THE WICHTERLE REACTION

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Dedicated to Otto Wichterle, the great teacher and experimentalist.

The Wichterle reaction is a conversion of vinylic chlorides to ketones by sulfuric acid. Most of the applications are transformations of γ-chlorocrotyl (3-chloro-2-butenyl) derivatives to 3-oxobutyl derivatives. The ketones thus formed may undergo subsequent reactions in compounds containing reactive centers. Thus intramolecular aldol-type condensations occur in compounds containing carbonyl groups, and Friedel–Crafts-type cyclizations in compounds containing aromatic rings. The reaction can be used as an alternative to Robinson's annelation.

The Wichterle reaction, conversion of vinylic halides to ketones with the possibility of additional cyclocondensation, is one of the organic name reactions that is insufficiently defined in the chemical literature. Let us take a closer look at this reaction, the more so in that its discovery happened at rather dramatic circumstances.

At the time Dr Otto Wichterle became an assistant professor at the Institute of Experimental Organic Chemistry at the Technical University in Prague, one of the students who wanted to work toward his doctor's degree in that institute was Ivan Vavrečka, a son of one of the directors of the huge Baťa Shoe Plant. When he was assigned, by the head of the institute, Professor Emil Votoček, a very outstanding carbohydrate chemist, a project concerning some rather exotic sugar derivatives, he asked innocently, whether he could not work on something practical. Such a request raised dramatically Votoček's level of adrenaline in blood. After the reaction has subsided, Votoček turned Ivan Vavrečka over to Wichterle to figure out for him some practical theme. This happened and Vavrečka collaborated with Wichterle later on.

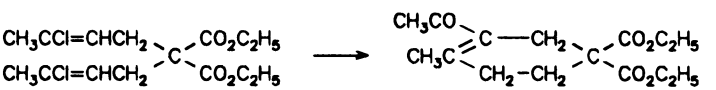
Vavrečka's connection with the industry proved of advantage. In the thirties, Baťa Shoe Plant, one of the largest, if not the largest in the world with subsidiaries all over the world, was diversifying in fields that were essential for the production of shoes. Anticipating problems with the import of natural rubber from the Far East in view of the imminent war, the directors decided to start manufacturing synthetic chloroprene rubber according to the Du Pont process. One of the byproducts was 1,3-dichloro-2-

butene, a compound that captured Wichterle's chemical imagination. He visualized at the first glance chemical potential of a compound that contained a double bond, a very reactive allylic chlorine and a rather unreactive vinylic chlorine. He started experimenting with this compound which was easily obtained from the Baťa company.

The first reaction tried was alkylation (γ-chlorocrotylation) of diethyl malonate to give diethyl bis(3-chloro-2-butenyl)malonate. In order to remove the distillation residue, Wichterle tried to dissolve it in concentrated sulfuric acid. A copious evolution of hydrogen chloride ensued. How many chemists would not hurl the contents of the flask down the drain? Instead, Wichterle added the distilled ester to concentrated sulfuric acid. A reaction, vigorous at the start, gradually subsided and required several days for completion. Meanwhile, on the 17th of November, 1939, the Czech universities were brutally raided by the Nazis and remained closed till the end of the war.

However, after several weeks, the university employees were allowed to remove their private property. Wichterle poured the reaction mixture on snow and smuggled it in a bottle in his laboratory coat together with his notebook out of the building, "penetrating through the Teutonic guards", as he recorded in his notebook. Soon after that, Wichterle got a position in Baťa's Research Institute of Rubber Technology in Zlín and over the rest of the war years worked on developing, among other things, his interesting reaction.

What happened when the diethyl bis(3-chloro-2-butenyl)malonate was treated with concentrated sulfuric acid? The primary reaction was probably addition of sulfuric acid to the double bond according to the Markovnikov rule[1]. Ejection of hydrogen chloride evidently converted the group –CCl=CH– to –CO–CH_2–, and since the two oxobutyl groups in the molecule were in a position allowing intramolecular aldol-type condensation to occur, a cyclic product was formed. It was isolated and identified as diethyl 3-acetyl-4-methyl-3-cyclohexene-1,1-dicarboxylate[1].



