made of distilled reagents, stored, and analyzed at room temperatures. (***WARNING***: 2-Chloroethyl sulfides are potent vesicants and must be handled in a closed system or in a hood with minimum velocity of 100 ft/min). Spectral identifications and peak assignments of the sulfonium cations were based on published data,[5] COSY, and heteronuclear correlated two-dimensional NMR experiments.

Both the H-2TG and the CH-TG salts shown in eq 3 and 4 were identified in the H–water mixtures. The EHT

$$S(CH_2CH_2Cl)_2 + 2S(CH_2CH_2OH)_2 \longrightarrow S[CH_2CH_2\overset{+}{S}(CH_2CH_2OH)_2]_2 + 2Cl^- \quad (3)$$

H-2TG

$$\begin{matrix} & CH_2CH_2Cl \\ S & \\ & CH_2CH_2OH \end{matrix} + S(CH_2CH_2OH)_2 \longrightarrow (CH_2CH_2OH)_2\overset{+}{S}CH_2CH_2SCH_2CH_2OH + Cl^- \quad (4)$$

CH-TG

sulfonium chloride shown in eq 5 and 2-hydroxyethyl ethyl sulfide (HEES) were the only compounds found by ^{13}C NMR immediately after the CEES–water samples (ranging from 2% to 50% by volume) became one phase. The other possible sulfonium cation, $CH_3CH_2\overset{+}{S}(CH_2CH_2Cl)CH_2CH_2SCH_2CH_3$ (ECT) was not detected in any of the samples. Presumably CEES was converted to HEES and EHT in the aqueous phase as soon as it was dissolved, and chemical reactions at the interface were the driving force for dissolution. In the 2% mixture, about 83 mol % of EHT and 17 mol % of HEES were found after the solution became one phase, but the EHT subsequently hydrolyzed to form HEES and HCl (eq 6) with a pseudo-first-order

$$\underset{\text{CEES}}{CH_3CH_2SCH_2CH_2Cl} + \underset{\text{HEES}}{CH_3CH_2SCH_2CH_2OH} \rightarrow \underset{\text{EHT}}{CH_3CH_2\overset{+}{S}(CH_2CH_2OH)(CH_2CH_2SCH_2CH_3)} + Cl^- \quad (5)$$

$$EHT + H_2O \rightleftharpoons 2CH_3CH_2SCH_2CH_2OH + H^+ \quad (6)$$

rate coefficient[6] of about 6×10^{-7} s^{-1}. Approximately 12 mol % of EHT was still present after 120 days. The hydrolysis rate apparently depended on the HCl contents in water, since 78 mol % of EHT was still present in the 50% sample after more than 2 years. Equation 6 is reversible since an aqueous mixture of 4 M HCl and 3 M HEES reacted to form 93 mol % of EHT sulfonium salt and 7 mol % of HEES, according to ^{13}C NMR analysis. NMR measured higher concentrations of EHT in samples of the same concentration of CEES which initially contained excess HEES. Although NMR is limited in detecting concentrations less than 1 mol %, conductivity measurements showed that the H^+ production from 2×10^{-4} M CEES was also lower in solutions of 6×10^{-4} M HEES than in pure water. Therefore, contrary to earlier observations, we believe that these sulfonium chlorides are significant initial products in dilute solutions and stable final products in concentrated aqueous solutions of 2-chloroethyl sulfides. We are currently attempting to isolate these sulfonium chlorides for further study.

The following are the NMR shifts of the salts identified in the reaction mixtures.

H-2TG: ^{13}C NMR (H_2O) δ 28.6 (2 C, SCH_2), 43.8 (2 C, $SCH_2CH_2S^+$), 46.4 (4 C, $^+SCH_2CH_2OH$), and 59.0 (4 C, CH_2OH); ^1H NMR (H_2O/TSP) δ 3.21 (t, 4 H, $SCH_2CH_2S^+$), 3.73 (t, 8 H, $^+SCH_2CH_2OH$), 3.85 (t, 4 H, $SCH_2CH_2S^+$), and 4.11 (t, 8 H, CH_2OH).

CH-TG: ^{13}C NMR (H_2O) δ 28.6 ($SCH_2CH_2S^+$), 36.3 (SCH_2CH_2OH), 44.2 ($^+SCH_2CH_2S$), 46.4 (2 C, $^+SCH_2CH_2OH$), 59.0 (2 C, $^+SCH_2CH_2OH$), and 63.2 (SCH_2CH_2OH); most of the ^1H signals were buried under the large peaks of H-2TG and TG.

