

on, as compared with the integrals in the normal spectrum. The irradiating field was gated off during acquisition of the fid.

²H NMR spectra were recorded in the Fourier mode on a Bruker WM 250 spectrometer, in 10-mm tubes. Details are shown in Figure 1.

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Thermal Isomerization of Quadricyclane to Norbornadiene Catalyzed by Copper(II) and Tin(II) Salts

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Abstract: Copper(II) salts and tin(II) chloride show exceptional heterogeneous catalytic behavior in converting quadricyclane to norbornadiene in benzene. The heterogeneous catalysis mechanism is described by the adsorption of quadricyclane on the salt surface by a combination of a one-site and a two-site coordination. The two-site-coordination process results in the formation of C₇H₈X₂ (X = Cl or Br) as a side product when CuCl₂ or CuBr₂ are used as catalysts. The rate constant for the disappearance of quadricyclane is much greater when CuCl₂ or CuBr₂ (~10⁻² min⁻¹ cm⁻²) is used than when CuSO₄ (~10⁻⁴ min⁻¹ cm⁻²) is used.

The reversible valence isomerization of norbornadiene¹ (NBD) to quadricyclane² (Q) has received considerable attention as an attractive system for solar chemical energy storage.³⁻⁵ Our studies have primarily involved the photosensitized isomerization of NBD to Q by copper(I) complexes.⁶ During these investigations it was observed that anhydrous copper(II) salts catalyzed the reverse isomerization of Q to NBD. This was extremely interesting in that previous studies^{5,7-11} have focused on more exotic and expensive catalysts (e.g., [(CF₃)₂C₂S₂]₃Mo,⁵ [Rh(CO)₂Cl]₂,⁸ (C-H₂=CHCN)₂Ni,⁹ cobalt(II) porphyrins,^{5,8} [(NBD)RhCl]₂,¹⁰ and [M(NO)₂(CH₃CN)₄](BF₄)₂ with M = Mo or W¹¹).

Recently it was reported that a solution of SnCl₂ and (Ph₃P)SnCl₂ in deuterated methanol catalyzed the isomerization of Q to NBD.⁷ However, a benzene solution of Q in contact with SnCl₂ was observed to be inactive.⁷ In view of our findings with CuCl₂, we assume that stannous chloride dihydrate was used. Indeed, we have found that SnCl₂·2H₂O does not catalyze the conversion of Q to NBD in benzene. Anhydrous SnCl₂ in benzene does catalyze the isomerization with the desired catalytic properties: (1) rapid and specific conversion of Q to NBD and (2)

Table I. Summary of Catalytic Properties of CuCl₂, CuBr₂, SnCl₂, and CuSO₄ in the Conversion of Quadricyclane, Q, to Norbornadiene, NBD, in Benzene

added salt	change in catalytic surface	remarks on kinetics
CuCl ₂ ·2H ₂ O, CuSO ₄ ·5H ₂ O, SnCl ₂ ·2H ₂ O	none	no reaction
CuCl ₂	brown to white	-rate Q > +rate NBD; C ₇ H ₈ Cl ₂ formed (-rate Q/rate NBD decreases with surface area of salt, with very small surface areas -rate Q ≈ +rate NBD)
CuBr ₂	black to white	-rate Q ≫ +rate NBD; C ₇ H ₈ Br ₂ formed (-rate Q/rate NBD decreases with surface area of salt, with very small surface areas -rate Q ≈ +rate NBD)
CuSO ₄	none	-rate Q = +rate NBD
SnCl ₂	none	-rate Q = +rate NBD

insolubility in the reaction medium.

Experimental Procedures

Materials. All materials were purchased commercially. Spectral grade benzene was dried by anhydrous cupric sulfate prior to the kinetic experiments. Anhydrous CuCl₂ was prepared by heating it in an oven at 160 °C for several hours. Anhydrous CuSO₄ was similarly heated prior to use. Powdered anhydrous CuSO₄ of approximately 400-600 mesh was used. The anhydrous CuCl₂ and CuBr₂ were 120-200 mesh and 50-70 mesh, respectively. Anhydrous SnCl₂ was used as purchased with the size of the crystals varying greatly from 2.5 to 0.2 mm.

