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271. Solvolysis and Isomerization of *cis*- and *trans*-1-Bromo-1-(*p*-anisyl)-propene (α-Bromoanethole)

Mesomeric Vinyl Cations, Part V

by **C. A. Grob** and **R. Nussbaumer**

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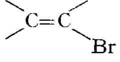
(6. X. 71)

Summary. The influence of a β-methyl group on the reactivity of two stereoisomeric vinyl bromides has been studied. In 80% ethanol *cis*-(**8**) and *trans*-α-bromoanethole (**9**) undergo first order reactions leading to *p*-methoxypropiophenone (**15**), 1-ethoxy-1-(*p*-anisyl)-propene (**16**) and *p*-anisylpropyne (**12**). Solvolysis of the *cis* isomer **8** is accompanied by isomerization to the more stable *trans* isomer **9** which is approx. eight times less reactive than **8**. *Cis-trans* isomerization is also observed in nitrobenzene at 150°.

These results are in agreement with the unimolecular substitution-elimination (S_N1-$E1$) mechanism which competes with *cis-trans* isomerization at the ion pair stage.

The solvolysis rate of **9** is slightly lower and that of **8** somewhat higher than the rate of α-bromo-*p*-methoxystyrene (**3c**). In the absence of other effects a β-methyl group therefore slightly depresses the ionization rate, presumably by steric hindrance of solvation. These results confirm the negligible polar influence of a β-methyl substituent on the stability of vinyl cations.

In previous papers it was shown that vinyl bromides **1** containing activating α-substituents, such as aryl (**1a**) or alkenyl (**1b**), possess considerable solvolytic



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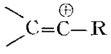

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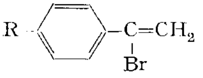

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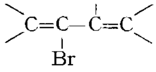


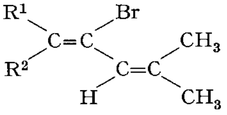
4

a) R = aryl
b) R = alkenyl

a) R = H
b) R = NH_2
c) R = OCH_3

reactivity [1] [2] [3]. In 80% ethanol they react by the S_N1–$E1$ mechanism *via* a mesomeric vinyl cation **2** to yield ketones, enol ethers and acetylene derivatives.

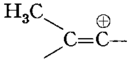
Certain substituents on the aryl group produce remarkable rate effects. Thus *p*-amino- (**3b**) and *p*-methoxy-α-bromostyrene (**3c**) react ca. 10^8 and 10^4 times, respectively, faster than α-bromostyrene (**3a**) [1]. Similarly, in the 2-bromo-1,3-diene series (**4**) one methyl substituent at C-4 increases the rate by ca. 10^2, two methyl groups by ca. 10^4 [2].



5

	k_{rel} 100°
a) $R^1 = R^2 = H$	1
b) $R^1 = H, R^2 = CH_3$	1.37
c) $R^1 = R^2 = CH_3$	1.42
d) $R^1 = CH_3, R^2 = H$	0.56

On the other hand methyl substituents at C-1 have little or no effect on the ionization rate of 2-bromo-1,3-dienes [2]. Thus *cis*-3-bromo-5-methyl-2,4-hexadiene (**5b**) and 3-bromo-2,5-dimethyl-2,4-hexadiene (**5c**), respectively, react only 1.37 and 1.42 times faster than 2-bromo-4-methyl-1,3-pentadiene (**5a**). *Trans*-3-bromo-5-methyl-2,4-hexadiene (**5d**), however, is *less* reactive than **5a** by a factor of almost two. From this it was concluded that a methyl group at C-1 actually decreases the rate but that this unspecified effect may be opposed by a rate enhancing steric effect when a methyl substituent is present *cis* to the second double bond, as in **5b** and **5c**. In this case steric interactions produce a departure from coplanarity and a concomitant increase in the ground state energy of the conjugated diene.



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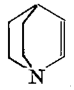
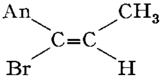


7

a) $R = CH_3$
b) $R = H$

The polar effect of methyl relative to hydrogen is still controversial [4]. However, when attached to an olefinic bond a methyl group is usually assumed to be electron releasing due to its inductive effect [5] or to hyperconjugation [6]; *e.g.* 3-methyl-2,3-dehydroquinuclidine (**7a**) (pK_A 10.11) is more basic by 0.23 unit than dehydroquinuclidine (**7b**) (pK_A 9.88)[1]. On the other hand the relative rates of the 2-bromodienes **5a**–**5b** suggest that the polar effect of a methyl group is negligible when located on the β-carbon atom of a vinyl cation **6**, a conclusion recently confirmed by molecular orbital calculations [7].