In compounds containing only one 3-chloro-2-butenyl residue, the 3-oxobutyl products are isolated unless they react with other functional groups present in the molecule[1 – 16] (Table I).

3-Chloro-2-butenyl derivatives of compounds containing functional groups, capable of reacting with the keto group of the 3-oxobutyl derivatives, usually underwent intramolecular aldol-type condensations. Such cyclization was not observed in the reaction with sulfuric acid of some methylated 2-(3-chloro-2-butenyl)cyclohexanones and -cyclohexenones[14 – 16] (last three entries in Table I). These 3-chloro-2-butenyl derivatives yielded δ-diketones.

TABLE I
The Wichterle reaction of 3-chloro-2-butenyl compounds
$CH_3CCl{=}CHCH_2R \longrightarrow CH_3COCH_2CH_2R$

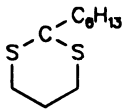
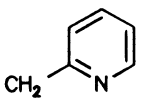
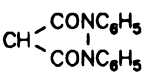
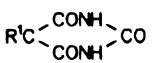
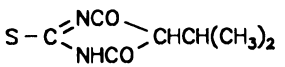
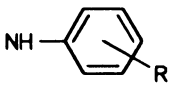
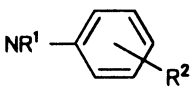
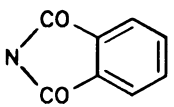
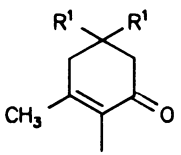
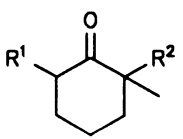
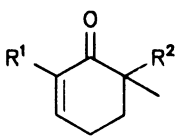
R	Yield, %	Ref.
C_4H_9	72	2
C_6H_{13}	52	2
C_6H_5	53	2
	32[a]	3
CO_2R^1 (R^1 = Me, Et, Pr, Bu, i-Bu, 3-methylbutyl)	77 (R^1 = Et)	4, 5
CH_2CO_2H		1
$CH(CO_2Et)_2$		6
$CH(CH_2)_4CO_2H$ CO_2H	83	7
	88	8
	92	5, 9
 (R^1 = H, Me, Et, i-Pr, Bu, cyclohexyl, allyl)	78 (R^1 = allyl)	10
	–	10

TABLE I
(*Continued*)

R	Yield, %	Ref.
	68 (R = H) 73 (R = H) 77 (R = 2-Me) 57 (R = 4-Me) 30 (R = 4-MeO)	11 12 12 11, 12 12
	56 (R^1 = Me, R^2 = H) – (R^1 = MeCO, R^2 = H) – (R^1 = MeCO, R^2 = 3-NO_2)	12 11 11
	54	13
$NHCOC_6H_5$	48	13
	72	13
	58 (R^1 = H) 91 (R^1 = Me)	14 14, 15
	44 (R^1 = H, R^2 = Me) 49 (R^1 = Me, R^2 = H)	16 16
	84 (R^1 = H, R^2 = Me) 88 (R^1 = R^2 = Me)	16 16

[a] R = $C_6H_{13}CO$ in the product.

In the majority of cases, spontaneous cyclization occurred, especially at higher temperatures (Table II). Thus, 6-chloro-5-hepten-2-one formed 3-methyl-2-cyclohexenone[17] (Eq. (*1*)), ethyl (3-chloro-2-butenyl)acetoacetate ethyl 4-methyl-3-cyclohexen-2-one-1-carboxylate and, on hydrolysis and decarboxylation, 3-methyl-2-cyclohexenone[18]; ethyl (3-chloro-2-butenyl)isopropylacetoacetate afforded piperitone after in situ hydrolysis and decarboxylation[19] (Eq. (*2*)). *S*-(3-Chloro-2-butenyl)isothiourea on treatment with sulfuric acid gave a chlorine-free product of unknown structure[20].