EHT: ^{13}C NMR (H_2O) δ 11.3 ($CH_3CH_2S^+$), 16.9 (CH_3CH_2S), 27.9, 28.0 (2 C, CH_2SCH_2), 37.4 ($CH_3CH_2S^+$), 42.6 ($SCH_2CH_2S^+$), 45.0 ($HOCH_2CH_2S^+$), 59.0 (CH_2OH); ^1H NMR (H_2O/D_2O/TSP) δ 1.24 (t, 3 H, CH_3CH_2S, J = 7.4 Hz), 1.47 (t, 3 H, $CH_3CH_2S^+$, J = 7.4 Hz), 2.66 (q, 2 H, CH_3CH_2S, J = 7.4 Hz), 3.05 (t, 2 H, SCH_2CH_2, J = 7.4 Hz), 3.47 (q, 2 H, $CH_3CH_2S^+$, J = 7.4 Hz), 3.58 (t, 2 H, $^+SCH_2CH_2OH$, J = 5.7 Hz), 3.68 (t, 2 H, $SCH_2CH_2S^+$, J = 5.7 Hz), 4.06 (t, 2 H, CH_2OH, J = 5.7 Hz).

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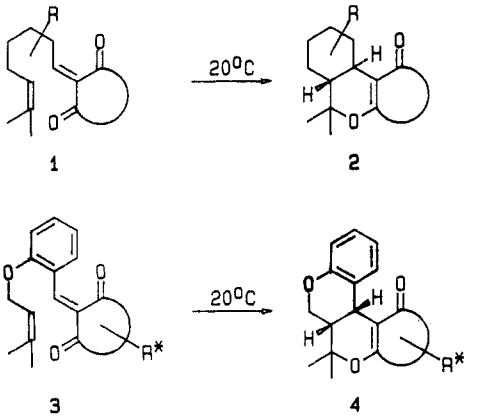
Stereospecificity in Intramolecular Hetero-Diels–Alder Reactions of 2-Benzylidene-1,3-dicarbonyl Compounds[†1]

Summary: The intramolecular hetero-Diels–Alder reaction of 2-benzylidene-1,3-dicarbonyl compounds proceeds via a concerted pathway; this has been shown by using ^{13}C-labeled dienophiles.

Sir: The intramolecular hetero-Diels–Alder reactions[2] of alkylidene- and 2-benzylidene-1,3-dicarbonyls **1** and **3**, which are easily obtainable by condensation of 1,3-dicarbonyls and aldehydes, proceed with high diastereoselectivity.[3] Thus, **1** leads exclusively to the trans-fused



dihydropyrans **2** (ni-de[4] > 98%),[5,6] whereas **3** gives the cis-fused cycloadducts **4** (ni-de > 98%).[7] In addition, chirality centers in the chain as well as in the 1,3-dicarbonyls allow a high asymmetric induction (i-de[4] > 95%).[1,5,6,8,9]

However, nothing is known so far about the degree of the concertedness[10,11] of these cycloadditions. Since the

[†] Dedicated to Professor George Büchi on the occasion of his 65th birthday.

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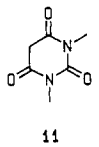
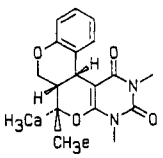
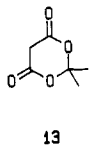
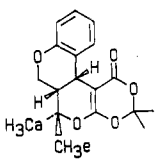
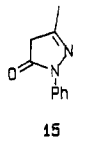
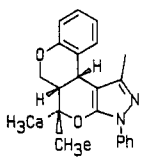
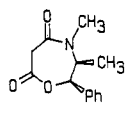
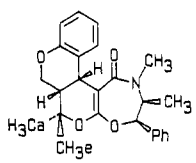
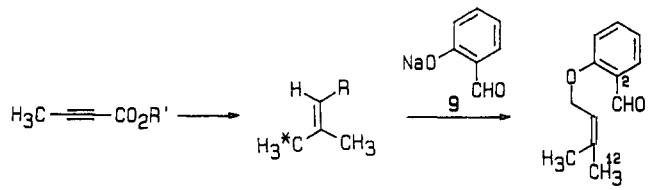
Table I. Reactions of 10 with 1,3-Dicarbonyl Compounds

entry	educts	products	% yield	condition[a] solvent	time	temp, °C	% of label in C-12 (as in 10) based on ^{1}H NMR	^{13}C NMR
	10 and						88.2	93.4
1	 11	 12	89	CH_3CN	4 h	20	88.6	91.5
2	11	12	88	CH_3CN	10 min	80	89.0	91.0
3	11	12	84	*o*-dichlorobenzene	5 min	140	88.5	91.0
4	 13	 14	81	CH_3CN	4 h	20	88.2	91.0
5	 15	 16	85	CH_3CN	16 h[b]	80	88.2	91.0
6	 17	 18	84	c, *d*			88.5	91.0

