einem *Erlenmeyer*-Kolben mit Stopfen im Dunkeln bei Raumtemperatur bis zur Einstellung des Sorptionsgleichgewichtes (ca. 4 Tage) geschüttelt. Dann wurde das angefärbte Sorbens abgetrennt und anhand einer Eichkurve photometrisch die Konzentration des Farbstoffs in der Lösung bestimmt. Aus der Differenz Δc_1^a wurde die auf dem Zinkoxid sorbierte Farbstoffmenge c^φ berechnet (vgl. Tabelle 5).

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132. Addition of a Functionalized Isoprene Unit to an Allyl Alcohol. III. The Reaction with Optically Active *cis*-Carveol

by **Alan F. Thomas** and **G. Ohloff**

Research Laboratories, *Firmenich & Cie*, 1211 Geneva 8

(29. IV. 70)

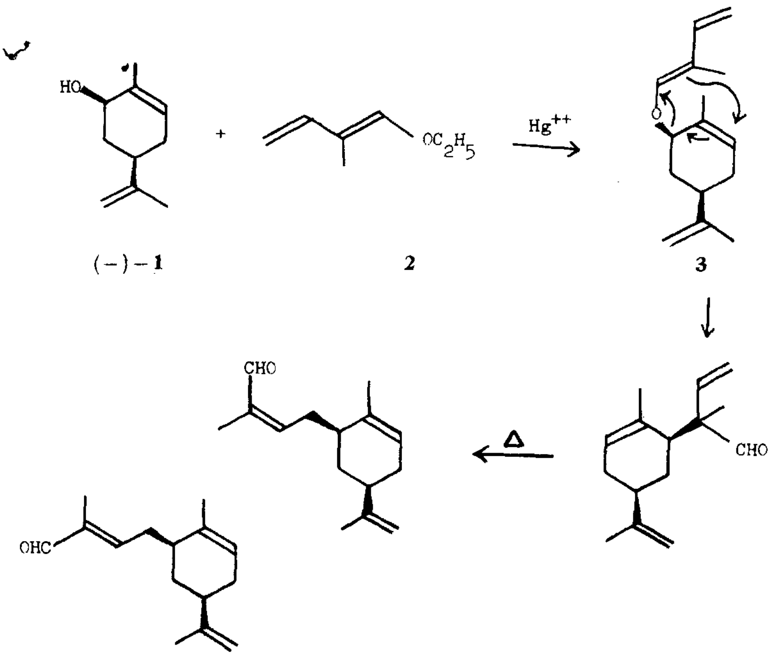
Summary. Provided the temperature is kept under 150°, diene ethers of allyl alcohols rearrange in the double *Claisen-Cope* reaction largely by a sigmatropic process in both stages. This was demonstrated by using the 2-methylbutadienyl ether of (–)-*cis*-carveol, when the product obtained after the two rearrangements was optically active. To check the extent of chirality loss, the same product was synthesized by a route involving only one sigmatropic reaction instead of two.

When the reaction occurs at higher temperature, much more chirality is lost, corresponding to the intervention of a diradical process.

Part I of this series was concerned with a general description of the double *Claisen-Cope* reaction of diene ethers of allyl alcohols [1], and part II illustrated the application of the reaction to heterocyclic compounds [2]. A sigmatropic process has been suggested for the reaction [3], with intervention of a diradical mechanism likely at higher temperatures. It remains to be shown whether the intermediate aldehyde, formed after the first stage of the reaction, can be isolated, and whether the *Claisen* and *Cope* steps are concerted. These points, and the evidence for the intervention of a different mechanism at higher temperature, are presented in this paper, using the reaction with optically active *cis*-carveol.

In connection with sigmatropic reactions of cyclohexenes, *Hill & Synerholm* have already shown [4] that the thermal rearrangement of optically active cyclohex-2-en-yl acetoacetate occurs with retention of optical activity. It is also known that both the *Claisen* [5] and the *Cope* [6] rearrangements occur with retention of configuration, although nothing is known of the combined reaction.