With cyclic ketones and β-keto esters, cyclization may lead to different condensation products depending mainly on the size of the rings[7] and, to a lesser extent, reaction

TABLE II
The Wichterle reaction of 3-chloro-2-butenyl ketones with subsequent cyclization via intramolecular aldol-type condensation

Reaction					Ref.
$CH_3CCl{=}CHCH_2CH_2COCH_3$				(*1*)	
		70%			17
CH_3CO / $CH_3CCl{=}CHCH_2{-}C(R)CO_2C_2H_5$				(*2*)	
R = H		38%[b]			18
R = *i*-Pr		40%[c]			19
	I	*II*	*III*	(*3*)	
n = 1 R = CO_2Et	48.5%				7
n = 2 R = CO_2Et	65%[d]				7
n = 3 R = CO_2Me		80%[e]			7
n = 8 R = CO_2Me		90%			7
n = 1 R = H			74%		7
n = 2 R = H			62%		7

TABLE II
(*Continued*)

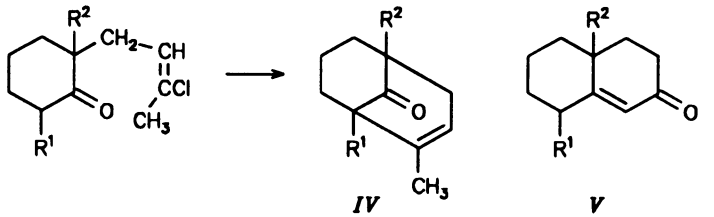
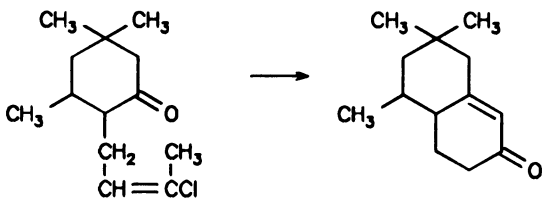
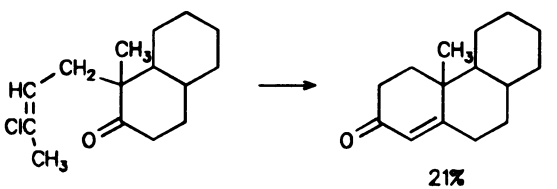
Reaction			Ref.
			(*4*)
	IV	*V*	
$R^1 = R^2 = H$		76%[f]	14
$R^1 = H; R^2 = Me$		20%[f]	14
$R^1 = H; R^2 = Me$	60%		16
$R^1 = Me; R^2 = H$		70%[a]	17
$R^1 = R^2 = Me$	93%		16
			(*5*) 14
			(*6*)
	21%		23

TABLE II
(*Continued*)

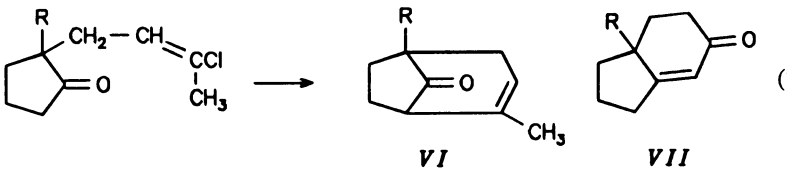
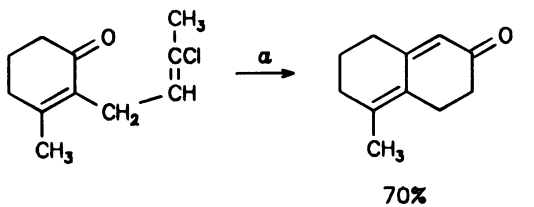
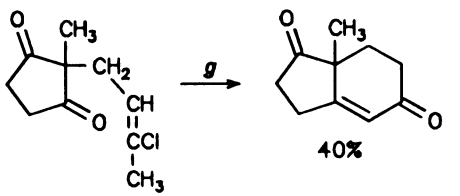
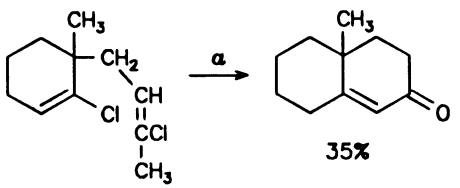
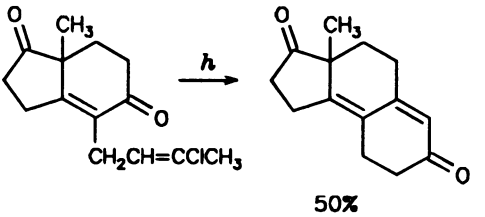
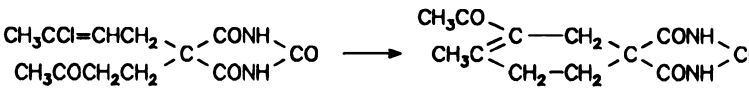
Reaction	Ref.
 (7)	
VI *VII*	
R = H 71%	21
R = Me 50%[a]	17
R = CO_2Et 32%	22
 (8)	
70%	17
 (9)	
40%	17
 (10)	
35%	17