In view of these somewhat conflicting results it was considered necessary to obtain further experimental data on the influence of a β-methyl substituent on the rate of solvolysis of an activated vinyl bromide. To this end *cis*- (**8**) and *trans*-1-bromo-1-(*p*-anisyl)-propene (**9**) (*cis*- and *trans*-α-bromoanethole) were chosen for study[2], since the lower homologue, *viz.* α-bromo-*p*-methoxystyrene (**3c**), had



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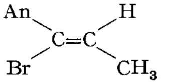
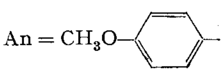


9



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[1] Unpublished work with *J. Zergenyi.*

[2] Taken from *Nussbaumer* [8].

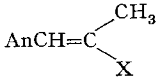
already been investigated and shown to react in a convenient temperature range [1]. A comparison of the rate and products of these geometrical isomers was also expected to shed light on steric factors[3]).

Syntheses. p-Methoxyphenylacetylene (**11**), obtained from *β*-bromo-*p*-methoxystyrene (**10**) by treatment with KOH in ethanol, was converted to *p*-anisylpropyne (**12**) by methylation with sodium and methyl iodide in tetrahydrofuran. Alternatively, **12** was prepared by dehydrochlorination of 2-chloro-1-(*p*-anisyl)-propene (**13**) by a modification of a known procedure. Addition of aqueous HBr to **12** yielded a mixture consisting of 55% *cis*- (**8**) and 45% *trans*-α-bromoanethole (**9**), which was separated by preparative gas chromatography. Treatment of **12** with HBr in ether also afforded **8** and **9**, but these were contaminated with 2-bromo-1-(*p*-anisyl)-propene (**14**) arising from a peroxide induced *anti-Markownikow* addition.

$AnCH{=}CHBr$ **10**

$AnC{\equiv}CH$ **11**

$AnC{\equiv}CCH_3$ **12**



$$AnCH{=}C(CH_3)X$$

13 X = Cl
14 X = Br

The α-bromoanetholes **8** and **9** undergo rapid decomposition when exposed to air. It is therefore necessary to prepare fresh samples for spectroscopic and solvolytic studies. The configuration of the two isomers was established by NMR. and UV. spectroscopy. Vinyl protons *cis* to bromine resonate at lower field than *trans* protons[4]). Since the quartets due to the vinylic protons in **8** and **9** are centered at 6.11 and 6.07 ppm, respectively, the former was assigned the *cis* configuration. The relative position of the doublets due to the protons of the *β*-methyl groups are reversed and are located at 1.65 and 1.90 ppm, respectively, in **8** and **9**. These assignments are supported by the hypsochromic shift of the UV. absorption maximum of **8** (243 nm) relative to that of the *trans* isomer **9** (263 nm). In addition, molecular models reveal that only in the *cis* isomer **8** is the anisyl ring twisted out of the plane of the vinyl group because of steric interference with the *β*-methyl group.

Table 1. *Reaction products (in %) of* cis-(**8**) *and* trans-α-*bromoanethanole* (**9**) *in 80 vol. % ethanol at 110°*

	equiv. $N(C_2H_5)_3$	$AnCOC_2H_5$	$AnC{\equiv}CCH_3$	$\underset{OC_2H_5}{AnC}{=}CHCH_3$	*trans*-α-bromoanethole (**9**)
cis-α-bromoanethole (**8**)	1	34	22	30	14
	2	37	20	28	15
	3	30	20	35	15
	5	21	23	41	15
trans-α-bromoanethole (**9**)	1	85	15	–	–
	2	49	23	28	–
	3	40	24	36	–
	5	38	29	33	–

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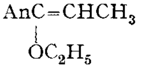
[3]) A short account of this work has appeared [9].

[4]) *E.g.* the *cis* and *trans* vinylic protons in 2-bromopropene ($CH_2{=}C(Br)CH_3$) give rise to signals at 5.52 and 5.33 ppm, respectively [10].

