30, 3146- 3151



Valdena apgriezenība

1906. gadā vācu ķīmiķis Emīls Fišers nosauca P. Valdena atklājumu par ***Valdena apgriezenību***

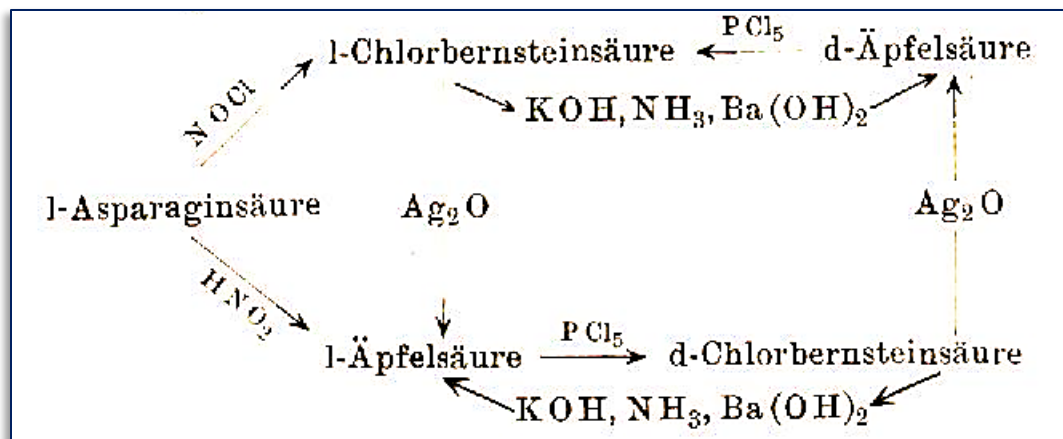


Waldensche Umkehrung
Walden-Umkehr
Waldensche Umkehr
Walden inversion

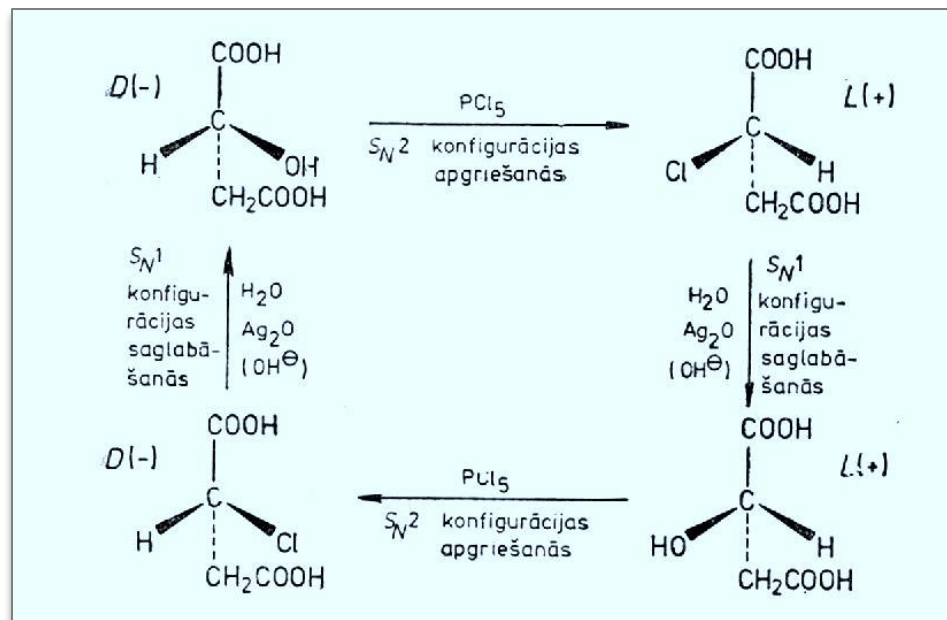
P. Walden. Optische Umkehrerscheinungen (Waldensche Umkehrung).
Braunschweig: Friedr. Vieweg & Sohn, 1919. 214 lpp.