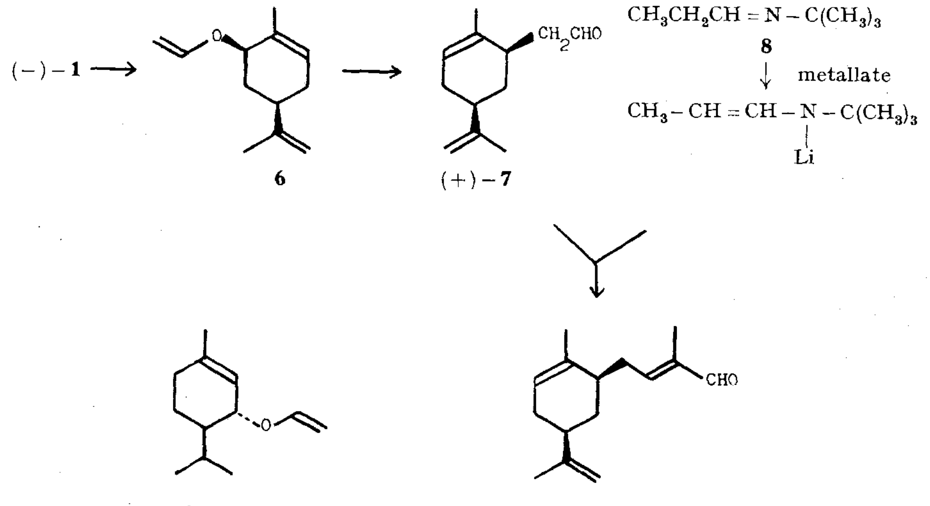
Results. – If (−)-*cis*-carveol (**1**) is heated to 100° with 1-ethoxy-2-methyl-butadiene (**2**) in the presence of mercuric acetate, the main product of rearrangement of the ether **3** is 2-[mentha-1′,8′-dienyl(-6′)]-2-methyl-3-butenal (**4**), having a rotation of the opposite sign to that of the original carveol. A small amount of carveyl formate was formed at the same time, and was separated by chromatography on silica gel. It was difficult, however, to free compound **4** from traces of impurity, and the combustion analysis was never completely satisfactory.



(−)-**1** **2** **3**

5b **5a** (+)-**4**

The spectra of the product (**4**), nevertheless, leave no doubt that the structural attribution is correct, and that the amount of impurity is very small. Pyrolysis of this compound at 400° yielded two aldehydes that appeared in the gas chromatograph as incompletely resolved peaks, the principal one of which was identified as 4-[mentha-1′,8′-dienyl(-6′)]-2-methyl-2-butenal (*trans*- about the 2,3-double bond, **5b**). The other peak was the corresponding *cis*-αβ-unsaturated aldehyde (**5a**), judging from its NMR. spectrum and precedents in the reaction [1] [7]. When prepared under these conditions, no rotation in compound **5b** was detected.



$CH_3CH_2CH{=}N-C(CH_3)_3$ **8**

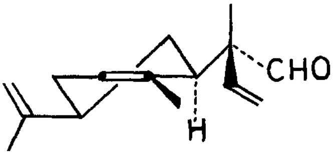
$CH_3-CH{=}CH-\underset{\displaystyle Li}{\underset{|}{N}}-C(CH_3)_3$

In order to examine whether this was because compound **5b** was actually a racemate, or whether it was merely of very low optical rotation, it was synthesized by a different route that would preserve its chirality. (−)-*cis*-Carveyl vinyl ether (**6**) was prepared under pyrolyzing conditions, when the aldehyde **7** was obtained, together with small amounts of an acetal (carveyl α-ethoxyethyl ether) formed by addition of carveol to the ethylvinyl ether used for the preparation of **6** (see exper. part). The structure of the aldehyde **7** (which has a rotation of +50°) was confirmed by its spectral properties and the formation of a semicarbazone. From this aldehyde **7**, the *Wittig* aldol reaction [8] with lithiated propylidene-*t*-butylamine (**8**) [9] yielded a single aldehyde with spectra identical to those of **5b**, this time having a rotation of +12°.