Results. When 0.1 M solutions of the α-bromoanetholes **8** and **9** were reacted in 80 vol.% ethanol at 110° for ten half lives in the presence of 1 to 5 equivalents of triethylamine, *p*-methoxypropiophenone (**15**) and *p*-anisylpropyne (**12**) were obtained (Table 1). As the concentration of triethylamine was raised, increasing amounts of 1-ethoxy-1-(*p*-anisyl)-propene **16** were also isolated. The enol ether **16** could not be separated from the ketone **15** by gas chromatography and its configuration therefore could not be determined. No enol ether was isolated from the *trans* isomer **9** in the presence of one equivalent of triethylamine. However, the more reactive *cis* isomer **8** afforded 30% enol ether **16** under these conditions. In general less enol ether **16** is obtained after prolonged reaction times, due to its hydrolysis to the ketone **15**.

$AnCOCH_2CH_3$

15

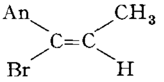
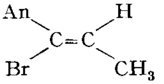
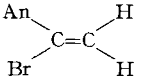


$$\underset{OC_2H_5}{AnC{=}CHCH_3}$$

16

Surprisingly, the reaction of *cis*-α-bromoanethole (**8**) also produced the *trans* isomer **9** in a constant yield of ca. 15% (Table 1). Solvolysis of **8** is thus accompanied by isomerization. Finally, reaction of **8** in 100% ethanol for four hours at 140° in the presence of five equivalents of triethylamine also afforded **9** (15%), in addition to **15** (7%), **12** (55%) and **16** (23%).

Table 2. *First order rate constants of* cis-(**8**) a) *and* trans-*α-bromoanethole* (**9**) b) *in 80 vol. % ethanol in the presence of one equiv. of triethylamine*

	temp. °C	k(s^{-1})	$k_{rel}^{100°}$	$E^{\ne}$ kcal	$S^{\ne}$ cal/°
 **8**	90.0	1.07×10^{-4}		25.05	−10.20
	100.0	2.59×10^{-4}			
	110.0	6.56×10^{-4} c)	8.3		
 **9**	110.0	7.92×10^{-5}	1	22.31	−21.53
	120.0	1.67×10^{-4}			
	130.0	3.39×10^{-4}			
 **3c**	110.0	9.64×10^{-5} d)	1.2	27.82	− 6.71

a) measured conductometrically, $c = 0.001$ M
b) measured titrimetrically, $c = 0.01$ M
c) calc. from measurements over three half lives
d) extrapolated from [1]

The first order rate constants of the α-bromoanetholes in 80 vol.% ethanol containing one equivalent of triethylamine were measured conductometrically for the *cis* isomer **8** and titrimetrically for the *trans* isomer **9** (Table 2). The rate constant for **8** at 110° decreased after about three half lives due to the isomerization to the less reactive **9**. At 120°, the rate constant for **8** (1.52×10^{-3}) dropped to that of **9** (1.67 ×

10^{-4}) after about thirty half lives. For comparison the rate constant for α-bromo-*p*-methoxystyrene (**3c**) at 100° [1] is also included in Table 2.

The rate and equilibrium constant K of *cis-trans* isomerization were measured in nitrobenzene, since solvolysis predominates in 80% ethanol. Between 150° and 170° isomerization could be fairly accurately followed by gas chromatography. Approximate rate constants k_1 and k_{-1} and the corresponding equilibrium constants K are listed in Table 3.

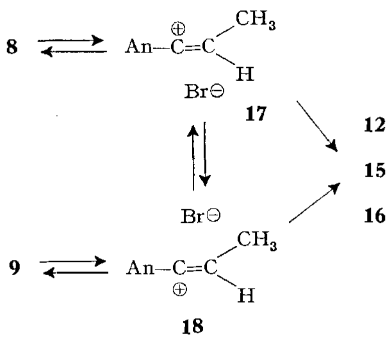
Table 3. *Rate of isomerization of* cis- *and* trans-α-*bromoanethole*, $c = 0.03$ M *in nitrobenzene: mean deviation* ± *5%*

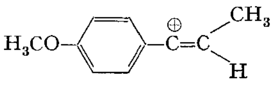
temp. °C	k_1 (s^{-1})	k_{-1} (s^{-1})	K
150	7×10^{-5}	1×10^{-5}	7.0
160	1.5×10^{-4}	2×10^{-5}	7.5
170	2.7×10^{-4}	3.5×10^{-5}	7.7

