standard reaction conditions were as follows. A suspension of **2** (1.4 mmol), **3** (1.4 mmol), and propylene oxide (0.5 mL) in 3.5 mL of 1,2-dichloroethane was gradually warmed at the rate of 2.5 °C/min at 25–60 °C, and the mixture was stirred under solvent reflux for 2 h. After workup, the yields of adducts **4** + **5** were: 44% from **2b**, 61% from **2c**, 70% from **2d**, 89% from **2e**, and 89% **4e** + **5e** from **1a**.

Diazotization of *o*-Nitroaniline (6). To a suspension of **6** (2.0 g, 14.5 mmol) in 40 mL of EtOH was added 6 mL of 35% HCl under ice cooling. Isoamyl nitrite (4.0 mL) was added dropwise over 1 min and the mixture was stirred under the conditions indicated in Table I. Although the reaction mixture was treated directly with phenol as described in the next paragraph, the addition of diethyl ether to the mixture separated colorless precipitates and an orange-colored aqueous layer. The former was proved to consist mainly of *o*-nitrobenzenediazonium chloride (**7**) and the latter of a mixture of *o*-chlorobenzenediazonium chloride (**8**) and **7**.

Coupling Reactions of 7 and 8 with Phenol. The solution of diazotized **6** prepared above was added to aqueous alkaline phenol (PhOH, 1.36 g, 14.5 mmol; NaOH, 1.16 g, 29 mmol; H_2O, 28 mL) under ice cooling. After stirring for 30 min, the deep-colored two-layered solution was altogether evaporated to dryness and the residue was chromatographed through a silica gel column (cyclohexane/EtOAc = 4:1) to separate 2-nitro-4′-oxyazobenzene (**9**) and 2-chloro-4′-oxyazobenzene (**10**). For the product ratio **10**/**9**, see Table I.

Methyl 3-Nitroanthranilate (11). This ester was prepared from **1a** according to the reported method:[9] yield 23%; mp (cyclohexane) 96–97 °C; NMR (δ, $CDCl_3$) 3.90 (3 H, s), 6.62 (1 H, t, *J* = 8 Hz), 8.27 (2 H, dt, *J* = 8 and 2 Hz). Anal. Calcd for $C_8H_8N_2O_4$: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.21; H, 4.30; N, 13.90.

Diazotization of 11. To a suspension of **11** (130 mg, 0.66 mmol) in 4 mL of EtOH was added 0.25 mL of 35% HCl (2.5 mmol) and isoamyl nitrite (0.19 g, 1.6 mmol) and the mixture was stirred for 2 min at 0 °C, 10 min at 15 °C, and 15 min at 35 °C. The suspension became a clear solution. Cooling the solution at this stage separated a yellow solid, which was identified as unreacted **11**. After additional stirring at 35 °C for 45 min, neither cooling the solution nor the addition of diethyl ether separated **11**. The ethanolic solution, thus prepared, was poured into an ice-cooled solution of phenol (PhOH, 62 mg, 0.66 mmol; Na_2CO_3, 140 mg, 1.3 mmol; H_2O, 3 mL) and the mixture was stirred for 10 min. After removing solvents in vacuum, the residue was chromatographed through a silica gel column (cyclohexane/EtOAc = 4:1) to give three fractions. The first eluate (yellow) consisted of **11** (54%), the second (slightly yellow) of methyl 2-chloro-3-nitrobenzoate (**14**, 10%), and the last (red) of 2-chloro-6-(methoxycarbonyl)-4′-oxyazobenzene (**13**, 36%). **14**: mp 68–69 °C; NMR ($CDCl_3$) δ 3.98 (3 H, s), 7.35–8.05 (3 H, m). Anal. Calcd for $C_8H_6NO_4Cl$: C, 44.57; H, 2.80; N, 6.50. Found: C, 44.91; H, 3.05; N, 6.21. **13**: mp 106–107 °C; NMR ($CDCl_3$) 3.75 (3 H, s), 6.85–7.80 (1 H each, a pair of d, *J* = 9 Hz, phenolic), 7.25–7.90 (3 H, m, benzoate nucleus). Anal. Calcd for $C_{14}H_{11}N_2O_3Cl$: C, 57.84; H, 3.81; N, 9.64. Found: C, 57.64; H, 3.96; N, 9.26.