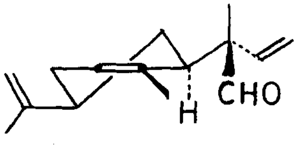
Examination of the by-products from the preparation of the aldehyde **4** (*i.e.* substances obtained when the temperature had not exceeded 100°) revealed the presence of a small amount of the aldehyde **5b**, the spectra of which were identical with those of the other samples of this substance, but whose rotation was −5°. When the aldehyde (+)-**4** was heated in a sealed tube at 150° for 2 hrs, there was also considerable conversion to **5b**, and, after careful purification by gas-liquid partition chromatography (glpc), this was now found to have a rotation of −8.4°.

trans-Carveol could not be induced to undergo these rearrangements.

Discussion. – The fact that only *cis*-carveol could be made to give a well-defined product under the conditions of the *Claisen* rearrangement is in accord with previous experiments of *Büchi* concerning the *cis*- and *trans*-vinyl ethers of piperitol, where only the *trans*-ether (**9**) was found to rearrange [10]1).



4a



4b

From the mode of its formation, the aldehyde (+)-**4** must be a mixture of diastereomers. The NMR. signal of the quaternary methyl group was sharp, and so was that of the methyl group of the isopropenyl substituent in the menthadiene part of the molecule. The signal of the methyl group on C-1, however, was double, corresponding to its two different environments, as shown in formulae **4a** and **4b**. The two different positions of the vinyl group result in a very complex set of signals, but it is somewhat unexpected that there is only a sharp singlet for the aldehyde proton.

Judging from the relatively high rotations of the aldehydes **4** and **7**, the first stage of the reaction must occur by a sigmatropic mechanism, in agreement with the findings of *Hill* [4] [5]. We are not, of course, able to state confidently how much chirality is retained in this step, although we are able to be fairly certain about the second step of the *Claisen-Cope* reaction (*i.e.* **4** to **5**). The *Wittig* aldol reaction from (+)-**7** cannot involve any loss in chirality, so the rotation of (+)-**5b** obtained in this way will be the true rotation, less any loss occuring between **6** and (+)-**7**. Since the conditions (150°) of the reaction to obtain (+)-**4** from **3** are approximately the same as those needed to convert **6** to **7**, the difference in rotation of the end product from the double *Claisen-Cope* reaction (*i.e.* (–)-**5b**) and (+)-**5b** produced by the *Wittig* aldol reaction must be due only to loss of chirality in the second step. When the double reaction occurs at temperatures of about 100°, therefore, at least 70% of the chirality is maintained2). Although under our conditions the error in reading the optical rotation is probably quite large, there seems little doubt that at 400° a large amount of the reaction must proceed *via* a symmetrical intermediate. The possible intervention of a diradical-like intermediate at higher temperature and sigmatropic reaction at lower temperature has already been suggested in the thermal rearrangement of caryophyllene [11] and in the *Claisen-Cope* reaction of furylmethanol [2].

Experimental. – Melting points were taken in capillaries and corrected. Infrared spectra were measured with a *Perkin-Elmer* Type 125 spectrophotometer. Nuclear magnetic resonance spectra were obtained with a *Varian* type A-60 instrument3). Mass spectra were measured on the

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1) We consider that the lack of reactivity of the *trans*-ether of carveol is occasioned by the desirability of the equatorial position for the isopropenyl group at C-4. This necessitates a pseudo-boat conformation in the case of the *cis*-ether, while the *trans*-ether leads to an intermediate of pseudo-chair conformation with very strong interference of the axial hydrogen at C-4 with the diene ether part of the molecule undergoing the sigmatropic rearrangement.