TABLE II
(*Continued*)

Reaction	Ref.
 (*11*)	17
 (*12*)	10

Yields are shown under the respective compound. [a] $HClO_4$–HCO_2H, reflux; [b] and 17% of the decarboxylation product; [c] of the decarboxylation product; [d] and 4.5% of the free acid; [e] and 12% of the free acid; [f] mixture of *IV* and *V*; [g] HBr–AcOH, reflux; [h] HBr–HCO_2H, reflux.

conditions[17]. A thorough study of such condensations, carried out by Prelog and coworkers, revealed that with cyclic ketones having six- and seven-membered rings, the double bond was formed in such a way as not to violate the Bredt rule. In rings of eight or thirteen members, the double bond occurred at the bridgehead[7] (Eq. (*3*)). In 2-(3-chloro-2-butenyl)cyclopentanones, the ring closure also occurred in different ways[17,21,22] depending on the size of the second group on carbon 2 (Eq. (*7*)).

Ethyl 2-(3-chloro-2-butenyl)cyclohexanone-2-carboxylate and ethyl 2-(3-chloro-2-butenyl)cycloheptanone-2-carboxylate cyclized to ethyl 4-methyl-9-oxobicyclo[3.3.1]-non-3-ene-1-carboxylate (*I*, n = 1, R = CO_2Et) and ethyl 7-methyl-10-oxobicyclo-[4.3.1]dec-7-ene-1-carboxylate (*I*, n = 2, R = CO_2Et), respectively[7], whereas ethyl 2-(3-chloro-2-butenyl)cyclooctanone-2-carboxylate and ethyl 2-(3-chloro-2-butenyl)cyclotridecanone-2-carboxylate gave 8-methyl-11-oxobicyclo[5.3.1]undec-7-ene-1-carboxylate (*II*, n = 3, R = CO_2Et) and ethyl 13-methyl-16-oxobicyclo[10.3.1]hexadec-12-ene-1-carboxylate (*II*, n = 8, R = CO_2Et), respectively. 2-(3-Chloro-2-butenyl)cyclohexanone and 2-(3-chloro-2-butenyl)cycloheptanone yielded ortho-condensed ring systems of 2,3,4,4a,5,6,7,8-octahydronaphthalen-2-one (*III*, n = 1, R = H) and bicyclo-

[5.4.0]undec7-en-9-one (*III*, n = 2, R = H), respectively[7] (Eq. (*3*)). Similarly, 2-(3-chloro-2-butenyl)cyclohexanones having hydrogen or methyl in position 2 gave bicyclic compounds *IV* and *V*. The presence of a bulky group at the bridgehead position seems to inhibit ring closure to the ortho-condensed ring system[7,14,16,17] *V* (Eq. (*4*)).