Registry No. **1a**, 606-18-8; **1b**, 50573-74-5; **1c**, 619-17-0; **1d**, 616-79-5; **1e**, 6388-47-2; **2b**, 70913-26-7; **2c**, 70913-27-8; **2d**, 70913-28-9; **2e**, 70913-29-0; **3**, 3854-96-4; **4b**, 65839-50-1; **4c**, 65839-53-4; **4d**, 65839-52-3; **4e**, 65911-33-3; **5b**, 65839-51-2; **5e**, 65911-31-1; **6**, 88-74-4; **7**, 70913-30-3; **8**, 70913-31-4; **9**, 2724-85-8; **10**, 6690-48-8; **11**, 57113-91-4; **13**, 70913-32-5; **14**, 53553-14-3; phenol, 108-95-2.

---

[9] F. J. Sowa and J. A. Nieuwland, *J. Am. Chem. Soc.*, **58**, 271 (1936).

Kinetic Study of the Dehydrochlorinations of 2,2-Diaryl-1,1,1-trichloroethanes by Ammonia and Methylamine

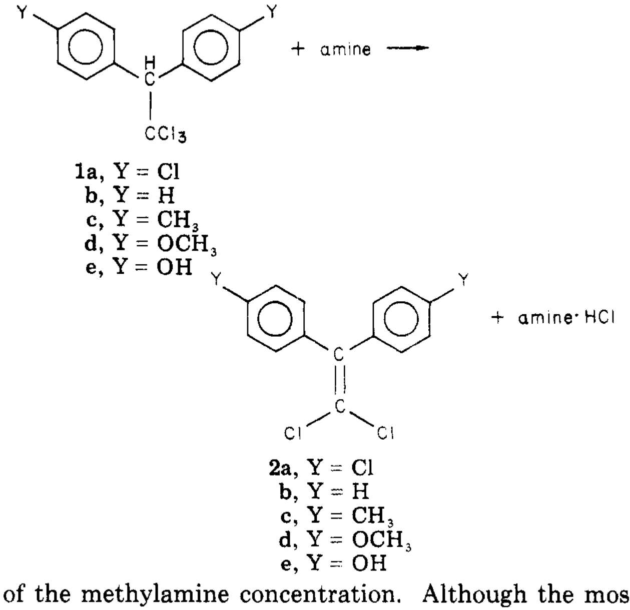
Michael R. MacLaury* and Anthony Saracino

Chemical Reactions and Systems Branch, General Electric Co., Schenectady, New York 12301

Received March 14, 1979

Amine-promoted dehydrochlorinations of $(p\text{-}YC_6H_4)_2CHCCl_3$ are consistent with a concerted E2 elimination. The observed rate law contains a third-order term that has not been observed for hydroxide- or alkoxide-promoted eliminations.

Recent articles by both Bordwell[1] and Saunders[2] have described the current evidence concerning base-initiated elimination reactions. Considerable study by McLennan et al.[3a] has led to the conclusion that the borderline between the concerted E2 and the carbanionic E1cB mechanisms occurs for the 2,2-diaryl-1,1,1-trichloroethane (DDT) and 2,2-diaryl-1,1-dichloroethane (DDD) type substrates. Most previously reported studies of these compounds have relied upon strong anionic bases in polar solvents (e.g., NaOH, NaOR, $NaOC_6H_5$, or $NaSC_6H_5$ in ROH) to effect elimination. We report herein the results of the reactions of ammonia and methylamine with 2,2-diaryl-1,1,1-trichloroethane derivatives (eq 1). Lord[4] has previously described the elimination reaction of **1a** by ammonia and methylamine in aqueous dioxane, and he curiously reports that the rate is dependent on the square of the methylamine concentration. Although the most common reaction between amines and halogenated



1a, Y = Cl
b, Y = H
c, Y = CH_3
d, Y = OCH_3
e, Y = OH

2a, Y = Cl
b, Y = H
c, Y = CH_3
d, Y = OCH_3
e, Y = OH

---

[1] F. G. Bordwell, *Acc. Chem. Res.*, **5**, 374 (1972).

[2] W. H. Saunders, *Acc. Chem. Res.*, **9**, 19 (1976).

[3] (a) A. Grout, D. J. McLennan, and I. H. Spackman, *J. Chem. Soc., Chem. Commun.*, 775 (1976); (b) D. J. McLennan and R. J. Wong, *J. Chem. Soc., Perkin Trans. 2*, 1373 (1974).