2) This is a figure distinctly lower than that of *Hill & Gilman* [6] for the single *Cope* step.

3) Measured in ppm with tetramethylsilane (internal) as 0.00 ppm.

Atlas CH4 mass spectrometer, using an inlet temperature of about 150° and electrons of 70 eV energy. Gas chromatography was carried out on a *Carlo Erba* Fractovap Type P (preparative) or a *Carlo Erba* Type GT (analytical and semi-preparative), using Carbowax 20M 15% on Chromosorb W 60–80 mesh, acid washed. The pyrolyses in gas chromatographs were carried out in a *Firmenich* model 59 T4), with an injection chamber that can be heated to 450°. All experiments leading to optically active products were carried out at least twice, and rotations were always measured by at least two different people on a *Schmidt & Haensch* polarimeter «Polatronic I».

(–)-cis-*Carveol* (**1**) [12]. Commercial (–)-carvone was reduced in ether with lithium aluminium hydride, then distilled. A fraction containing less than 5% of the *trans*-isomer (by glpc) was used in all experiments, and it had $[\alpha]_D^{22} = -41°$ ($c = 8$ in $CHCl_3$).

trans-*2-[Mentha-1′,8′-dienyl(-6′)]-2-methyl-but-3-en-al* (**4**). A mixture of 30 g of (–)-*cis*-carveol, 75 g of 1-ethoxy-2-methyl-buta-1,3-diene [1], 6 g of mercuric acetate, and 6 g of sodium acetate was heated at 100° for 17 hrs, then filtered. A fraction weighing 37.4 g was distilled rapidly, bp. 60–85°/0.005 Torr, and consisted mainly of the title product. For analysis, the substance was purified by chromatography on silica gel in petroleum ether (bp. 80–100°) after which it exhibited a single spot on thin-layer chromatography $d_4^{22} = 0.9505$; $\alpha_D^{22} = +66.3°$ (neat). NMR. spectrum 1.09 (3H, *s*, $CH_3{-}\overset{/}{\underset{\backslash}{C}}{-}$), 1.45 and 1.51 (3H, $CH_3{-}\overset{/}{C}{=}$, 2 isomers), 1.69 (3H, *s* + fine structure, $CH_3{-}\overset{/}{C}{=}$), 4.63 (2H, broad *s*, $H_2C{=}C{<}$), 4.85–6.20 (4H, *m*, $-CH{=}CH_2$ and $-CH{=}C{<}$), 9.32 (1H, *s*, $-CH{=}O$). Mass spectrum: *m/e* (% relative abundance) 93 (100), 107 (62), 135 and 55 (30), 91 (24), 41 and 79 (22), 77 (17), 43 and 134 (16), 105 and 119 (11), 218 ($M^{+\cdot}$, 1.5).

$C_{15}H_{22}O$ Calc. C 82.51 H 10.16% Found C 81.66 H 10.09%

$C_{16}H_{25}N_3O$ [*semicarbazone*, mp. 134–135° (MeOH)]

Calc. C 69.78 H 9.15 N 15.26% Found C 69.90 H 9.51 N 15.03%

Carveyl formate. Immediately after compound **4** had been eluted from the silica gel column in the previous experiment, a second substance was eluted that could be purified for analysis by glpc. NMR. spectrum: 1.60 and 1.67 (6H, $CH_3{-}\overset{/}{C}{=}$), 4.64 (2H, *s*, $H_2C{=}C{<}$), 5.25–5.7 (2H, broad *m*, $-CH{=}\overset{/}{C}{-}$ and $>CH{-}OCHO$), 7.83 (1H, *s*, $-O{-}CH{=}O$). Mass spectrum: 119 (100), 134 (96), 91 (87), 84 (86), 41 (80), 43 (64), 92 (60), 55 (55), 93 (52), 39 (49), 29 (40), 27 (37), 56, 77, 78 and 105 (33), 79 (31), remainder of spectrum very complex, with 180 ($M^{+\cdot}$, <1).

