1-Methoxycarbonylbicyclo[2.2.1]heptane-*endo,endo*-2,3-dicarboxylic Anhydride (3). To a 500-mL round-bottom flask was added 9.50 g (0.0428 mol) of 2 and 250 mL of dry EtOAc. The flask was purged with dry N_2 and stirred to affect solution, and then 0.95 g of 5% Pd/C was added. The mixture was hydrogenated at 1 atm pressure. After 30 min the calculated amount of H_2 was consumed. The mixture was filtered, the solvent volume was reduced by 70% in vacuo, and the product was allowed to crystallize. A total of 9.46 g (99%) of large white crystals, mp 157–158 °C, was recovered: IR (2% in KBr) 1865 and 1800 (anhydride C=O), 1730 (ester C=O), and 1080 (C–O) cm^{-1}; NMR ($CDCl_3$) δ 4.07–3.37 (m, 2, H-2 and H-3), 3.78 (s, 3, $-OCH_3$), 2.90 (m, 1, H-4), 2.15–1.50 (m, 6, $-CH_2-$); mass spectrum (70 eV), *m/e* (relative intensity) 224 (M^+, 0.1), 193 (16), 152 (25), 124 (100), 93 (18), 91 (9), 79 (16), 65 (11), 59 (16), and 28 (20). Anal. Calcd for $C_{11}H_{12}O_5$: C, 58.93; H, 5.36. Found: C, 58.88; H, 5.33.

1-Methoxycarbonylbicyclo[2.2.1]hept-2-ene (4). To a 250-mL round-bottom flask attached to a gas collection apparatus was added 9.45 g (0.042 mol) of 3, 5.39 g (0.008 mol) of freshly prepared $(Ph_3P)_2Ni(CO)_2$,[10] and 75 mL of anhydrous diglyme (freshly distilled from sodium). The stirred solution was heated at reflux and the effluent gas collected. The reaction mixture turned from yellow to brown to black as the heating was continued. After 6 h, 1880 mL of gas (1 equiv each of CO and CO_2) had been collected. The diglyme was removed in vacuo through a short-path apparatus, codistilling the product [bp 40 °C (2.5 mm)]. Then 2-(2-ethoxyethoxy)ethanol (2 × 25 mL) was added and distilled to dryness [bp 51 °C (0.02 mm)]. The combined distillates were poured into 800 mL of water and extracted with pentane[11] (4 × 100 mL). The combined pentane layers were washed with water (4 × 75 mL) and then with saturated brine and dried ($MgSO_4$).

The pentane was removed in vacuo to yield 5.82 g (91%) of a clear oil with a fruity odor: IR (liquid film) 3080 (olefin), 1740 (C=O), 1575 (olefin), 1110 (C–O), and 705 (olefin) cm^{-1}; NMR ($CDCl_3$) δ 6.10 (m, 2, C=CH), 3.72 (s, 3, $-OCH_3$), 2.92 (m, 1, H-4), and 2.20–0.92 (m, 6, $-CH_2-$); mass spectrum (70 eV), *m/e* (relative intensity) 152 (M^+, 8), 124 (100), 121 (11), 96 (28), 79 (25), 77 (14), 64 (25), 59 (21), 39 (14), 32 (42), 31 (55), 29 (22), and 28 (55).

Registry No.—1, 35730-27-9; 2, 66483-32-7; 3, 66551-63-1; 4, 15023-46-8; cyclopentadiene, 542-92-7; maleic anhydride, 108-31-6; $ClCO_2CH_3$, 79-22-1.

References and Notes

(1) This work was supported by USPHS-NIH Training Grant GM 1341 and research grants from the American Heart Association Kansas Affiliate and the University of Kansas General Research Fund.

(2) (a) W. R. Boehme, *J. Am. Chem. Soc.*, **80,** 4740 (1958); (b) *ibid.*, **81,** 2762 (1959); (c) H. Kwart and G. Null, *ibid.*, **80,** 248 (1958); (d) *ibid.*, **81,** 2765 (1959); (e) J. W. Wilt, C. T. Parsons, C. A. Schneider, D. G. Schultenover, S. J. Wagner, and W. J. Wagner, *J. Org. Chem.*, **33,** 694 (1968).

(3) R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23,** 742 (1958).