[4] K. A. Lord, *J. Chem. Soc.*, 1657 (1948).

0022-3263/79/1944-3344$01.00/0

Table I. Second-Order Rate Constants for the Dehydrochlorination of $(p\text{-}YC_6H_4)_2CHCCl_3$ by Ammonia and Methylamine

	10^6k_2,[a] M^{-1} s^{-1}			10^6k_2,[a] M^{-1} s^{-1}	
Y	CH_3NH_2[b]	NH_3[c]	Y	CH_3-NH_2[b]	NH_3[c]
Cl	423.9	688	OCH_3	4.6	12
H	22.7	48	OH	0.62	3.2
CH_3	8.0	18	*o,p*-OH	0.32	

[a] Pseudo-first-order reaction conditons ([amine]/[reactant] > 20). $k_2 = k_1$/[amine]: correlation coefficients >0.992. [b] $[CH_3NH_2]$ = 1.48 M in THF at 25 °C. [c] $[NH_3]$ = 24 M in CH_3CN at 50 °C, 170-psi pressure, 50% (v/v).

compounds is displacement to form the alkylamine, there are several other examples of dehydrohalogenations by ammonia.[5]

We have found that the ammonia- and alkylamine-promoted[6] elimination reactions for the substrates shown in Table I and eq 1 are remarkably clean and free of side reactions.[7] Kinetic analysis of the rates under pseudo-first-order conditions are linear for at least 3 half-lives for all compounds studied.

Activation parameters for **1a** and **1e** are dramatically different from the corresponding values reported previously for the NaOH/CH_3OH system. Cristol[8] reported activation energies (E_a) and entropies of activation ($\Delta S^{\ddagger}$) between 18 and 20 kcal/mol and −3 and −5 eu, respectively, for this series of compounds, whereas we have found activation energies of 8.3–10.9 kcal/mol and entropies of activation of −49 to −55 eu (Table II). Our very negative entropies indicate that the transition state is considerably more ordered and polarized when amines are used to dehydrochlorinate than when hydroxide is used. The Hammett ρ values[9] of 1.96 for methylamine and 1.77 for ammonia are consistent with the idea that these reactions do not go through a fully developed carbanion and are significantly lower than the previously reported value[8b] of 2.73 for sodium hydroxide in ethanol. The rates are much less dependent upon Y when ammonia or methylamine is used than when hydroxide or alkoxide effect the elimination.

The combination of a low ρ value together with such a large negative entropy of activation is consistent with an E2 transition state for this series of compounds. This is in contrast with the conclusion of McLennan[3b] that base-promoted elimination from DDT-type compounds proceeds by an E1cB mechanism.

Table II. Activation Parameters and Second-Order Rate Constants for the Dehydrochlorination of $(p\text{-}YC_6H_4)_2CHCCl_3$ by Ammonia and Methylamine

Y	amine	*T*, °C	10^6k_2,[a] M^{-1} s^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu
Cl	CH_3NH_2[b]	0	78.1		
		24	300.5	8.3	−49
		44	641.1		
OH	CH_3NH_2[c]	25	0.62	10.9	−52
		50	2.87		
OH	CH_3NH_2[d]	30	15.38		
		40	26.09	9.8	−50
		50	41.28		
OH	NH_3[e]	26.5	1.61		
		39.5	2.77	9.6	−55
		50	5.01		

[a] Pseudo-first-order conditons. $k_2 = k_1$/[amine]: correlation coeffcients >0.993. [b] $[CH_3NH_2]$ = 0.77 M in THF, [methylamine]/[reactant] = 27/1. [c] $[CH_3NH_2]$ = 1.40 M in THF, [methylamine]/[reactant] = 45/1. [d] $[CH_3NH_2]$ = 22.5 M (liquid methylamine), [methylamine]/[reactant] = 240/1. [e] $[NH_3]$ = 48 M (liquid ammonia) [ammonia]/[reactant] = 58/1.