In contrast to the (3-chloro-2-butenyl)isophorone which gave a δ-diketone[14,15] (Table I), (3-chloro-2-butenyl)dihydroisophorone cyclized to 5,7,7-trimethyl-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-one[14] (Table II, Eq. (*5*)). Condensation of (3-chloro-2-butenyl)decahydronaphthalenones can be used for construction of the A ring in steroids[23] (Table II, Eq. (*6*)). (3-Chloro-2-butenyl)cyclopentanones and their alkyl 2-carboxylates cyclize similarly but not without side reactions. The structure of the products depends on the structure of the starting material and to a certain extent on the reaction conditions[17,21,22]. Whereas 2-(3-chloro-2-butenyl)cyclopentanone and its 2-methyl homolog cyclized to indenones[17,21] *VII* (Table II, Eq. (*7*)), ethyl 2-(3-chloro-2-butenyl)cyclopentanone-2-carboxylate yielded ethyl 4-methyl-8-oxobicyclo[3.2.1]oct-3-ene-1-carboxylate[22] *VI* (Table II, Eq. (*7*)). More examples of cyclizations of (3-chloro-2-butenyl)cyclopentanones and -cyclohexenones are shown in Eqs (*8*) – (*11*).

Cyclization to a 3-acetyl-4-methyl-3-cyclohexene derivative occurred with (3-chloro-2-butenyl)-(3-oxobutyl)barbituric acid, prepared by treatment of (3-oxobutyl)barbituric acid with 1,3-dichloro-2-butene[10] (Eq. (*12*)).

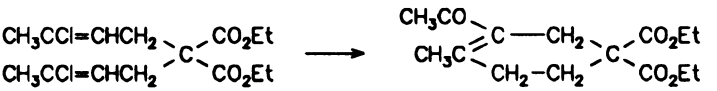
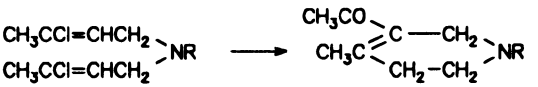
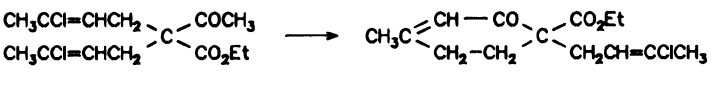
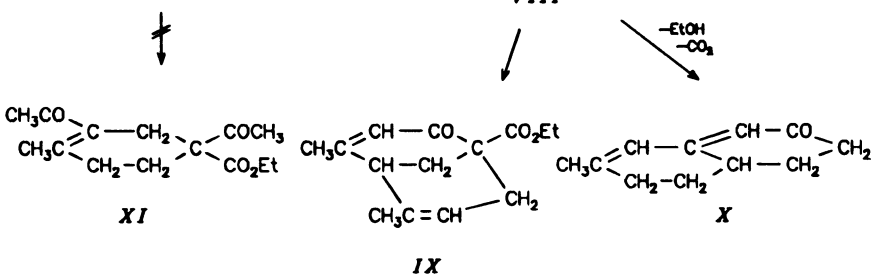
When two 3-chloro-2-butenyl residues are present in the molecule, autocondensation takes place between the two 3-oxobutyl chains (Table III). This is the case of the conversion of diethyl bis(3-chloro-2-butenyl)malonate to 3-acetyl-4-methyl-3-cyclohexene-1,1-dicarboxylate, the first example of the Wichterle reaction[1] (Eq. (*13*)).

Cyclization of bis(3-chloro-2-butenyl)amines and amides was very sluggish at room temperature and required warming of the reaction mixture to about 50 °C. Bis(3-chloro-2-butenyl)amine yielded 3-acetyl-4-methyl-1,2,5,6-tetrahydropyridine[13], bis(3-chloro-2-butenyl)methylamine 3-acetyl-1,4-dimethyl-1,2,5,6-tetrahydropyridine[13], 1,1-bis(3-chloro-2-butenyl)piperidinium chloride 3-acetyl-4-methyl-1,1-pentamethylenepiperidinium hydrogen sulfate[13], *N*,*N*-bis(3-chloro-2-butenyl)benzamide 3-acetyl-1-benzoyl-4-methyl-1,2,5,6-tetrahydropyridine[13] and *N*,*N*-bis(3-chloro-2-butenyl)-4-toluenesulfonamide 3-acetyl-4-methyl-1-(4-toluenesulfonyl)-1,2,5,6-tetrahydropyridine[13]. *N*,*N*-(3-chloro-2-butenyl)benzylamine cyclized at 80 °C to 3-acetyl-1-benzyl-4-methyl-1,2,5,6-tetrahydropyridine which decomposed at higher temperatures to 2,3,4-trimethylpyridine[24] (Eq. (*14*)).