Conversion Rates. Dried benzene was added to a predetermined amount of copper(II) or tin(II) salt weighed in a nitrogen-dried 10-mL volumetric flask. Quadricyclane dissolved in benzene was then added to the volumetric flask, with approximately 10-15 s required to achieve mixing. The heterogeneous solution was continuously stirred except for 5- to 10-s intervals when ~0.3 μL of solution was withdrawn for analysis.

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(2) Tetracyclo[2.1.0.0^{2,7}.0^{4,6}]heptane.

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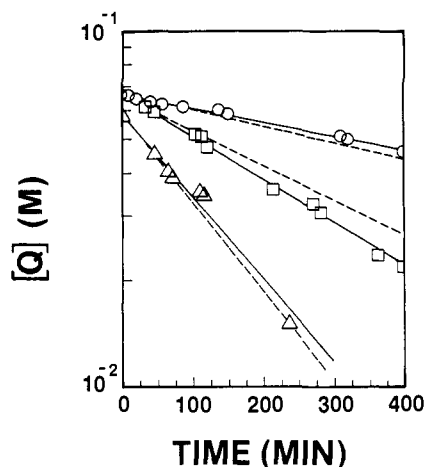


Figure 1. Catalyzed conversion of Quadricyclane (Q) to norbornadiene (NBD) with CuSO_4 in 10 mL of benzene (O, 0.0326 g; \square , 0.0643 g; Δ , 0.1424 g of CuSO_4). Solid lines are the linear least-squares fit of $\log [Q]$, vs. time. Dashed lines are modeling fit by using eq 1.

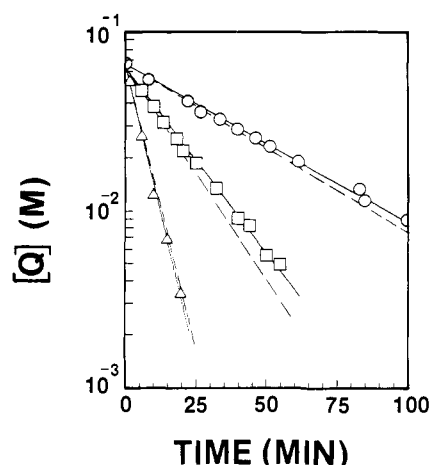


Figure 2. Catalyzed conversion of quadricyclane (Q) to norbornadiene (NBD) with CuSO_4 in 10 mL of benzene (O, 0.3767 g; \square , 0.6891 g; Δ , 1.2143 g of CuSO_4). Solid lines are the linear least-squares fit of $\log [Q]$, vs. time. Dashed lines are modeling fit by using eq 1.

The concentrations of Q and NBD were determined at various times during the catalyzed conversion using a Hewlett-Packard 5880-A gas chromatograph with a flame ionization detector. An OV-101 fused silica capillary column was used to separate the isomers with toluene used as an internal standard. Calibration of the GC response showed a 1:1 correspondence for NBD and Q to toluene concentration. A LKB 2091 GC/MS system was also used in identification of products. In order to observe the parent peak of the $\text{C}_7\text{H}_8\text{Br}_2$ product, we used a 18-20 eV EI source instead of the standard 70 eV source.

Results

Anhydrous CuSO_4 , CuCl_2 , CuBr_2 , or SnCl_2 added to benzene solutions of Q produced NBD even though the salts are very insoluble. The rate of conversion of Q to NBD is dependent on the amount of salt in contact with the solution. Copper(II) sulfate pentahydrate, copper(II) chloride dihydrate, and tin(II) chloride dihydrate under analogous conditions did not catalyze the isomerization. It is therefore apparent that a coordination site on the metal must be available to catalyze the isomerization of Q to NBD. Table I shows a summary of the observed catalytic behavior of these salts.