Table III. Rate Constants for the Reaction of $(ClC_6H_4)_2CHCCl_3$ (DDT) in THF with a Range of Concentrations of CH_3NH_2 at 25 °C

$[CH_3NH_2]$, M	$[CH_3NH_2]$/[DDT][a]	10^6k_1, s^{-1}	10^6k_2, M^{-1} s^{-1}
0.0303	1		89.8[c]
0.0594	2		82.7[c]
0.1404	5		107.8[c]
		15.0	106.7[d]
0.515	55	121	235.0[d]
0.772	55	232	300.5[d]
1.545	55	886	573.5[d]

[a] Molar ratio. [b] Pseudo-first-order rate constant; correlation coefficients >0.996. [c] Second-order rate constant calculated by the method of Cristol.[9a] Plot of log $\dfrac{1 - [\mathrm{DDT}]/[\mathrm{CH_3NH_2}]}{1 - \phi}\phi$ vs. time, where ϕ = fraction of DDT consumed. [d] $k_2 = k_1/[CH_3NH_2]$.

The second-order rate constants for the elimination reactions of **1a** and **1e** increase with methylamine concentration. Data presented in Table III indicate that k_2 for the reaction of **1a** (DDT) increases almost sevenfold as the methylamine concentration increases from 0.03 to 1.5 M. We have observed similar results for the reaction of **1e** with methylamine in such solvents as THF and CH_3CN. Curiously, the effect of increasing ammonia concentration on k_2 is negative; that is, the second-order rate constant is decreased as ammonia concentration increases. This may be the result of a decrease in effective base strength due to the self-association of ammonia by hydrogen bonding.

These results are consistent with the mechanism proposed in Scheme I. The amine and the trichloroethane compounds form a complex,[10] in a preequilibrium step, that either reacts via the usual E2 concerted elimination (overall second order) or via an amine-assisted solvation of the leaving chloride in a third-order elimination. The rate expression for this scheme given in eq 2, yields an

$$\text{rate} = K(k_2{}^0 + k_3[\text{amine}])[\text{amine}][\text{trichloroethane compound}] \tag{2}$$

---

(5) (a) L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents", Wiley, New York, N.Y., 1953, p 87; (b) Belgian Patent 831 679, April 12, 1974; (c) British Patent 1 147 258, September 21, 1967; (d) German Offen. 2 204 708, August 9, 1973; (e) Y. Urata, Mem. Def. Acad., *Math., Phys., Chem. Eng., Yokosuka, Jpn.*, **13**, 387 (1973); (f) G. Friedman, C. Cohen, D. Wolf, and G. M. J. Schmidt, *Isr. J. Chem.*, **10**, 559 (1972); (g) A. Factor, M. R. MacLaury, J. L. Webb, U.S. Patent 4 097 538, June 27, 1978.

(6) Ammonia and methylamine afford the cleanest products. Other primary and secondary amines react to afford the dichloroethylenes, but significant side products and uncharacterized colored materials are formed also.

(7) Products and reactants for all reactions were identified by GC/MS, and ^{13}C and ^1H NMR spectra of isolated products are consistent with those of reported material.

(8) (a) S. J. Cristol. *J. Am. Chem. Soc.*, **67**, 1494 (1945); (b) S. J. Cristol, N. C. House, A. J. Quant, H. W. Miller, K. R. Eilar, and J. S. Meek, *ibid.*, **74**, 3333 (1952).

(9) The ρ values are the slopes of the plots of log k_2 vs. 2σ for Y = Cl, H, CH_3O, and CH_3. The correlation coefficients for methylamine and ammonia are 0.981 and 0.979, respectively, whereas the reported[8b] correlation value for NaOH was 0.971. The data for Y = OH were excluded because it was not immediately obvious which σ value should be used. The data for the ammonia reaction are consistent with phenol ($2\sigma = -0.74$); however, the methylamine results suggest that the phenoxide is fully formed and that one should use $2\sigma = -1.04$ for the Hammett plot.

(10) C. Jayne Biaselle and J. G. Miller, *J. Am. Chem. Soc.*, **96**, 3813 (1974).

$$k_2^{\text{obsd}} = K(k_2^0 + k_3[\text{amine}]) \qquad (3)$$

observed second-order rate constant (eq 3) that is consistent with our results[11] and the previously reported[4] elimination kinetics of 1a. The second- and third-order rate constants for **1a** and **1e** are summarized in Table IV. The third-order pathway is dominant for **1a** in THF while for **1e** it is the minor reaction path in both THF and acetonitrile.