In ethyl bis(3-chloro-2-butenyl)acetoacetate with one keto group present in the molecule and two more generated in the reaction with sulfuric acid, several ring closures were possible[18].

It is likely that the first cyclization occurred between the methyl group of the acetyl and the incipient keto group in one of the 3-chloro-2-butenyl chains, thus forming ethyl 1-(3-chloro-2-butenyl)-4-methyl-2-oxo-3-cyclohexene-1-carboxylate (Table III, Eq.

TABLE III
The Wichterle reaction of bis- and tris(3-chloro-2-butenyl) compounds

Reaction		Ref.
	(13)	1
	(14)	
R = H[a]	–	13
R = Me[b]	50%	13
R = $(CH_2)_5$	[c]	13
R = benzoyl	11%	13
R = 4-toluenesulfonyl	–	13
R = benzyl[d]	30%	24
	(15)	
		18

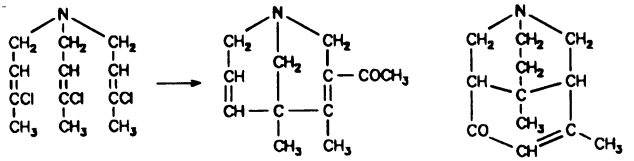
VIII

XI

IX

X

TABLE III
(*Continued*)

Reaction	Ref.
 (*16*)	
XII *XIII*	26
27%	25

Yields are shown under the respective compounds. [a] As a hydrochloride; reaction temperature 50 °C; [b] reaction temperature 50 – 55 °C; [c] as a picrate; [d] reaction temperature 80 °C.

(*15*), compound *VIII*). This compound, still containing one 3-chloro-2-butenyl residue, reacted with the newly formed 3-oxobutyl chain to form a bicyclic product, ethyl 4,6-dimethyl-2-oxobicyclo[3.3.1]nona-3,6-diene-1-carboxylate (*IX*).

There was, however, another possibility to close the second ring in such a way as to form an ortho-condensed ring system of two six-membered rings. Such a reaction was unlikely in the case of the ester, because the ester group inhibits cyclization to an ortho-condensed ring system, as shown in other examples[7] (Table II, Eq. (*3*)). However, when the ester group was removed by hydrolysis and decarboxylation, as it happened under the conditions used, then the cyclic ketone reacted with the second 3-oxobutyl group to form 7-methyl-2-oxo-2,3,4,4a,5,6-hexahydronaphthalene[18] (*X*).

The other alternative sequence of the intramolecular reaction of the two 3-chloro-2-butenyl groups to give ethyl 1,3-diacetyl-4-methyl-3-cyclohexene-1-carboxylate (*XI*) followed by the subsequent reaction with the 1-acetyl group, is less likely as it would violate the Bredt rule or require a shift of the double bond.

A compound containing three 3-chloro-2-butenyl groups linked to nitrogen, tris(3-chloro-2-butenyl)amine, gave a complex molecule, originally assumed[25] to be a bicyclic amine *XII* but later proven[26] to be a tricyclic compound *XIII* (Table III, Eq. (*16*)).

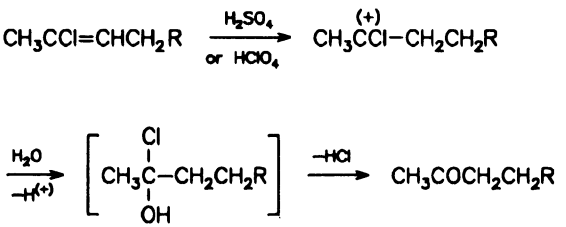
The chemical procedure of the Wichterle reaction is treatment of a vinylic chloride with concentrated sulfuric acid. An interesting modification is the use of other strong acids such as perchloric acid and hydrobromic acid combined with formic and acetic acid. Such a modification gave reasonable yields and, in some cases, more uniform products[17] (Table II, Eqs (*8*) – (*11*)).