The catalytic conversion of Q to NBD with use of anhydrous CuSO_4 appears to be a 1:1 conversion process with no side products observed. The rate of disappearance of Q is equal to the rate of formation of NBD, with the mass balance $[Q] + [\text{NBD}]$ remaining constant within experimental error throughout all conversions catalyzed by CuSO_4 . The rate of conversion increases with the amount of CuSO_4 , and the rate appears to remain pseudo

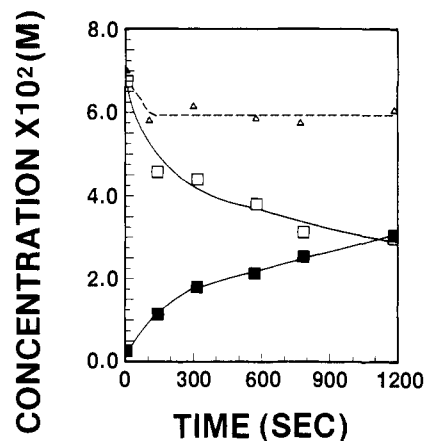


Figure 3. Catalyzed conversion of quadricyclane (Q) to norbornadiene (NBD) with 0.0265 g of CuCl_2 in 10 mL of benzene: \square , [Q]; \blacksquare , [NBD]; Δ , [Q] + [NBD].

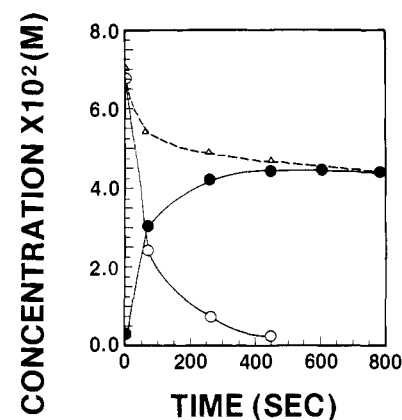


Figure 4. Catalyzed conversion of quadricyclane (Q) to norbornadiene (NBD) with 0.1272 g of CuCl_2 in 10 mL of benzene: O, [Q]; \bullet , [NBD]; Δ , [Q] + [NBD].

first order over the weight range of 0.03 to 1.2 g as shown in Figures 1 and 2. A benzene solution of anhydrous CuSO_4 at its solubility limit was observed to have a pseudo-first-order rate constant of only $2 \times 10^{-5} \text{ min}^{-1}$ (i.e., the maximum value for a homogeneous reaction) in comparison to the slowest rate shown in Figure 1 of $9 \times 10^{-4} \text{ min}^{-1}$ for 0.0326 g of CuSO_4 .

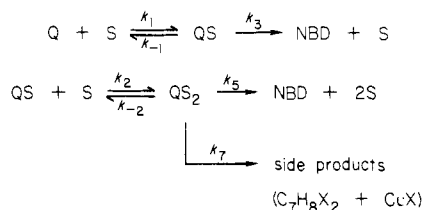
The addition of anhydrous CuCl_2 or CuBr_2 to benzene solutions of Q gives quite different results in comparison to CuSO_4 . The brown CuCl_2 or black CuBr_2 crystals are gradually displaced by a white precipitate. The reaction of the crystals is accompanied by a decrease in Q concentration. The rate of disappearance of Q increases with the amount of CuX_2 ($X = \text{Cl}$ or Br); however, $-\text{d}[Q]/\text{d}t$ is considerably greater than $\text{d}[\text{NBD}]/\text{d}t$. Norbornadiene is produced in the catalytic process, but a side product results from the addition of chlorine or bromine respectively to quadricyclane. A GC/MS analysis of this product shows two isomers with the proper isotopic ratios for the mass weight corresponding to $\text{C}_7\text{H}_8\text{X}_2$. Analysis of the white precipitate formed in the reaction of the cupric halide with quadricyclane shows multiple mass units of CuX when heated in the solid inlet probe of the mass spectrometer. An IR of a halocarbon oil suspension of the precipitate showed no absorbance other than the halocarbon. These observations infer that the white precipitate formed in the reaction is copper(I) halide. The yield of NBD produced by the CuX_2 -catalyzed conversion varies with the amount of CuX_2 added to the solution. With very small surface areas of the CuX_2 catalyst available, $-\text{d}[Q]/\text{d}t \approx \text{d}[\text{NBD}]/\text{d}t$. As the surface area of CuX_2 is increased in proportion to the amount of Q available, $-\text{d}[Q]/\text{d}t$ becomes progressively greater than $\text{d}[\text{NBD}]/\text{d}t$ and the $\text{C}_7\text{H}_8\text{X}_2$ product becomes dominant. For CuBr_2 , no production of NBD is observed for very large amounts of CuBr_2 while with CuCl_2 the relative yield of NBD appears to be approaching a constant value