Valdena apgriezenība

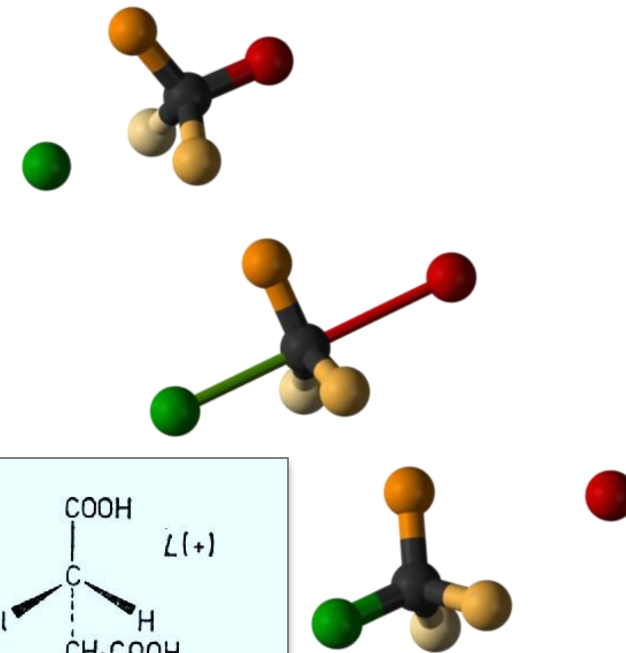
Valdena cikla shematiski skaidrojumi



P. Walden. Optische Umkehrerscheinungen
(Waldensche Umkehrung). Braunschweig: Friedr.
Vieweg & Sohn, 1919. 25. lpp.

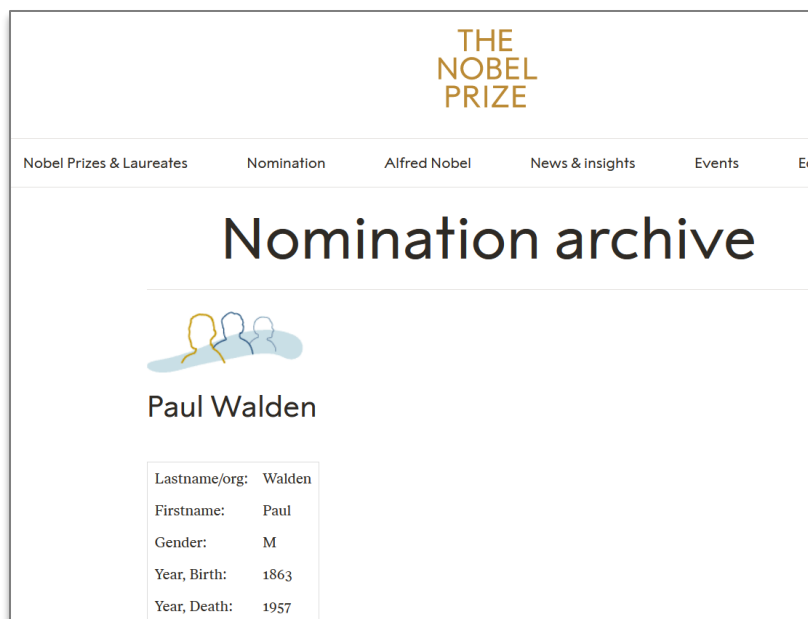


O. Neilands. Organiskā ķīmija. Rīga: Zvaigzne,
1977. 608. lpp.



Nominācijas Nobela prēmijai ķīmijā


P. Valdens 7 reizes tika nominēts Nobela prēmijai, bet to nesaņēma



THE NOBEL PRIZE

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Nomination archive



Paul Walden

Lastname/org:	Walden
Firstname:	Paul
Gender:	M
Year, Birth:	1863
Year, Death:	1957

Nominee in 9 nominations:

- Chemistry 1914 by Giacomo Ciamician
- Chemistry 1920 by Carl Drucker
- Chemistry 1920 by Wilhelm Böttger
- Chemistry 1927 by Wilhelm Böttger
- Chemistry 1934 by Carl Blacher
- Chemistry 1934 by Waldemar Fischer
- Chemistry 1947 by Nil Dhar
- Chemistry 1948 by Jean Timmermans
- Chemistry 1954 by Charles Dufraisse

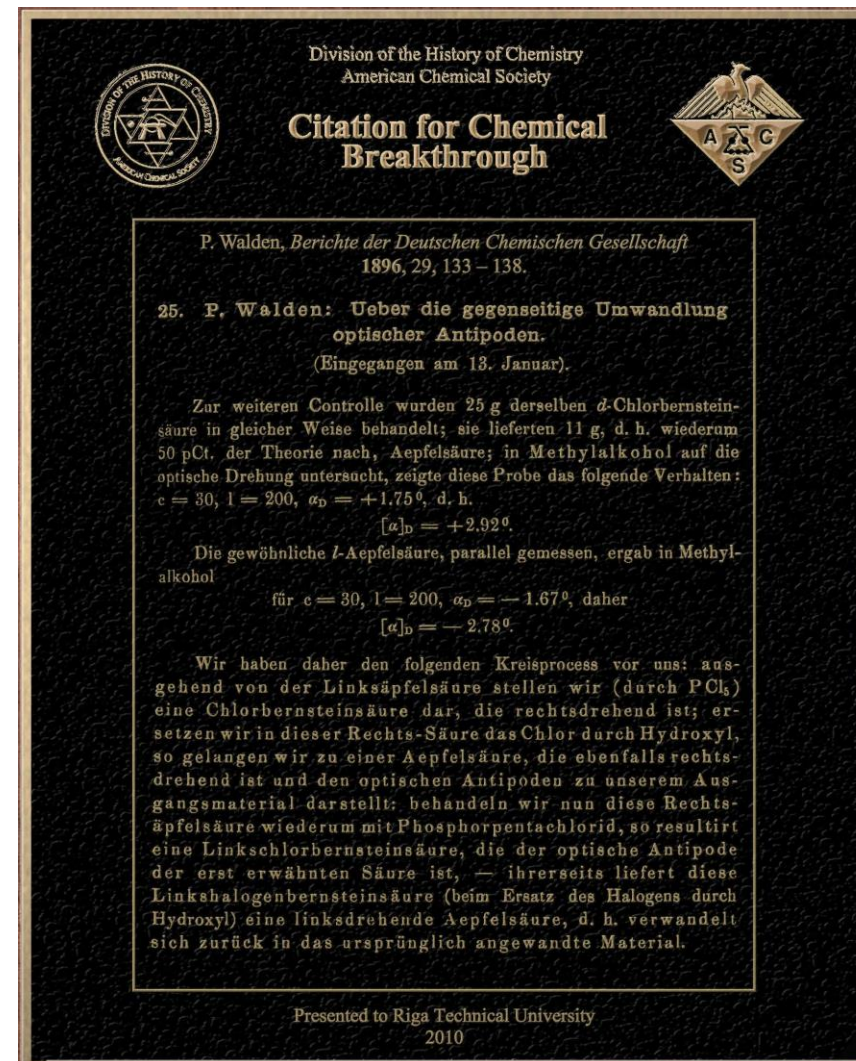
Nominator in 2 nominations:

- Chemistry 1904 for Wilhelm Ostwald
- Chemistry 1911 for Alfred Werner

https://www.nobelprize.org/nomination/archive/show_people.php?id=9940

Award of Citation for Chemical Breakthrough 2010

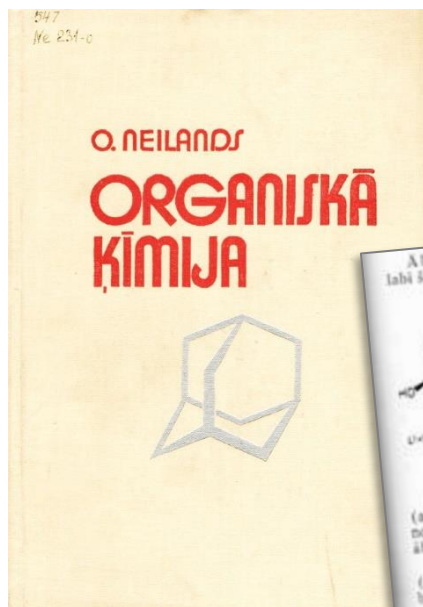
Amerikas Ķīmijas biedrības balva par publikāciju, kas izraisījusi *pavērsienu zinātnieku domāšanā*



DIVISION OF THE HISTORY OF CHEMISTRY		
ENHANCED BY Google		
Citations for Chemical Breakthrough Awards		
2010 Awardees		
NOTE: Text in COLOR indicates a "live" link.		
Scientists/Inventors	Breakthrough Publication (If text is in color, this is a live link to the plaque.)	Location of Award (If text is in color, this is a live link to photographs and other materials related to the presentation.)
P. Walden	"Ueber die gegenseitige Umwandlung optischer Antipoden," <i>Ber. Deutsch. Chem. Gesell.</i> 1896 , 29, 133 - 138.	Riga Technical University, Latvia Chem. Eng. News article about Paul Walden
V. Grignard	"Sur quelques nouvelles combinaisons organométalliques du magnésium et leur application à des synthèses d'alcools et d'hydrocarbures." <i>Comptes Rendus</i> 1900 , 130, 1322 - 1324.	University of Lyon
M. Tswett	"Adsorptionsanalyse und chromatographische Methode. Anwendung auf die Chemie des Chlorophylls," <i>Ber. Deutsch. Bot. Gesell.</i> 1906 , 24, 384 - 393.	University of Warsaw
J. B. Sumner	"The Isolation and Crystallization of the Enzyme Urease," <i>J. Biol. Chem.</i> 1926 , 69, 435 - 441.	Cornell University
J. C. Sheehan and K. R. Henery-Logan	"The Total Synthesis of Penicillin V," <i>J. Am. Chem. Soc.</i> 1957 , 79, 1262 - 1263.	Massachusetts Institute of Technology



Valdens apgriezenība modernajās mācību grāmatās



Abolskābe ir bezkrāsas kristāliska viela ar patīkamu skābu garšu, labi šķīst ūdenī.

CC(=O)O
 L(+)-Abolskābe

CC(O)C(=O)O
 D(-)-Abolskābe

D(-)-abolskābe — kušanas temperatūra 99...100 °C, [α]_D²⁰ = -5,7° (acetona šķīdumā; ūdens šķīdumā griešanās leģa ietilums ļoti atkarīgs no koncentrācijas); iegūta no dabas produktiem (sastopama negatīvas aboles, ērkšķogās, pilādžu ogās, maborkā) vai arī no (±)-abolskābes.

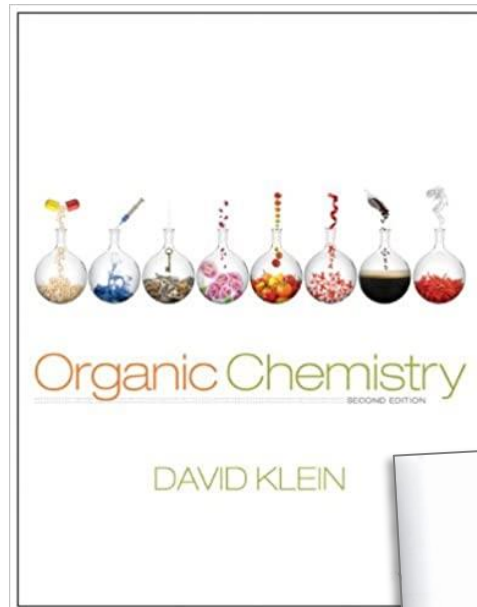
L(+)-abolskābe — kušanas temperatūra 99...100 °C, [α]_D²⁰ = +5,7° (acetona šķīdumā); iegūstama no (±)-abolskābes vai arī no (+)-vīnskābes, reducējot to ar HI.