The examples shown so far were cyclizations via intramolecular aldol-type condensation. 3-Chloro-2-butenyl compounds containing aromatic rings undergo in concentrated sulfuric acid Friedel–Crafts-type condensations (Table IV). Such is the reaction of 2-chloro-5-phenyl-2-pentene (prepared from 1,3-dichloro-2-butene and benzylmagnesium chloride), that gave 1-methyl-3,4-dihydronaphthalene[27] (*XIV*) which disproportionated to 1-methylnaphthalene (*XV*) and 1-methyl-1,2,3,4-tetrahydronaphthalene (*XVI*, Eq. (*17*)).

Aromatic 3-chloro-2-butenylamines yielded derivatives of dihydroquinolines and quinolines. *N*-(3-Chloro-2-butenyl)aniline afforded ultimately lepidine[11] (*XVII*), and *N*-(3-chloro-2-butenyl)-*p*-toluidine 4,6-dimethylquinoline[11] (Eq. (*18*)). The (3-oxobutyl)-amines were intercepted as intermediates[12] (Table I). *N*-(3-Chloro-2-butenyl)-1-naphthylamine was converted to 4-methylbenzo[*h*]quinoline[11] (Eq. (*19*)).

The vast majority of the Wichterle reaction has been performed on 3-chloro-2-butenyl derivatives, prepared readily from the commercially available 1,3-dichloro-2-butene. There are very few examples of the Wichterle reaction with other vinylic chlorides such as 2-chloroallyl chlorides[11,28]. Examples are shown in Table V, Eq. (*20*). The cyclizations were effected not only with sulfuric acid but also with polyphosphoric acid[28].

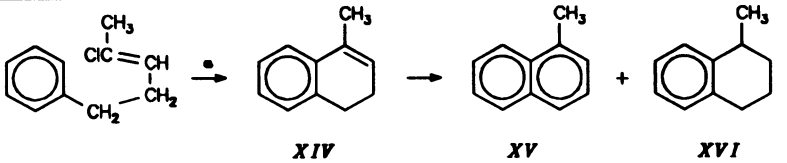
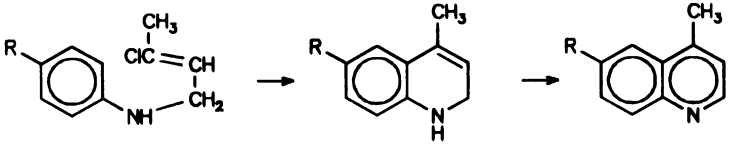
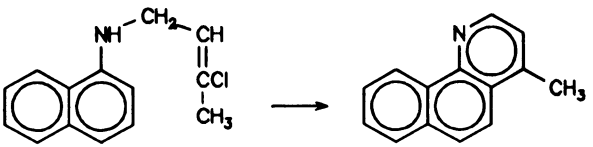
The mechanism of the Wichterle reaction is still a matter of speculation. It seems probable that the first step is protonation of the olefinic carbon β to chlorine and formation of a carbocation at the carbon linked to chlorine[17,28]. The suggested "hydrolysis" step leading to the ketonic product would necessarily require a molar quantity of water. But under the most common reaction conditions, this is not always the case. The hydrogen chloride starts evolving immediately after mixing the vinylic halide with concentrated sulfuric acid, and the amount of water in the concentrated sulfuric acid used is sometimes insufficient (Scheme 1).



SCHEME 1

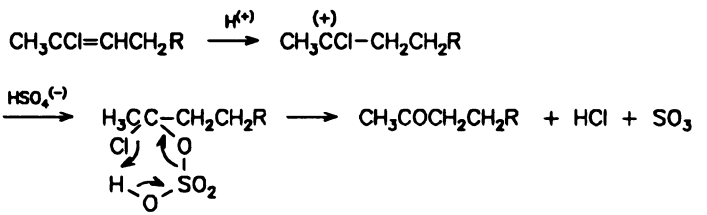
TABLE IV

The Wichterle reaction of 3-chloro-2-butenyl compounds with subsequent cyclization via intramolecular Friedel–Crafts reaction

Reaction	Ref.
	(*17*)
XIV 20%	27
XV + ***XVI*** 57%[b]	2
	(*18*)
R = H — ***XVII*** 91%	11
R = Me — –	11
	(*19*)
12%	11

Yields are shown under the respective compounds. [a] 70% H_2SO_4; [b] mixture of *XV* and *XVI*.