We have observed a large rate enhancement for the reaction of **1e** in liquid ammonia and methylamine upon the addition of soluble salts such as sodium chloride or lithium chloride. Even the addition of excess amine-hydrochlorides accelerates the rate of dehydrochlorination. Under pseudo-first-order conditions when ammonia was used as both solvent and reactant, the half-life of the reaction of **1e** decreased from 53 min at 50 °C to 25 min upon increasing the concentration of ammonium chloride to 1.3 M. The same rate enhancement was observed when ammonium chloride was added to liquid methylamine; that is, the half-life for the reaction of **1e** at 50 °C decreased from 12 to 9 min upon the addition of ammonium chloride to the methylamine.

The unusual sensitivity of dehydrochlorinations to both amine concentrations and dielectric strength effects allows one to consider these reaction conditions as useful for the synthesis of olefins from halogenated precursors.

Experimental Section

2,2-Diaryl-1,1,1-trichloroethanes. These materials were prepared by the acid-catalyzed condensation of trichloroacetaldehyde and the appropriately substituted benzene[14] or phenol.[15] Mass, ^{13}C NMR and ^{1}H NMR spectra are consistent with the structures shown in eq 1.

Dehydrochlorination Reactions. Ammonia or methylamine (Matheson) was condensed at −78 °C under a nitrogen atmosphere into a glass pressure vessel (Fisher-Porter). The reaction vessel was sealed to a stainless steel manifold equipped with a pressure gauge, needle valve, and a ball valve fitted with a rubber septum through which a needle could be inserted for sampling. The reactor was placed in a constant-temperature bath (±0.1 °C) and allowed to warm up to the desired temperature. A stable pressure reading was assumed to mean thermal equilibrium had been reached. At 50 °C the gauge pressure for anhydrous ammonia and methylamine was 300 and 100 psi, respectively. When acetonitrile or THF was used as solvent, the pressures were considerably reduced. The diaryltrichloroethane reactant (ca. 0.5 g) was separated from the solution by a small glass cup which was held upright with magnets until thermal equilibrium had been achieved. Samples were withdrawn for analysis periodically through a valved 71-cm 18-gauge needle (Becton-Dickinson 1431 Brockenbrough Needle) which was inserted through the rubber-septum-sealed ball valve in the pressure manifold. The samples were quenched in glacial acetic acid.

2,2-Diaryl-1,1-dichloroethylenes. Preparative-scale reactions (>1 g) of all the trichloroethanes with both anhydrous ammonia and methylamine afforded greater than 90% isolated yields after recrystallization. The melting points and ^{13}C NMR, ^{1}H NMR, and mass spectra are consistent with the previously reported dichloroolefins.[16] GC/MS and analytical high-pressure LC indicated no products from side reactions except for the reaction of **1e** with anhydrous methylamine at 100 °C. In this case 2,2-bis(4-hydroxyphenyl)-1-chloroethylene was formed in about 1.5% isolated yield.

Scheme I

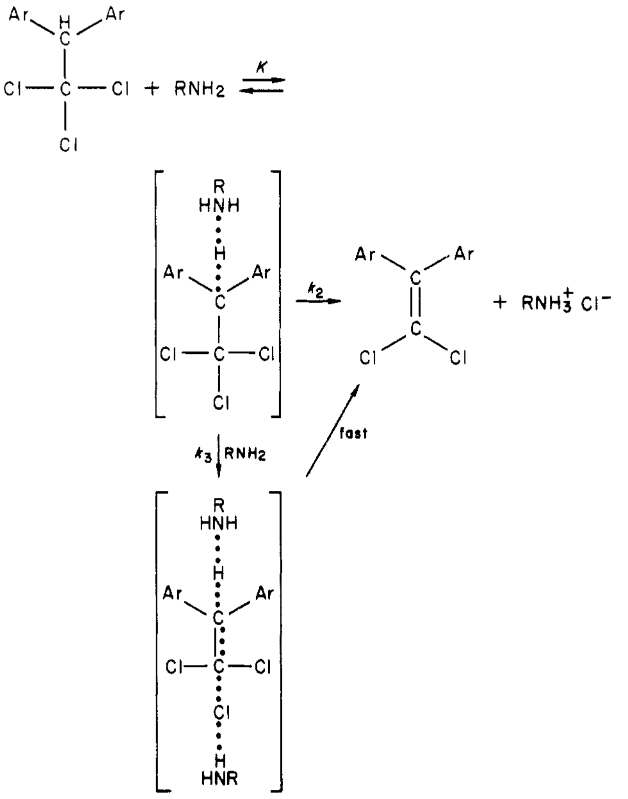


Table IV. Methylamine and Ammonia Concentration Effects on Elimination Rates of $(YC_6H_4)_2CHCCl_3$ ($k_2^{\text{obsd}} = k_2^0 + k_3[\text{amine}]$)