(4) B. M. Trost and F. Chen, *Tetrahedron Lett.*, 2603 (1971).

(5) (a) K. Wiesner, P-T. Ho, R. C. Jain, S. F. Lee, S. Oida, and A. Phillipp, *Can. J. Chem.*, **51,** 1448 (1973); (b) W. G. Dauben, G. T. Rivers, R. J. Tweig, and W. T. Zimmerman, *J. Org. Chem.*, **41,** 887 (1976).

(6) J. Thiele, *Chem. Ber.*, **34,** 68 (1901).

(7) (a) D. Peters, *J. Chem. Soc.*, 1757 (1959); (b) *ibid.*, 1761 (1959).

(8) O. W. Webster, *J. Am. Chem. Soc.*, **88,** 3046 (1966).

(9) If the Diels-Alder reaction is run at higher temperatures, a significant amount of 5-methoxycarbonylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride was formed due to the presence of the tautomeric 2-methoxycarbonylcyclopenta-1,3-diene.

(10) J. D. Rose and F. S. Statham, *J. Chem. Soc.*, 69 (1950).

(11) It was found that hexane was less efficient for this extraction than pentane.

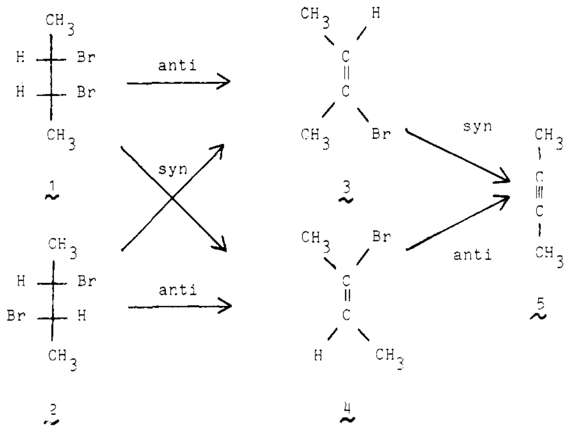
Heterogeneous Reactions. 5. The Anti Orientation of Elimination for the Dehydrobromination of *meso*- and *dl*-2,3-Dibromobutane and (*E*)- and (*Z*)-2-Bromobut-2-ene with Solid Potassium *tert*-butoxide

Michael J. Tremelling,* Steven P. Hopper, and
Paul C. Mendelowitz

Department of Chemistry, Vassar College,
Poughkeepsie, New York 12601

Received February 21, 1978

Scheme I



One of the most important stereochemical features of bimolecular base promoted β-elimination reactions is the relative orientation of the leaving groups. An important factor which is associated with the E2 reaction is the transition state stabilization derived from the partially developed double bond, and in order to maximize this stabilization the leaving groups must be periplanar. The periplanar requirement may be satisfied with the dihedral angle between these two groups being either 0° (syn) or 180° (anti).[1] In systems where both carbon centers involved in the elimination are chiral, a specific relative orientation of the leaving groups for diastereomeric reactants will dictate a different product selection (for example see Scheme I). In most solution reactions involving the dehydrohalogenation of alkyl halides the stereochemistry of the elimination has been shown to be predominantly antiperiplanar.[2–5]

We have recently reported a heterogeneous reaction system which has proven to be very efficient for effecting the base-promoted dehydrohalogenation of alkyl halides.[6] This heterogeneous reaction system utilizes solid phase alkoxide bases and vapor phase alkyl halides. Since the conditions of the heterogeneous reaction system are quite different from the more common solution reactions, it is important to determine the stereochemical requirement for these dehydrohalogenations. In fact, a syn elimination involving the simultaneous stabilization of the leaving groups by the anion and cation of the solid base is an attractive possibility under heterogeneous conditions.