$C_{11}H_{16}O_2$ Calc. C 73.30 H 8.95% Found C 72.88 H 8.86%

cis-*5-[Mentha-1′,8-dienyl(-6′)]-2-methyl-but-2-*cis-*en-al* (**5a**) and (–)-cis-*5-[mentha-1′,8′-dienyl-(-6′)]-2-methyl-but-2-*trans-*en-al* (**5b**). – *a*) After compound **4** and carveyl formate had been eluted from the silica gel column described above, the column was treated with petroleum ether-benzene (9:1), when compound **5b** was obtained, having $d_4^{22} = 0.9548$; $[\alpha]_D^{22} = -5.0°$ ($c = 10$ in $CHCl_3$). The NMR. and mass spectra were identical with those of the substance described under b). – b) The aldehyde **4** (0.5 g) was heated for 2 hrs in a sealed glass tube at 150°, then purified by two passages through the glpc column. Two peaks were collected that were in the ratio of about 1:4. The first of these, purified with some difficulty, was ascribed the structure of the 2-*cis*-enal (**5a**) on the basis of the following NMR. spectrum [5]: 1.68–1.70 (9H, $CH_3{-}\overset{/}{C}{=}$), 4.62 (2H, *s*, $H_2C{=}C{<}$), 4.8 (broad, $w_1/_2 = 8.5$ Hz, $CH_2{-}CH{=}C{<}$), 6.30 (1H, *t*, $J = 8$ Hz, $CH_2{-}CH{=}\overset{/}{C}{-}CHO$), 10.00 (1H, *s*, $CH{=}\overset{/}{C}{-}CHO$, *cis*). The second peak was easier to purify by a second passage on the glpc column, and was ascribed the structure of the *trans*-enal (**5b**), the NMR. spectrum indicating the complete absence of any *cis* compound. $\alpha_D^{21} = -8.4°$ (neat); NMR. spectrum: 1.67, 1.68, 1.70, superimposed (9H, $CH_3{-}\overset{/}{C}{=}$), 4.62 (2H, *s*, $CH_2{=}C{<}$), 5.5 ($w_1/_2 = 8.5$ Hz, $CH_2{-}CH{=}C{<}$), 6.41 (1H, *t*, $J = 6$ Hz, $CH_2{-}CH{=}\overset{/}{C}{-}CHO$), 9.32 (1H, $CH{=}\underset{CH_3}{C}{-}CHO$ *trans*). Mass spectrum: 93 (100), 107 (64), 55 (29), 135 (25), 41, 79, 91 (22), 77 (17), 43 (15), 134 (12), 105, 119 (10), 218 ($M^{+\cdot}$, 7.3).

(±)-cis-*5-[Mentha-1′,8′-dienyl(-6′)]-2-methyl-but-2-*trans-*en-al* (**5b**). The aldehyde **4** was pyrolysed by injecting it into the evaporation chamber of a gas chromatograph at 400°. Two peaks

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4) Built by *E. Palluy, Firmenich & Cie.*

were observed, the first of which was never obtained completely pure in this experiment, but which was similar to the first peak of the previous experiment, and had an NMR. spectrum with a signal at 10.01 ppm; it was accordingly assigned the 2-*cis*-enal structure (**5a**). The second peak had indentical IR., NMR. and mass spectra with those described above for **5b**, but had $\alpha_D^{21} = \pm 0°$ (neat).