Y	T, °C	amine	[M]	solvent	$10^6 k_2^0$, M^{-1} s^{-1}	$10^6 k_3$, M^{-2} s^{-1}
Cl	25	CH_3NH_2	1.5	THF	73	328
OH	53	CH_3NH_2	2.7	THF	2.3	0.41
OH	53	CH_3NH_2	1.7	CH_3CN	4.8	1.1

[a] All rates were measured under pseudo-first-order conditions and $k_2^{\text{obsd}} = k_1/[\text{amine}]$; correlation coefficients >0.988. [b] Maximum molar concentration for which this relationship was tested.

Analytical Method for Kinetic Analysis. The reactions were monitored by isocratic high-pressure liquid chromatography by using a Waters Associates μC_{18} Bondpak column and a 254-nm UV detector. The eluting solvent was 50% methanol for the bis(phenols) (**1e** and **2e**) or 50% acetonitrile for the other reactants and products; the flow rate was 2.0 mL/min. The UV detector was interfaced to an electronic integrating system (Spectra-Physics SP 4000) and the peak area/concentration responses were found to be linear over the concentration range used. Response factors for all compounds were determined with authentic samples of both the trichloroethanes and the dichloroethylenes. The acetic acid quenched samples were filtered before injection onto the column.

Methylamine Titration. THF and acetonitrile were saturated with anhydrous methylamine at 25 °C. A 1.0-mL aliquot of the solution was diluted with 20 mL of water and titrated[17] to a phenolphthalein end point with 0.1 N HCl. For all kinetic re-

---

[11] An alternate explanation for these results is the change in ionic strength in the solvent as methylamine concentration increases. However, this "salt effect"[12] is an unlikely explanation as this is a concerted reaction between two neutral molecules, and the Debye–Hückel theory predicts no effect of ionic strength on rate.[13]

[12] A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78, 2763 (1956).

[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd ed, Wiley New York, N.Y., p 150.

[14] O. Zeidler, Ber. Dtsch. Chem. Ges., 7, 1180 (1874).

[15] E. ter Meer, Ber. Dtsch. Chem. Ges., 7, 1201 (1874).

[16] D. J. McLennan and R. J. Wong, J. Chem. Soc., Perkin Trans. 2, 279 (1972).

[17] A referee correctly pointed out that this method of titration is not optimum; however, the error involved is less than 15%, when compared to a standard potentiometric titration using perchloric acid. Since serial dilutions were made from the analyzed stock solution, the concentration vs. rate relationship remains valid.

actions, these stock solutions were serially diluted, and concentrations were calculated on the basis of the volume ratios.

Acknowledgment. We thank J. A. Cella for fruitful discussion and encouragement and C. G. Overberger for the significant suggestion that initiated this work.

Registry No. **1a**, 50-29-3; **1b**, 2971-22-4; **1c**, 4413-31-4; **1d**, 72-43-5; **1e**, 2971-36-0; **2a**, 72-55-9; **2b**, 2779-69-3; **2c**, 5432-01-9; **2d**, 2132-70-9; **2e**, 14868-03-2; 2-(*o*-hydroxyphenyl)-2-(*p*-hydroxyphenyl)-1,1,1-trichloroethane, 6621-68-7; methylamine, 74-89-5; ammonia, 7664-41-7; 2,2-bis(4-hydroxyphenyl)-1-chloroethylene, 68118-92-3; trichloroacetaldehyde, 75-87-6; chlorobenzene, 108-90-7; benzene, 71-43-2; methylbenzene, 108-88-3; methoxybenzene, 100-66-3; phenol, 108-95-2; 2-(*o*-hydroxyphenyl)-2-(*p*-hydroxyphenyl)-1,1-dichloroethene, 71032-16-1.