Discussion. Cis- (**8**) and *trans*-α-bromoanethole (**9**) undergo first order reactions in 80 vol.% ethanol affording the ketone **15**, the acetylene derivative **12** and the enol ether **16** (Table 1). Since the rate is not affected by triethylamine, a unimolecular substitution-elimination mechanism of the S_N1–$E1$ type is operative as in the case of the α-bromostyrenes **3** [1] [3] and the 2-bromo-1,3-dienes **4** [2]. A novel result is the isomerization which accompanies solvolysis of **8**, and permits the isolation of ca. 15% **9** after ten half lives. This *cis-trans* isomerization produces a decline of the observed rate constant, since the solvolysis rate of **9** is lower by a factor of 8.3.

These findings are in accord with an isomerization-solvolysis mechanism (Scheme 1) involving two discrete ion pairs **17** and **18** in which the vinyl cation and the bromide ion are still in close contact (intimate ion pairs)[5]. Rotation of the bromide ion around the face of the vinyl cation leads to one or the other of **17** and **18**. Recombination of these respective ion pairs results in the formation of the α-bromoanetholes **8** and **9**. In nitrobenzene at 150° an equilibrium of 88% *trans* and 12% *cis* isomers is reached. This corresponds to an equilibrium constant K of **7** (Table 3) and a free energy difference of 1.65 kcal.

Scheme 1





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[5] Ion pairs have recently been invoked by *Rappoport* & *Apeloig* in the observed *cis-trans* isomerization of 1,2-dianisyl-2-phenylvinyl bromide in 80% ethanol [11].

In 80% ethanol dissociation of the ion pairs **17** and **18** competes with recombination and produces the ketone **15**, the enol ether **16**, and the acetylene derivative **12** by reaction with the solvent. The higher ratios of ketone to acetylene obtained from **9** (Table 1) are due to the longer reaction time which permits increased hydrolysis of **16** to **15**. It is therefore difficult to ascertain whether the same solvated vinyl cation **19** is involved in the formation of products from both isomers. Failure to isolate pure enol ether **16** precluded attempts to determine its configuration. The indications are, however, that one stereoisomer predominated[6]).

As shown in Table 2 the thermodynamically less stable *cis*-α-bromoanethole (**8**) reacts 8.3 times as fast as the *trans* isomer **9**[7]). This rate difference is attributable to steric interaction between the anisyl and the β-methyl groups on the same side of the double bond in **8** and the resultant departure of the molecule from coplanarity. This view is supported both by the higher energy of **8** and by the hypsochromic shift of 20 nm in its UV. spectrum relative to **9**. Furthermore, a non-planar conformation of the molecule will enhance the ability of the anisyl group to donate electrons to the incipient *p*-orbital of the α-carbon atom in the transition state of ionization.

Finally, the ionization rate of the *trans* isomer **9** is 1.2 times *lower* than that of α-bromo-*p*-methoxystyrene (**3a**), while that of the *cis* isomer **8** is 6.4 times higher. It follows that when a β-methyl substituent does not give rise to steric acceleration it causes a slight rate depression. This result confirms our earlier conclusion [2] that a β-methyl group confers no extra stabilization on a vinyl cation.

The small rate depressions observed in the solvolysis of *trans*-α-bromoanethole (**9**) and of the 2-bromodiene (**5d**) [2] do not warrant any revision of current concepts concerning the polar effect of methyl groups. The positive charge generated on the α-carbon atom of both systems is delocalized into the adjacent aryl or alkenyl substituent and, consequently, makes little or no electronic demand on the β-methyl group. It would therefore seem more appropriate to ascribe these modest rate-depressing effects of a β-methyl group to steric hindrance of solvation, as previously suggested [12].

Financial support from *CIBA-GEIGY AG*, Basel, and from the «*Schweizerischer Nationalfonds*» is gratefully acknowledged.

Experimental

M.p.'s were determined on a *Kofler*-Block and are corrected; accuracy below 200 °C ± 1°. Spectral and gas chromatographic analyses were carried out as previously described [2].

Syntheses. – p-*Methoxyphenylacetylene* (**11**) was prepared by the procedure of *Manchot & Oltrogge* [13]. Yield 60%, b.p. 95–97°/14 Torr (Lit. [13]: b.p. 96–98°/15 Torr). NMR. spectrum in CCl_4 (ppm): 2.83 (*s*, 1H), 3.75 (*s*, 3H), 7.04 (*m*, 4H).