(±)-abolskābe — kušanas temperatūra 129...130 °C, iegūstama no bromdintarskābes, hidrolizējot to ar ūdeni, vai arī no malēnskābes, pievienojot tai ūdeni:

CC(O)C(=O)O + H2O <-> CC(O)C(=O)O

Izmanto par starpproduktu organiskajā sintēzē un medicīnā.

Abolskābes reakcijas pētīti, P. Valdens Abolskābes reakcijām var iegūt (-)-izomērus no (+)-abolskābes var iegūt (+)-hlordintarskābi un no (-)-abolskābi. Savukārt no (+)-abolskābes var iegūt (-)-hlordintarskābi un tālāk (-)-abolskābi. Tādā veidā var panākt konfigurācijas apgriešanos. Šo parādību vēlāk nosauca par Valdens apgriezenību.



7.4 The S_N2 Mechanism

Stereospecificity of S_N2 Reactions

There is another crucial piece of evidence that led Ingold and Hughes to propose the concerted mechanism. When the α position is a chirality center, a change in configuration is generally observed, as illustrated in the following example:

CC(Br)C + [SH-] >> CC(S)C + [Br-]

Back-side attack

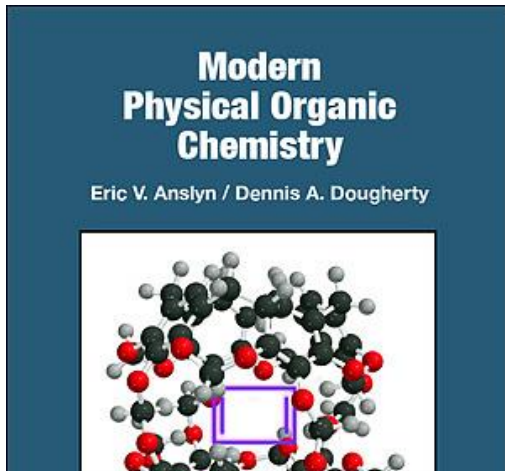
Front-side attack

The reactant exhibits the *S* configuration, while the product exhibits the *R* configuration. That is, this reaction is said to proceed with **inversion of configuration**. This stereochemical outcome is often called a Walden inversion, named after Paul Walden, the German chemist who first observed it.

The requirement for inversion of configuration means that the nucleophile can only attack from the back side (the side opposite the leaving group) and never from the front side (Figure 7.4). There are two ways to explain why the reaction proceeds through **back-side attack**:



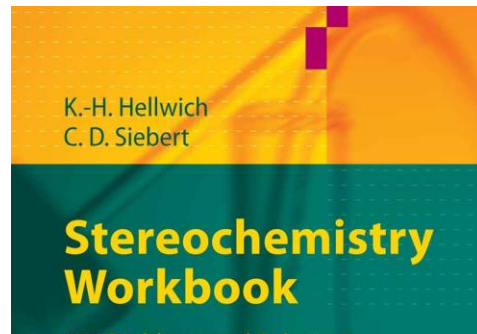
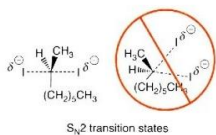
Valdena apgriezenība modernajās mācību grāmatās