$C_{15}H_{22}O$ Calc. C 82.51 H 10.16% Found C 82.58 H 10.21%

Reaction of (–)-cis-*carveol* (**1**) *with ethyl vinyl ether*. 55 g of (–)-*cis*-carveol, 110 g of ethyl vinyl ether, 6 g of mercuric acetate, and 6 g of sodium acetate were heated together in a sealed tube at 120° for 24 hrs. Filtration and distillation yielded 44.9 g of a mixture with bp. 107–123°/10 Torr. On thin-layer chromatography there were two new spots, together with unchanged starting material. Chromatography in benzene on silica gel gave the material constituting the main spot, which was distilled to yield 22 g of pure (+)-trans-*2-[mentha-1′,8′-dienyl(-6′)]-acetaldehyde* (**7**), bp. 121 – 122°/10 Torr; $n_D^{20} = 1.4922$; $d_4^{20} = 0.9570$; $\alpha_D^{23} = +50°$. NMR. spectrum: 1.67 (6H, mult., $J = < 2$ Hz, 2CH_3–C=), 4.64 (2H, *s*, CH_2=C<), 5.5 (broad, 1H, $\mathrm{CH_2}$–C*H*=C<), 9.72 (1H, *t*, $J = 1.5$ Hz, $\mathrm{CH_2}$–CHO). Mass spectrum: 81 (100), 97 (60), 93 (42), 41 (37), 119 (34), 135 (32), 91 and 134 (28), 82 (27), 79 (26), 67 (24), 105, 39 and 67 (21), 107 and 77 (20), 53, 80 and 92 (18), 55 (16), 117, 95 and 43 (11), 178 ($M^{+\cdot}$, 2.2).

$C_{12}H_{18}O$ Calc. C 80.85 H 10.18% Found C 80.34 H 9.79%

$C_{13}H_{21}N_3O$ [*semicarbazone*, mp. 169–170° (EtOH)]

C 66.35 H 9.00 N 17.86% Found C 66.25 H 9.26 N 18.30%

Continued elution of the silica gel column with benzene-chloroform (9:1) gave 3 g of the by-product, after distillation, bp. 118–120°/10 Torr, which was characterized as *carveyl α-ethoxyethyl ether*; $d_4^{20} = 0.9300$; $\alpha_D^{24} = -55°$. NMR. spectrum: 1.14 (3H, *t*, $J = 7$ Hz, CH_3–$\mathrm{CH_2}$), 1.24 (3H, *d*, $J = 5$ Hz, CH_3–CH<), 1.73 (6H, *s* + further coupling, CH_3–$\overset{/}{\mathrm{C}}$=), 3.48 (2H, *q*, $J = 7$ Hz, $\mathrm{CH_3}$–CH_2–O; the presence of a shoulder on each signal of this quartet shows that two diastereomers are present), 4.67 (2H, *s*, CH_2=C<), 4.77 (1H, *q*, $J = 5$ Hz, $\mathrm{CH_3}$–C*H*$<^{\mathrm{O}}_{\mathrm{O}}$), 5.39 (1H, broad, $w_{1/2} = 9$ Hz, $\mathrm{CH_2}$–C*H*=C<). Mass spectrum: 73 (100), 45 (81), 93 (17), 31 (10), 107 (10), 178 (3.6), 224 ($M^{+\cdot}$, < 1).