1-(p-Anisyl)-propyne (**12**). – a) *From* **11**. The entire operation was carried out under dry nitrogen. 2.9 g (0.123 mol) of sodium were pulverized under boiling xylene. After replacing the xylene with 130 ml of abs. tetrahydrofuran 16.2 g (0.123 mol) of *p*-methoxyphenylacetylene (**11**) in 30 ml of abs. tetrahydrofuran were added with stirring through a dropping funnel during 30 min. During addition the temperature rose to 55°. The brown suspension was heated to gentle reflux (58°) for 1.5 h. After cooling to 20° 30.0 g (0.211 mol) of methyl iodide in 25 ml of abs. tetrahydro-

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[6]) Presumably, this is the *cis* isomer since attack by ethanol at the less hindered side of **19** should be favoured.

[7]) A similar rate ratio for **8** and **9** was observed by *Rappoport & Apeloig* employing sodium acetate as the base (personal communication from Prof. *Z. Rappoport*).

furan were added dropwise during 45 min. The mixture was stirred under reflux (58°) for one hour. After cooling, 250 ml of water were slowly added. A brown, oily layer separated which was extracted with ether. The washed and dried ether extract was evaporated and the oily residue destilled through a *Vigreux* column. Yield 13.0 g (72%) **12**, b.p. 117–119°/13 Torr (Lit. [14]: b.p. 115–117°/9 Torr). NMR. spectrum in CCl_4 (ppm): 1.98 (*s*, 3H), 3.72 (*s*, 3H), 6.95 (*m*, 4H).

$C_{10}H_{10}O$ (146.19) Calc. C 82.16 H 6.90% Found C 82.44 H 7.13%

b) *From 2-chloro-1-*(p-*anisyl*)*-propene* (**13**). 110 g (0.6 mol) of **13** [14] were boiled under reflux with 99 g (1.7 mol) of KOH in 165 ml methanol for 15 h. The mixture was diluted with 500 ml of ice water and extracted with four 200 ml portions of ether. The extracts were washed with 2N sulfuric acid and then with water. After drying over magnesium sulfate the ether was evaporated. The oily residue was distilled through a *Vigreux* column at 14 Torr, yielding 90 g of a mixture, b.p. 120–136°, consisting of ca. 70% of **12** and 30% starting material. Redistillation through a 1 meter spinning band column (reflux ratio 1:40) at 10 Torr gave pure anisylpropyne (**12**), b.p. 108.6–110.3° (Lit. [14]: b.p. 115–119°/9 Torr).

cis- *and* trans-*α-Bromoanethole* (**8** *and* **9**). A solution of 5.67 g (0.07 mol) dry HBr in 30 ml of freshly distilled ether was slowly added to an ice-cooled solution of 7.8 g (0.054 mol) 1-*p*-anisylpropyne (**12**) in 40 ml distilled ether. After $3^1/_2$ h at 20° in the dark the solution was evaporated in vacuo to dryness. The solution of two residue in ether was washed with 10% $NaHCO_3$ solution and water, dried over $MgSO_4$, and evaporated to dryness in vacuo. The light, liquid residue was distilled in a high vacuum, b.p. 82–84°/0.05 Torr, yield 6.4 g.

$C_{10}H_{11}BrO$ (227.11) Calc. C 52.88 H 4.88 Br 35.19% Found C 53.22 H 4.85 Br 34.88%

Better results were obtained when 6.0 g (0.041 mol) of **12** were shaken with 6 ml (0.077 mol) of 63% aqueous HBr for 1 h at –15° and 2 h at 20°. The mixture was diluted with water, extracted with ether and worked up as described above.

In both cases the ratio of *cis*-(**8**) to *trans*-(**9**) α-bromoanetholes was 55:45 as determined by gas chromatography. Separation was achieved on a preparative scale employing a 3 m aluminium column packed with 10% silicone rubber SE 52 on Chromosorb, with helium (200 ml/min).

From 150 mg of the mixture of **8** and **9** 55 mg of the *cis* isomer **8** were obtained. NMR. spectrum in CCl_4 (ppm): 1.65 (*d*, 3H), 3.77 (*s*, 3H), 6.11 (*q*, 1H), 6.97 (*m*, 4H). The second fraction, 60 mg, consisted of the *trans* isomer **9**. NMR. spectrum in CCl_4 (ppm): 1.90 (*d*, 3H), 3.77 (*s*, 3H), 6.07 (*q*, 1H), 7.03 (*m*, 4H).