11.5 NUCLEOPHILIC ALIPHATIC SUBSTITUTION REACTIONS

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What mechanism does Ingold's observation support? First, it shows that a simple S_N1 mechanism is not operating. The creation of a carbenium ion that is not in a solvent cage with the leaving group would lead to an equal amount of both enantiomers of the product for each incorporation of radioactive iodide, and hence racemization at exactly the same rate as radioactive iodide incorporation. The experimental observation also rules out frontside attack by the nucleophile, because the stereochemistry would be retained when the radioactive iodide is incorporated. Finally, the result does support a mechanism with backside attack, because each radioactive iodide incorporation inverts the stereochemistry of the reactant. This was a landmark experiment that helped to solidify the notion of backside attack in S_N2 mechanisms. It has been validated repeatedly in a wide range of systems. S_N2 reactions always proceed with inversion of configuration. S_N2 reactions are 100% stereospecific. Interestingly, the inversion of stereochemistry in aliphatic substitution reactions was first reported in 1893 by Walden, and in honor of this discovery, the stereochemical outcome of S_N2 reactions is termed the **Walden inversion**.

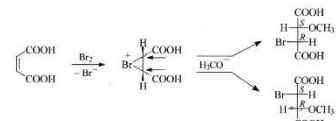


191 Problems

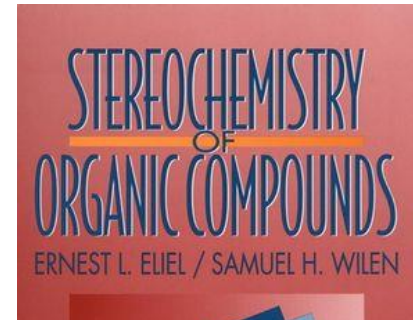
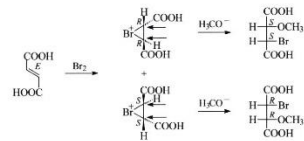
Answer 112 125

112

a) The cyclic bromonium ion produced from maleic acid is mirror symmetrical. Since there is equal probability that subsequent nucleophilic attack by methanolate can take place at either carbon atom, the product is a racemate. The reaction is not enantioselective but it is stereoselective since the *u*-configured racemate is formed exclusively as a product because the ring opening reaction proceeds with Walden inversion.



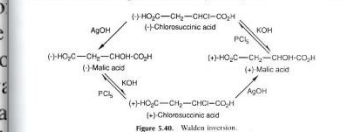
b) The cyclic bromonium ion produced from fumaric acid has only a two-fold proper axis of symmetry. Thus it will exist as a pair of enantiomers. Since there is equal probability that subsequent nucleophilic attack by methanolate can take place at either C2 and C3 of either enantiomer, the same *l*-configured product will be obtained in either case and consequently, overall a racemate will be obtained. The reaction is not enantioselective but is stereoselective. Since maleic acid and fumaric acid are stereoisomers and since the product obtained here is stereoisomeric to that obtained from maleic acid, the reaction is therefore also stereospecific.



The primitive notion that all displacement reactions proceed homofacially was dispelled by Walden (1896, 1897) who, at the end of the nineteenth century, performed the sequence of reactions shown in Figure 5.40. The enantiomeric (–)-chlorosuccinic and (+)-chlorosuccinic acids obviously have opposite configurations; thus if the AgOH reaction proceeds with retention, the KOH and PCl_5 reactions must proceed heterofacially. Unfortunately, it was not known at the time that two possibilities were the correct one and it was not until the work of Phillips (1923, 1925) that the stereochemical course of the reaction proceeding at a stereogenic center was elucidated.