of approximately 60% as the amount of CuCl_2 in contact with the solution is increased. Some of the data for CuCl_2 are shown in Figures 3 and 4. The relative rates of the CuX_2 catalysis are difficult to measure as the amount of surface area, as well as the Q concentration, is changing during the course of the reaction. By using the initial rates of $-d[Q]/dt$ divided by the initial [Q] concentration and surface area available, an approximation to the relative rates of catalysis can be made. With the error that is involved in the calculation of the surface area from the crystal size, the first-order rate for the disappearance of Q divided by the surface area only shows that the rates are approximately the same order of magnitude for CuCl_2 and CuBr_2 ($\sim 10^{-2} \text{ min}^{-1} \text{ cm}^{-2}$). However, the same analysis for CuSO_4 shows that the CuSO_4 pseudo-first-order rate for the disappearance of Q divided by surface area is approximately two orders of magnitude slower ($\sim 10^{-4} \text{ min}^{-1} \text{ cm}^{-2}$).

Insoluble SnCl_2 in benzene catalyzes the isomerization of Q to NBD in the same manner as described for anhydrous CuSO_4 . Analysis of the products from the SnCl_2 -catalyzed isomerization in benzene shows essentially total conversion of Q to NBD. No addition of chlorine to quadricyclane was noted. A very minor side product observed had a parent peak at 110 mass units. This is believed to be the addition of water to quadricyclane probably resulting from a small amount of water present in the reaction system.

Discussion

The catalytic conversion of Q to NBD with the anhydrous copper(II) and tin(II) salts is clearly a surface-mediated reaction. The solubility of these inorganic salts in benzene is extremely small, and the rate of conversion of Q to NBD is dependent on the amount of salt present in contact with the solution. The results of this study are best described in terms of a heterogeneous catalysis mechanism that involves the adsorption of quadricyclane on the surface by combination of a one-site and a two-site coordination.



Q = quadricyclane; NBD = norbornadiene; S = active surface sites; QS, QS_2 = charge-transfer complex on the surface

The first-order dependence shown in Figures 1 and 2 suggests that only a small fraction of the surface is ever covered under the conditions shown. When the assumptions that the fraction of the surface area covered by Q is extremely small and the adsorption equilibria are not disturbed significantly by the occurrence of the reactions (k_3 , k_5 , and k_7) are made, then the mechanism shown gives

$$-d[Q]/dt = \{K_1 k_3 S + K_1 K_2 (k_5 + k_7) S^2\} [Q]$$

where $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$. The number of active surface sites should be directly proportional to the weight of the given catalyst, assuming a consistent crystal size distribution in the sample used. Thus,

$$-d[Q]/dt = \{k'_{1Q}(\text{wt}) + k'_{2Q}(\text{wt})^2\} [Q] \quad (1)$$

where $k'_{1Q} = cK_1 k_3$, $k'_{2Q} = c^2 K_1 K_2 (k_5 + k_7)$, wt = weight of catalyst used, and c = proportionality constant between the weight and surface area. This analysis would predict pseudo-first-order kinetics

$$\ln ([Q]_0/[Q]_t) = \{k'_{1Q}(\text{wt}) + k'_{2Q}(\text{wt})^2\} t$$

$$\text{with a slope} = k'_{1Q}(\text{wt}) + k'_{2Q}(\text{wt})^2$$

As the weight of the catalyst is increased the squared term will

become dominant; with small weights the $k'_{1Q}(\text{wt})$ term will have a significant contribution. In the case of CuSO_4 where no side products are observed (k_7 being insignificant) the total surface area of the salt remains constant during the catalysis, and eq 1 can be easily tested. The pseudo-first-order slopes in Figures 1 and 2 are fit well by a quadratic function of the weight of CuSO_4 used in the catalysis. A least-squares fit of the quadratic equation minimizing the relative deviations of slopes gives $k'_{1Q} = 2.9 \times 10^{-2} \text{ min}^{-1} \text{ g}^{-1}$ and $k'_{2Q} = 7.3 \times 10^{-2} \text{ min}^{-1} \text{ g}^{-2}$ (with a 400-mesh crystal size, $k_{1Q} = 6.6 \times 10^{-5} \text{ min}^{-1} \text{ cm}^{-2}$ and $k_{2Q} = 3.8 \times 10^{-7} \text{ min}^{-1} \text{ cm}^{-4}$). The dashed lines in Figures 1 and 2 show the fit of the data when this analysis is used. At the lowest weight of CuSO_4 (0.0326 g) the isomerization proceeds 95% through a one-surface-site step, but with the highest of CuSO_4 (1.214 g) the isomerization proceeds only 25% through a one-surface-site step. Neither a one-site nor a two-site mechanism alone will fit the rate data over the entire weight range of CuSO_4 . Also, if the one-surface-site step (k_3) were eliminated from the mechanism, steady-state kinetics would predict a surface area squared dependence at low weights of CuSO_4 and a linear dependence at high weights of CuSO_4 . This analysis does not fit the experimental data.