The *cis* isomer **8** solidified to a wax at –70°, the *trans* isomer **9** showed a m.p. 12–13°.

1-Ethoxy-1-(p-*anisyl*)*-propene* (**16**) was prepared in analogy to the procedure of *Zoss & Hennion* [15] from anisylpropyne (**12**) and abs. ethanol in the presence of boron trifluoride etherate and mercuric oxide. The crude liquid, b.p. 72–74°/0.04 Torr, was purified by gas chromatography. NMR. spectrum in CCl_4 (ppm): 1.23 (*t*, 3H), 1.72 (*d*, 3H), 3.63 (*q*, 2H), 3.82 (*s*, 3H), 5.08 (*q*, 1H), 7.33 (*m*, 4H).

Preparative solvolysis. – 0.05M solutions of **8** and **9** in 80 vol. % ethanol, containing 1 to 5 equiv. of triethylamine, were heated in sealed glass tubes at 110°. After 3 h (*cis* isomer) and 24 h (*trans* isomer), respectively, the mixture was evaporated to dryness in vacuo. The residue was taken up in pentane and the solution washed with water and dried over Na_2SO_4. After concentration the solution was injected into the gas chromatograph. The individual peaks were identified by comparison of the retention times and the IR. and NMR. spectra with those of authentical samples. Peak areas were evaluated by the method of *Condal-Bosch* [16]. Each determination was repeated at least once (accuracy ± 4%). Product composition as a function of base concentration is listed in Table 1.

Kinetic measurements. – Rate constants for the *cis* isomer **8** were determined by the conductometric method as desrcibed in Part II [2]. The change in conductivity was followed during the first three half lives. The final value λ_∞ was calculated with formula (1), where λ_1, λ_2, λ_3

$$(1)\quad \lambda_\infty = \lambda_1 + \frac{(\lambda_2 - \lambda_1)^2}{2\lambda_2 - (\lambda_1 + \lambda_3)} \qquad (2)\quad k = \frac{2 \cdot 302}{t} \log \frac{\lambda_\infty - \lambda_0}{\lambda_\infty - \lambda_t}$$

represent conductivity after t_1, t_2 and t_3 seconds, respectively. Rate constants k were calculated with formula (2). The mean deviation was ± 0.6%. A downward trend of the rate constants due to isomerization was noticeable above 110°.

Rate constants for the *trans* isomer **9** were determined titrimetically by following the appearance of bromide ion in 5 ml samples sealed in glass ampoules [1]. Titrations were carried out with 0.01 N or 0.005 N $AgNO_3$ solution after acidification with 2 N HNO_3 and employing an automatic Potentiograph E 336 (*Metrohm*). Reactions were followed to 80% completion. The mean deviation was ± 0.5% at 111°, ± 1.4% at 120 and 130°.

Cis-trans isomerization was followed kinetically at 120.1° by following the decrease of the observed rate constant during 30 half lives and starting with pure *cis* isomer **8**, as shown in Table 4.

Table 4. *Observed first order rate constant*[a]) *for the* cis *bromide* **8** *in 80 vol. % ethanol at 120.1° with 1 equiv.* NEt_3

t (s)	$k \times 10^4$ (s^{-1})	t(s)	$k \times 10^4$ (s^{-1})	t(s)	$k \times 10^{-4}$
0[b])	–	960	7.2	4200	3.6
240	9.6	1500	5.8	7200	2.5
480	9.4	1800	5.6	10800	1.9
720	8.3	3000	4.2	∞	1.6

[a]) titrimetric

[b]) measurements began after one half life.

Isomerization in nitrobenzene. – 0.03 M solutions of the *cis* isomer **8** in nitrobenzene were heated at 150°, 160° and 170° (± 0.5°) for 12 and 8 h, respectively. At certain time intervals samples were taken and the amount of *trans* isomer formed determined by gas chromatography. The rate constants k_1 and k_{-1} (Table 3) were calculated with formulae (3) and (4), X_e and X being the concentration of **9** at equilibrium and at time t, respectively.

$$(3) \quad \ln \frac{X_e}{X_e - X} = (k_1 + k_{-1})t \quad , \qquad (4) \quad \frac{k_1}{k_{-1}} = K$$

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