Of the four reactions involved in Phillips' experiment, *p*-toluenesulfonylation, and oxidation of the

Determination of Relative Configuration of Saturated Aliphatic Compounds 135



involve breaking of bonds to the chiral center and, therefore, must proceed heterofacially (with retention of configuration). It follows that (–)-2-octyl acetate and (–)-2-octyl *p*-toluenesulfonate (tosylate) have the same configuration (i.e., *l*), and that the reaction of the latter with acetate to give (+)-2-octyl acetate therefore proceeds with inversion of configuration (heterofacially, indicated by a looped arrow in Fig. 5.41). The conclusion that nucleophilic displacement reactions of the type shown in Figure 5.41 proceed with inversion of configuration was later extended, by analogy, to the reaction of 2-octyl tosylate with halide ions (Hosono, Phillips, et al., 1929) and the configuration of 2-halooctanes were thus assigned. The correctness of the argument was put on a firmer basis by the work of Hughes et al. (1935), shown in Figure 5.42. Optically active 2-octanone, when treated with iodide ion, is racemized because inversion of configuration occurs in the displacement and eventually one-half of the molecules will have a configuration opposite to that of the other one-half. At this point the system is in equilibrium. Treatment of 2-octanone with radioiodide (I^*) leads to exchange and incorporation of radioiodine into the organic material. The rate of racemization can be measured polarimetrically and the rate

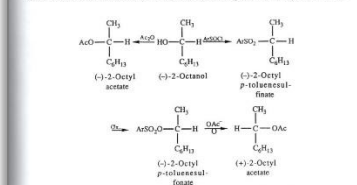


Figure 5.41. Inversion in the reaction of (–)-2-octyl *p*-toluenesulfonate with acetate.



Valdena apgriezenība RTU Primo

The screenshot displays the RTU Primo search interface. At the top left is the RTU logo and name. Navigation links include 'MEKLĒT', 'E-RESURSI A-Z', 'TIEŠĀ MEKLĒŠANA', and 'PĀRLŪKOT'. User options 'Ienākt' and 'Izvēlne' are on the right. The search bar contains 'walden inversion' with a search icon and a 'Viss' dropdown. Below the search bar, a filter bar shows 'Atlasīts 0 LAPA 1' and '1-10 of 69 Rezultāti' (circled in red), along with a 'Personalizēt' toggle. The main results area lists two articles. The first article is titled 'Dynamical barrier and isotope effects in the simplest substitution reaction via Walden inversion mechanism' by Zhao, Zhiqiang; Zhang, Zhaojun; Liu, Shu; Zhang, Dong H. The second article is 'Revisiting the bromination of 3β-hydroxycholest-5-ene with CBr₄/PPh₃ and the subsequent azidolysis of the resulting bromide, disparity in stereochemical behavior' by Schumacher, Christian; Ward, Jas S; Rissanen, Kari; Bolm, Carsten; Aly, Mohamed Ramadan El Sayed. A right-hand sidebar offers filters: 'Pielāgot rezultātus', 'Izvērst manus rezultātus', 'Kārtot pēc: Atbilstība', 'Pieejamība' (with sub-items: 'Pilnais teksts tiešsaistē (69)', 'Recenzētie žurnāli (59)', 'Brīvpieejas'), 'Resursa veids' (with sub-items: 'Raksti (62)', 'Grāmatas (4)', 'Konferenču materiāli (2)', 'Recenzijas (1)'), and 'Priekšmets' (with sub-item: 'Science & Technology (45)').

Valdena apgriezenība d/b EbscoHost

The screenshot displays the EBSCOhost search interface. At the top left, the EBSCOhost logo is visible. The search bar contains the text "Walden inversion", which is circled in red. To the right of the search bar is a "Search" button. Below the search bar, there are options for "AND" and "Select a Field (optional)". The search results are displayed in a list format. The first result is titled "1. Does the $\text{Cl} + \text{CH}_4 \rightarrow \text{H} + \text{CH}_3\text{Cl}$ Reaction Proceed via Walden Inversion?". The second result is titled "2. Quantum dynamics of the Walden inversion reaction $\text{Cl}[\sup -] + \text{CH}[\sub 3]\text{Cl} \dots \text{ClCH}[\sub 3] + \text{Cl}[\sup -]$ ". The search results are also circled in red. On the left side, there is a "Refine Results" panel with options for "Current Search", "Boolean/Phrase", "Expanders", and "Limit To". The "Limit To" section includes checkboxes for "Full Text", "References Available", and "Peer Reviewed". The "From:" and "To:" fields are set to "1923" and "2023" respectively. The "Scientific Library of Riga Technical University" logo is visible in the top right corner.