The dehydrobromination of the diastereomeric *meso*-2,3-dibromobutane (**1**) and *dl*-2,3-dibromobutane (**2**) and the determination of any stereochemical selection from the analysis of the resulting (**E**)-2-bromobut-2-ene (**3**) and (**Z**)-2-bromobut-2-ene (**4**) provides a system which allows an examination of the syn vs. anti selection under heterogeneous conditions. These results yield a useful comparison with similar solution reactions.[2–5] Subsequent reaction of both **3** and **4** is also possible to yield but-2-yne (**5**). These reactions involve the elimination of a second molecule of HBr and provide a system which compares the syn vs. anti elimination of vinyl halides.[7,8]

Results and Discussion

Samples of **1** and **2** were prepared via the bromination of (**E**)- and (**Z**)-but-2-ene, respectively. The resulting dibromides were shown to have an isomeric purity of greater than 95% by ^1H NMR.[9] The *meso* and *dl* diastereomers, **1** and **2**, were reacted separately with solid potassium *tert*-butoxide at 100 °C according to methods which have been previously described.[6,11] The products of the dehydrobromination reaction for each isomer were analyzed by gas chromatography. Reactions for the preparation of **3** and **4**, according to the method of Bordwell and Landis, were not totally stereospecific.[3] The reactions yielded **3** which was found to be contaminated with 9% **4** and **4** which was found to be contaminated with 3% **3**.

0022-3263/78/1943-3076$01.00/0

Table I. Results of the Heterogeneous Dehydrobromination of *meso*- and *dl*-2,3-Dibromobutane and (E)- and (Z)-2-Bromobut-2-ene with Potassium *tert*-Butoxide at 100 °C[a]

reactant	registry no.	% 3[b]	% 4[b]	% 5[b]
1[c]	5780-13-2	67	trace	10
2	598-71-0	trace	28	72[f]
3[d,e]	3017-71-8	83	trace	17
4[e]	3017-68-3	trace	18	82

[a] All yields were determined by VPC internal standard yield analysis using toluene as the standard. [b] Percentage composition of recovered product. Overall mass balances for all reactions ranged from 70 to 90% based on starting material. [c] Reaction product contained 23% unreacted 1. [d] The reactant contained a 9% contamination of 4. [e] Product mixture contained less than 3% but-1,2-diene. [f] registry no. 503-17-3.

After quantifying the isomeric purity of 3 and 4 they were reacted with solid potassium *tert*-butoxide at 100 °C.

The possible modes of elimination (syn vs. anti) and their stereochemical implications are summarized for each isomer in Scheme I. The results of reactions with 1, 2, 3, and 4 under heterogeneous conditions are shown in Table I.

The results from Table I would imply that the elimination of HBr from 1 and 2 is proceeding with a preferred anti orientation of the leaving groups. A comparison of the reactions for 3 and 4 shows that 4 is far more reactive to elimination under these conditions than 3. The fact that unreacted 3 is recovered in very high yield while 4 reacts almost completely to yield 5 would indicate that the rate for anti elimination is much greater than the rate for syn elimination. The amount of alkyne observed in the reaction of 3 is amplified by a 9% contamination of 4 in the starting material. However, even if the results are corrected for this contamination it is apparent that 3 is not inert to the reaction conditions and must also be labile to some mode of elimination. Since 3 is thermally inert in the absence of base, it is possible that 3 is reacting directly via a syn elimination or that 3 undergoes a base promoted isomerization to 4 which subsequently reacts via an anti elimination to yield the alkyne.[8] The results shown in Table I are consistent with a high selectivity for anti elimination under heterogeneous reaction conditions.

The direct comparisons for the heterogeneous reactions of 1 and 2 with their reactions in solution would be the results obtained for the Bordwell and Landis procedure for the preparation of 3 and 4. The reactions of 1 and 2 under both heterogeneous and solution reaction conditions yield products that are consistent with a preferred anti mode of elimination. The analogous comparisons for the reactions of 3 and 4 under heterogeneous and solution conditions are also complementary. The solution studies of Miller and Staley have also shown the vinyl halide isomer that will allow anti elimination is more reactive than the isomer that requires syn elimination.[7,8]

Conclusions

The preferred anti orientation of the groups being eliminated in the heterogeneous system is parallel to that for similar reactions in solution.[2–5,7,8] Although the selection for the anti orientation of leaving groups is parallel for both the heterogeneous and solution reactions of alkyl and vinyl halides, the complex balance of factors that determines this syn vs. anti selection may not be the same.[1] These factors that determine the relative free energies of the isomeric transition states do, however, favor the anti orientation of elimination for both reaction systems regardless of their inherent differences.

Experimental Section

All ^{1}H NMR were recorded using a Varian T-60 NMR spectrometer. Analytical gas chromatography was carried out on a Perkin-Elmer Model 3920 gas chromatograph using a ⅛ in. × 12 ft 6% DC 200/12500 column. All GC traces were recorded using a Houston Instrument Omniscribe recorder with integrator.