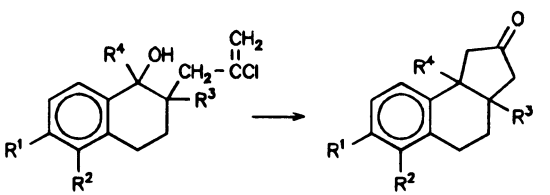
It is not out of the question that, in the originally suggested mechanism[1], the first step, the addition of sulfuric acid across the double bond, as is documented in other cases, is followed by a concerted elimination of hydrogen chloride and sulfur trioxide (Scheme 2). This is, however, only a conjecture and is to be proven.



SCHEME 2

The procedure for the Wichterle reaction is very simple. The vinylic chloride is added gradually to stirred concentrated (90 – 97%) sulfuric acid with or without cooling. Evolution of hydrogen chloride is often very vigorous but soon subsides. It is of advantage to pass a current of dry air or nitrogen through the reaction mixture and thus

TABLE V
The Wichterle reaction of 2-chloro-2-propenyl compounds

Reaction		Ref.
 (20)		
$R^1 = R^3 = H$; $R^2 = MeO$, $R^4 = Me$	40%[a]	29
$R^1 = MeO$, $R^2 = R^4 = H$, $R^3 = Me$	40%[b]	29

Yields are given under the respective compounds. [a] 95% polyphosphoric acid, 96 °C; [b] 90% H_2SO_4, 0 °C.

carry away the hydrogen chloride. By passing the gas mixture through a solution of sodium hydroxide of known titre it can be found out by titration when no more hydrogen chloride is being evolved. This may take a few hours or few days. Sometimes, like in the case of (3-chloro-2-butenyl)amines, elevated temperatures (50 – 80 °C) are necessary. After the reaction is over, the mixture is poured onto ice, the organic layer (in the case of amines after alkalization) is separated and the aqueous layer is extracted. The yields vary over a wide range because of some side reactions. The strongly acidic medium, especially combined with elevated temperatures, may be a cause of hydrolysis and decarboxylation where feasible. β-Keto esters were partly converted to acids[7] and ketones[18] (Table II, Eq. (*3*); Table III, Eq. (*15*), respectively). From 3-acetyl-1,4-dimethyl-1,2,5,6-tetrahydropyridine (Table III, Eq. (*14*)), up to 20% of the acetyl group was eliminated[13]. Also *p*-toluic acid was found as a byproduct[18], probably formed by intramolecular condensation of two 3-chloro-2-butenyl chains, as has been demonstrated by treatment of 1,4-bis(dimethylamino)-2-chloro-2-butene with sulfuric acid[29].

In all the examples of the Wichterle reaction the vinylic halides have chlorine at a carbon without hydrogen. Compounds with chlorine at a carbon carrying hydrogen should give aldehydes, but this did not occur. Such compounds lose hydrogen chloride very sluggishly, approximately fifty times more slowly that their analogs giving ketones, and no expected products were isolated[30,31].

After reading about conversions of many 3-chloro-2-butenyl derivatives to 3-ketobutyl derivatives, it is surprising that no mention is found in the literature of the Wichterle reaction with 1,3-dichloro-2-butene itself. The reaction was tried by the author of this review, and undoubtedly by a few others. It was extremely vigorous and led to an intractable tar, probably because the intermediate, assumed to be methyl vinyl ketone, polymerized very rapidly. Preparative conversion of 1,3-dichloro-2-butene to methyl vinyl ketone was achieved by treating 1,3-dichloro-2-butene with water in the presence of catalysts[31]. But this procedure does not possess the features of the Wichterle reaction.

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