Stereochemistry of Diels–Alder Reactions at High Pressure. 4. Asymmetric Induction in High-Pressure Cycloadditions of (*R*)-(−)-Menthyl Glyoxylate and Symmetric 1,3-Dienes[1]

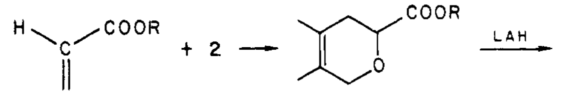
Janusz Jurczak* and Marek Tkacz

Institute of Organic Chemistry, Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland

Received December 18, 1978

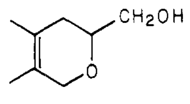
High-pressure cycloaddition of (*R*)-(−)-menthyl glyoxylate and 2,3-dimethylbuta-1,3-diene and cyclohexa-1,3-diene was studied. Optical yields of the cycloadditions were 2.4–20.9%, and the induced absolute configuration was *R* in all cases. Results were interpreted by using the concept of parallel formation of four endo boundary active complexes corresponding to the transoid and cisoid conformation of (*R*)-(−)-menthyl glyoxylate in the transition state.

We have recently observed the considerable effect, heretofore unreported, of high pressure on the direction and magnitude of asymmetric induction in the Diels–Alder reaction between unsymmetric 1-methoxybuta-1,3-diene and the heterodienophile (*R*)-(−)-menthyl glyoxylate (**1c**).[1,2]



1a, R = CH_3
b, R = n-C_4H_9
c, R = $C_{10}H_{19}$
= (−)-menthyl

4a, R = CH_3
b, R = n-C_4H_9
c, R = $C_{10}H_{19}$
= (−)-menthyl



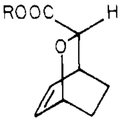
5

It would be worthwhile to extend stereochemical studies to high-pressure [2 + 4] heterocycloaddition of symmetric 1,3-dienes in order to describe more precisely the cycloaddition transition states.

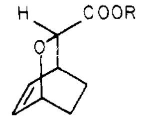
In this study we have selected two representative symmetric dienes: 2,3-dimethylbuta-1,3-diene (**2**) and cyclohexa-1,3-diene (**3**). Compound **2** is known[3] to react with alkyl glyoxylates (**1a**,**b**) at high temperatures (140 °C), affording low yields of the racemic esters of 4,5-dimethyl-2,3-dihydro-2*H*-pyran-2-carboxylic acid (**4a**,**b**), which have only one chiral center at atom C-2. Reduction of adducts **4** with lithium aluminum hydride leads to the racemic alcohol **5**.

Drastic conditions (140 °C) and low product yields of the thermal reaction between **1a** and **2** exclude its application to stereochemical studies. Under the reaction conditions the products of cycloaddition are very likely to be partly decomposed. On the other hand, application of high pressure allows the reaction to occur under mild conditions. Thus, use of (*R*)-(−)-menthyl glyoxylate (**1c**) under such mild conditions could be expected to bring about asymmetric induction.

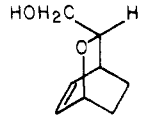
The second symmetric 1,3-diene which we selected, cyclohexa-1,3-diene (**3**), reacts with **1b** at 120 °C in satisfactory yield affording a mixture of endo (**6a**) and exo (**7a**) adducts in a ratio of 9:1.[4] Lithium aluminum hydride reduction of endo adduct **6a**, separable by column chromatography from exo adduct **7a**, affords alcohol **8**. Clearly it is necessary to establish only the absolute configuration of atom C-3, since the configuration of the other two chiral centers results from the diastereomeric geometries of the molecules.



6a, R = n-C_4H_9
b, R = $C_{10}H_{19}$
= (−)-menthyl
c, R = H



7a, R = n-C_4H
b, R = $C_{10}H_{19}$
= (−)-menthyl
c, R = H



8

Thermal endo addition at 120 °C of **1c** and **3** gives both diastereomers of adduct **6b** in equal amounts, which after reduction afford racemic alcohol 8. The same considerations apply to exo addition. Thus, asymmetric induction could be expected from application of high pressure.

Results and Discussion

Determination of the absolute configuration of ester **4c**, formed by asymmetric synthesis, was based on analysis of the optical and spectral properties of alcohol **5** as compared

---

[1] Part 3: J. Jurczak, *Pol. J. Chem.*, in press.

[2] J. Jurczak and B. Baranowski, *Pol. J. Chem.*, **52**, 1857 (1978).

[3] O. Achmatowicz Jr., M. Chmielewski, J. Jurczak, L. Kozerski, and A. Zamojski, *Org. Magn. Reson.*, **4**, 537 (1972).

[4] O. Achmatowicz Jr., J. Jurczak, and J. St. Pyrek, *Rocz. Chem.*, **49**, 1831 (1975).