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Walden inversion TX All Text Search

AND Select a Field (optional) Clear ?

AND Select a Field (optional) + -

[Basic Search](#) [Advanced Search](#) [Search History](#)

Refine Results

Current Search

Boolean/Phrase:
[TX Walden inversion](#)

Expanders
Apply equivalent subjects

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Full Text
 References Available
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From: 1923 To: 2023

Search Results: 1 - 20 of 322

1. Does the $\text{Cl} + \text{CH}_4 \rightarrow \text{H} + \text{CH}_3\text{Cl}$ Reaction Proceed via Walden Inversion?

By: Krotos, László; Czakó, Gábor. Journal of Physical Chemistry A, 12/14/2017, Vol. 121 Issue 49, p9415-9420, 6p; DOI: 10.1021/acs.jpca.7b10226, Database: Applied Science & Technology Source

Subjects: Chemical reactions; Potential energy surfaces; Substitution reactions; Collisions (Physics); Walden inversion

2. Quantum dynamics of the Walden inversion reaction $\text{Cl}[\sup -] + \text{CH}[\sub 3]\text{Cl} \dots \text{ClCH}[\sub 3] + \text{Cl}[\sup -]$.

By: Clary, David C.; Palma, Juliana. Journal of Chemical Physics. 1/8/1997, Vol. 106 Issue 2, p575. 9p. 1 Diagram, 2 Charts, 11 Graphs. DOI: 10.1063/1.473397. . Database: Academic Search Complete

Subjects: SCATTERING (Physics); WALDEN inversion; CHEMICAL reactions

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Valdena apgriezenība d/b Web of science

<input type="checkbox"/> 6	Walden-inversion -enforced transition-state stabilization in a protein tyrosine phosphatase	88 Citations
	Alhambra, C; Wu, L; (...); Gao, JL	92 References
	Apr 29 1998 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 120 (16) , pp.3858-3866	
	The initial step of the dephosphorylation reaction of a tyrosine phosphate substrate catalyzed by the low molecular weight bovine protein tyrosine phosphatase (BPTP) has been studied, making use of a combined quantum mechanical and molecular mechanical approach in molecular dynamics simulations. It was found that the enzyme favors a dianion substrate in the dephosphorylation reaction, whir ... Show more	
	Full Text at Publisher ...	Related records
<input type="checkbox"/> 7	The S(N)2 reaction and its relationship with the Walden inversion , the Finkelstein and Menshutkin reactions together with theoretical calculations for the Finkelstein reaction	5 Citations
	Alkorta, I and Elguero, J	79 References
	Oct 2021 Jul 2021 (Early Access) STRUCTURAL CHEMISTRY 32 (5) , pp.1755-1761	
	Enriched Cited References	
	This communication gives an overview of the relationships between four reactions that although related were not always perceived as such: S(N)2, Walden , Finkelstein, and Menshutkin. Binary interactions (S(N)2 & Walden , S(N)2 & Menshutkin, S(N)2 & Finkelstein, Walden & Menshutkin, Walden & Finkelstein, Menshutkin & Finkelstein) were reported. Carbon, silicon, nitrogen, and phosphorus as central ... Show more	
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Piemineklis Paulam Valdenam

Atklāts – 2003. gada 14. oktobrī

Atrašanās vieta – Kronvalda bulv. 4

Pieminekļī atainota Valdena
apgriezenība

*“..Pauls Valdens Rīgā ir izdarījis nozīmīgāko
atklājumu organiskajā ķīmijā..” R. Valters*

1895./1898. gadā atklātā Valdena apgriezenība
Rīgu neizdzēšami ierakstīja ķīmijas vēsturē.



Paldies par uzmanību!



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