The addition of chlorine or bromine when CuCl_2 or CuBr_2 is used as the catalyst strongly suggests the formation of a charge-transfer complex between Q and the Cu(II) salt as an intermediate in the catalysis mechanism. Quadricyclane can be converted to NBD as a consequence of the charge transfer to the transition metal. Norbornadiene, having a very low binding affinity for Cu(II), is released into the solution phase as it is formed. With Cu(II) halides, the halide can be transferred to the hydrocarbon during the formation of the charge-transfer complex, thus resulting in the ultimate reduction of the copper(II) halide to copper(I) halide and the addition of the halide to quadricyclane. The change in the rate of $-d[Q]/dt$ in comparison to $d[\text{NBD}]/dt$ (Table I, Figures 3 and 4) with surface area of the CuX_2 salts suggests that the addition of halide is only favorable when quadricyclane is coordinated to two surface sites. This is not surprising since the balanced oxidation-reduction process would require two CuX_2 molecules per Q ($\text{C}_7\text{H}_8 + 2\text{CuX}_2 \rightarrow \text{C}_7\text{H}_8\text{X}_2 + 2\text{CuX}$). The chloride or bromide addition to quadricyclane was an interference for the isomerization study and as such was not studied further to assess the exact nature of the products. The cupric halide salt was inactive with norbornadiene in benzene. However, Onoe, Uemura, and Okano¹³ have found that norbornadiene can be chlorinated with CuCl_2 in CH_3CN at 80 °C. This is a homogeneous reaction and only two products were obtained: *trans*-3,5-dichloronorbornadiene, and *exo-cis*-3,5-dichloronorbornadiene. These products would be consistent with a two-site mechanism and our GC-MS results.

Large surface areas of CuBr_2 produce only the $\text{C}_7\text{H}_8\text{Br}_2$ product which infers $k_7 \gg k_5$. With CuCl_2 an equilibrium of $\sim 60\%$ NBD production was observed with large surface areas of CuCl_2 which gives $k_5/(k_5 + k_7) \approx 0.6$ or $k_5/k_7 \approx 1.4$. SnCl_2 reduction is apparently not energetically favorable for addition of chlorine to quadricyclane since no addition product is observed ($k_5 \gg k_7$). As more surface becomes available with increasing weights of cupric chloride, increased ratios of chloride addition to isomerization are observed. Quantitative values for the rates would be difficult to unravel since the chloride addition results from production of cuprous chloride which is an inactive surface for the isomerization (i.e., the surface becomes poisoned).

The clean catalytic conversion of Q to NBD by CuSO_4 becomes an excellent example of surface reactions. The simplest treatment of the surface reaction involving a competitive one-adsorption- and two-adsorption-site process can be used to adequately describe the results. If Q is only very weakly adsorbed on the surface (i.e., the fraction of the surface sites occupied is extremely small), the

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derivation of eq 1 is greatly simplified.

Low-valence transition-metal compounds have been shown to be effective in the photosensitized isomerization of NBD to Q (e.g., CuCl_2 and copper(I) phosphine complexes⁶). The results of this study indicate that the presence of higher valence states of the metal may inhibit the production of quadricyclane; therefore, oxygen and other oxidizing agents would have to be rigorously excluded in the photosensitized conversion of NBD to Q by

transition-metal compounds.

Acknowledgment. We gratefully acknowledge financial support from Frank J. Seiler Research Lab (Air Force Systems Command), Utah Consortium for Energy Research and Education, and the Utah State University Research Office.