Materials. The *cis*- and *trans*-but-2-ene were obtained from Union Carbide and used without further purification. The solid potassium *tert*-butoxide was obtained from Aldrich.

***meso*-2,3-Dibromobutane (1).** A 500-mL flask was charged with 53.2 g (0.33 mol) of bromine and 250 mL of CCl$_4$. The *trans*-but-2-ene was then added until the bromine color was discharged. The CCl$_4$ was removed under vacuum and the product was vacuum distilled, bp 29 °C (2.2 mm), yielding 64.4 g (90%) 1. The purity of the product was checked by ^{1}H NMR and found to be greater than 95% 1.[9]

***dl*-2,3-Dibromobutane (2).** The bromination of *cis*-but-2-ene using 49.3 g (0.31 mol) of bromine, under the same conditions as described above, yielded 53.2 g (80%) of 2, bp 27 °C (2.9 mm). The purity of the product was also checked by ^{1}H NMR and found to be greater than 95% 2.[9]

(E)-2-Bromobut-2-ene (3) and (Z)-2-Bromobut-2-ene (4). These vinyl halides were prepared according to the method of Bordwell and Landis.[3] Their purities were determined by VPC and ^{1}H NMR.[11] The reaction for the preparation of 3 was found to yield both 3 and 4 in the amounts of 91 and 9%, respectively. The reaction for the preparation of 4 yielded 3 and 4 in the amounts of 3 and 97%, respectively.

But-2-yne (5). The heterogeneous reaction of 4 yielded 5 directly as product. The condensate from the heterogeneous reaction of 4 was distilled at ambient temperature condensing the distillate at 0 °C. An isolated yield was not determined since 5 was needed only in sufficient quantities for identification by ^{1}H NMR (δ = 1.69 s) and the determination of a response factor for the internal standard analysis.

Heterogeneous Dehydrohalogenation Reactions. The design of the apparatus and the procedure of the reaction system have been described in detail previously.[6,10] Each reaction used 5 g (0.045 mol) of potassium *tert*-butoxide and 2–3 g of 1, 2, 3, or 4. All reactions were run at 100 ± 5 °C. The mass balance for all reactions ranged from 70 to 90%, based on starting material. Control experiments were performed on pure samples of each reagent to insure that there was no thermal isomerization under the conditions of the reaction.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for support of this research.

Registry No.—*trans*-But-2-ene, 624-64-6; *cis*-but-2-ene, 590-18-1; potassium *tert*-butoxide, 865-47-4.

References and Notes

(1) W. H. Saunders and A. F. Cockerill, "Mechanisms of Elimination Reactions", Wiley, New York, N.Y., 1973; J. Sicher, *Rev. Pure Appl. Chem.*, **25**, 655 (1971); *Angew. Chem., Int. Ed. Engl.*, **11**, 200 (1972), and references therein.

(2) M. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Am. Chem. Soc.*, **73**, 3329 (1951).

(3) F. G. Bordwell and P. S. Landis, *J. Am. Chem. Soc.*, **79**, 1596 (1957).

(4) D. J. Cram, F. D. Greene, and C. H. DePuy, *J. Am. Chem. Soc.*, **78**, 790 (1956).

(5) R. A. Bartsch, *Tetrahedron Lett.*, 297 (1970); *J. Am. Chem. Soc.*, **93**, 3683 (1971).

(6) M. J. Tremelling, S. P. Hopper, and J. E. Evans, *Tetrahedron Lett.*, 1153 (1976).

(7) S. J. Miller and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 629 (1952); S. J. Miller, *J. Org. Chem.*, **26**, 2619 (1961).

(8) S. W. Staley and R. F. Doherty, *Chem. Commun.*, 288 (1969).

(9) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1469 (1969).

(10) S. P. Hopper and M. J. Tremelling, *Synth. React. Inorg. Met.-Org. Chem.*, **7**, 157 (1977); S. P. Hopper, M. J. Tremelling, R. J. Ginsberg, and P. C. Mendelowitz, *J. Organomet. Chem.*, **134**, 173 (1977).

(11) J. H. Richards and W. F. Beach, *J. Org. Chem.*, **26**, 623 (1961).