$C_{14}H_{24}O_2$ Calc. C 74.95 H 10.78% Found C 74.67 H 10.80%

(+)-cis-*5-[Mentha-1′,8′-dienyl(-6′)]-2-methyl-but-2*-trans-*en-al* (**5b**). To 20 ml of absolute ether and 770 mg of lithium, cut into small pieces, was added 8.23 g of methyl iodide in 15 ml ether, while the temperature was maintained below –10°. After 30 min at 0°, the solution was cooled to –10°, and over 20 min, a solution of 5.56 g of diisopropylamine in 10 ml of ether was added. The mixture was maintained at 0° until the evolution of methane had ceased (about 45 min), when, at –10°, a solution of 7.40 g of propylidene-*t*-butylamine [13] in 20 ml ether was added over 10 min. After keeping the solution at 0° for 20 min, it was cooled to –60°, and 10.0 g of (+)-*trans-2-*[mentha-1′,8′-dienyl(-6′)]-acetaldehyde (**7**) in 20 ml ether were added over 20 min. After allowing to come to room temperature, the solution was kept at that temperature for one hr, then a solution of 30 g of oxalic acid in 400 ml water was added. The mixture was stirred for 20 min, and the product extracted in ether. Washing (sodium hydrogen carbonate solution, water), drying and concentrating the ether yielded 11.6 g of crude material that was chromatographed in benzene solution on a column of silica gel. The eluate was distilled to give 6.1 g of the pure title product having a single peak in the gas chromatogram; bp. 84–85°/0.001 Torr, $d_4^{20} = 0.9482$; $\alpha_D^{24} = +12.0°$ (neat). The NMR., IR., and mass spectra of this substance were identical in all respects with those of the compound assigned the (–)-*trans-* and (±)-*trans-*2-en-al structures (**5b**) in the earlier experiments.

$C_{15}H_{22}O$ Calc. C 82.51 H 10.16% Found C 82.75 H 10.30%

$C_{16}H_{25}N_3O$ [*semicarbazone*, mp. 160–161° (EtOH), $[\alpha]_D^{22} = -37°$ ($c = 5$ in $CHCl_3$)]

Calc. C 69.78 H 9.15 N 15.26% Found C 69.74 H 9.35 N 15.35%

$C_{21}H_{26}N_4O_4$ [*2,4-dinitrophenylhydrazone*, mp. 152–153° (EtOH)]

Calc. C 63.30 H 6.58 N 14.06% Found C 63.20 H 6.42 N 13.77%

Acknowledgement. We are indebted to the following for experimental help: Miss *W. Bucher*, Miss *G. Spalinger*, Miss *R. Dubini*, and Mr. *M. Ozainne* and Mr. *M. Jaccard*.

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133. Die Tautomeriegleichgewichte von Dihydrochinoxalinen

von **M. Schellenberg**

Forschungsabteilung der *CIBA Photochemie AG*, Fribourg

(14. V. 70)

Summary. The primary product of the two step reduction of 2-phenylquinoxaline is the 1,4-dihydrocompound which undergoes a tautomeric rearrangement to the thermodynamically more stable 1,2-dihydro-3-phenylquinoxaline. The 1,4-dihydro compound is an extremely reactive reducing agent whereas the 1,2-dihydro form is almost inert against oxidizing agents. Both dihydro forms are in a kinetically hindered equilibrium. The rearrangement requires a transfer of a proton from a nitrogen to a carbon atom and is therefore relatively slow even at pH 0.

The 1,2-dihydro compound cannot take part in redox reactions directly. If this compound is oxidized, the rate determining step is always the reversed tautomeric rearrangement.

The effect of the kinetics of the tautomeric rearrangement on the polarographic behavior of the 2-phenylquinoxaline system is discussed.

1. Einleitung. – Wie alle 1,4-Diazine bilden Chinoxaline zweistufige Redoxgleichgewichte. Die relevanten Redox- und Protonierungsreaktionen sind in [1] summarisch besprochen worden. Allgemein kann ein Chinoxalin (A) durch Aufnahme eines Wasserstoffatoms in ein Radikal (AH) und dieses durch Aufnahme eines weiteren Wasserstoffatoms in ein Dihydrochinoxalin (AH_2) übergehen.

$$A \underset{\varepsilon'\,(\mathrm{pH})}{\overset{e,\,H^+}{\rightleftarrows}} \cdot AH \underset{\varepsilon''\,(\mathrm{pH})}{\overset{e,\,H^+}{\rightleftarrows}} AH_2$$

Die üblichen Methoden zur Ermittlung der Normalpotentiale (ε' und ε'') eines derartigen Redoxsystems sind Potentiometrie und Polarographie. Beide Verfahren müssen bei völlig reversiblen Systemen und nach Kompensation aller möglichen Fehler zu identischen Resultaten führen.