Registry No. CuCl_2 , 7447-39-4; CuSO_4 , 7758-98-7; SnCl_2 , 7772-99-8; CuBr_2 , 7789-45-9; quadricyclane, 278-06-8; norbornadiene, 121-46-0.

Diastereoselective Benzyloxymercuration/Demercuration of Derivatives of γ -Alkyl- δ -hydroxy- α,β -unsaturated Esters. A New Strategy for the Synthesis of Aldol-Type Products

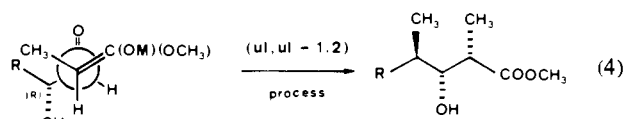
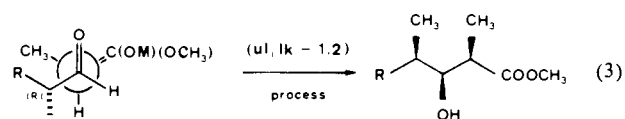
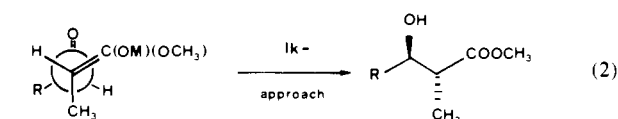
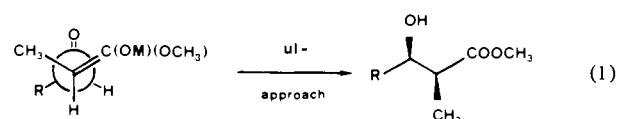
Suvit Thaisrivongs and Dieter Seebach*

Contribution from the *Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, CH-8092 Zürich, Switzerland. Received April 18, 1983*

Abstract: The diastereoselective construction of open-chain carbon skeletons with three or more consecutive asymmetric centers—bearing alternating oxygen (RO) and alkyl (R) substituents—by the aldol addition reaction still poses considerable problems (eq 3 and 4). An alternative route to some products with this substitution pattern and with certain relative configurations is the α -alkylation of β -hydroxy esters followed by two-carbon chain extension via Wittig olefination and benzyloxylation via the title reaction (Scheme I and Chart I; cf. **5** \rightarrow **12** \rightarrow **21**). Readily available enantiomerically pure starting materials can be employed. It is demonstrated by the examples described here that the addition of benzyloxy groups to the β -position of unsaturated esters and of enones with δ -RO groups is mainly directed by the γ -substituent. With conversions of 60–85%, the chemical yields are in the order of 85–95%, and the major diastereomers of certain configuration prevail to the extent of >90% with γ -methyl and >95% with γ -ethyl groups (Chart I). The configuration of the products is assigned by conversion to cyclic acetals or hemiacetals (Chart II) and 300-MHz ^1H NMR spectroscopy. From this assignment, the relative topicity of benzyloxylation is specified as *ul*-1,2 (eq 8).

There has been a keen interest in acyclic stereoselection due largely to the determination of synthetic chemists to construct acyclic or macrocyclic target molecules that contain a large number of centers of chirality. Some of these natural products, such as macrolide and ionophore antibiotics, have attracted considerable attention, which led to a renaissance of the aldol reaction as a highly desirable method for stereochemical control in syntheses of conformationally flexible compounds. In fact, advances in the enantioselective and diastereoselective execution of aldol additions have been impressive and culminated in the total syntheses of many structurally intriguing molecules.¹⁻³ As exemplified in 1 and 2 for the addition of a methyl propionate metal enolate to an aldehyde, each component has two enantiotopic faces, and the two possible relative topicities give rise to two diastereomers.⁴ Many ingenious procedures now exist that provide one of the adducts directly or indirectly with high diastereoselectivity.¹⁻³

However, a more difficult problem arises if the aldehyde contains one or more centers of chirality. In addition to the relative topicity, with which the two trigonal centers combine, the process must also secure a preference for one of the two possible relative topicities within the aldehyde; i.e., the attacking enolate must exhibit diastereoface selection.⁵ This is demonstrated with an



α -methyl-branched aldehyde in eq 3 and 4. In this case, the relative configuration on *three* consecutive centers is to be established in a *single* step. There are more or less useful solutions to fulfill this task.^{1-3,6}

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