[a] For condensation reactions catalytic amounts of ethylenediammonium diacetate (EDDA) are used. [b] Condensation 30 min, 20 °C then 16 h, 80 °C. [c] Acetonitrile, EDDA, molecular sieves, 3 Å, 20 °C, 14 h, isolation of the benzylidene-1,3-dicarbonyl (*Z* configuration), 83%. [d] 1,2-Dichloroethane, diethylaluminum chloride, molecular sieves 3 Å, 80 °C, 4 h.

heterodiene is highly polarized, betains[12] or diradicals[13] may act as intermediates, resulting in a loss of the steric information of prochiral dienophiles. In this paper we describe investigations on the stereochemical course of the cycloaddition by employing the ^{13}C-labeled aldehyde **10**. The use of labeled dienophiles, which is the first example of this kind, allows us to avoid misinterpretations, which may be due to the influence of substituents at the dienophile on the stability of the transition state.



5 10

6, R = CO_2R'
7, R = CH_2OH
8, R = CH_2OMs

The aldehyde **10** was obtained by alkylation of the sodium salt of 2-hydroxybenzaldehyde (**9**) with the mesylate **8** (DMF, 5 °C, 14 h, 64%). **8** was synthesized without isolation from the allylic alcohol **7**, which could be prepared by syn addition of [^{13}C]dimethylcopper lithium to butynoic ester **5** and subsequent reduction with aluminum hydride[14] followed by treatment with methanesulfonyl chloride (CCl_4, NEt_3, −10 °C, 30 min). Quantitative analysis of the

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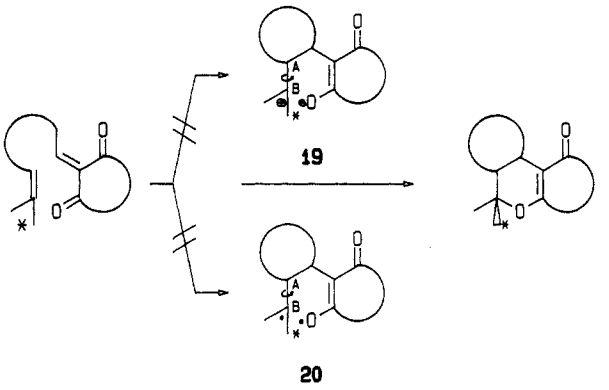
^{13}C NMR and ^{1}H NMR spectra has shown that during the synthesis of **10** some scrambling had occured. The distribution of the label was determined by integration[15] of the ^{13}C-satellites in the ^{1}H NMR spectrum for C-12 at δ 1.81 (J_{CH} = 126.5 Hz) and for C-13 at δ 1.75 (J_{CH} = 126.5 Hz) as 88.2:11.8. From the ^{13}C NMR spectrum of **10**, a ratio of 93.4:6.6 for C_{12}/C_{13} was found. The higher values determined from the ^{13}C spectra can be explained by different T_1 values of labeled and unlabeled methyl groups as pointed out by Benn.[16]

The aldehyde **10** was condensed with dimethylbarbituric acid (**11**), Meldrum's acid (**13**), the pyrazolone **15**, and the enantiomerically pure oxazepandione **17**, yielding the cycloadducts *rac*-**12**,[7a] *rac*-**14**,[7a] *rac*-**16**,[7b] and **18**[8] via the primarily formed 2-benzylidene-1,3-dicarbonyls, which were however not isolated except in the case of **17** (Table I). The percentage of the label in the equatorial methyl group at the dihydropyran ring in the cycloadducts was determined by comparison of the heights of the peaks for the equatorial and axial methyl groups in the ^{13}C NMR spectra as well as by integration of the appropriate ^{13}C-satellites in the ^{1}H NMR spectra. Generally the signals of the equatorial, predominately labeled methyl group appear at lower field in the ^{1}H and ^{13}C NMR spectra than the axial. The assignment has been confirmed by one- and two-dimensional NOE experiments of **12** and **16**. They clearly show that in **12** the β-methyl group (δ 1.60) is in close vicinity to H-6a. A NOE between the α-methyl group (δ 1.20) and H-6a could not be detected. However, in **16** the resonance of the two methyl groups is reversed, because of a different conformation of the pyranopyran system, since both methyl groups show NOE effects to H-5a. Also, a NOE is observed between H-11b and the high field methyl group at C-5, which carries the ^{13}C-label. This experiment therefore, demonstrates the cis relationship between the labeled methyl group and H-5a. There is no NOE between H-11b and the α-methyl group.

In all reactions the ratio of the labels in the two methyl groups has not been altered. Even high reaction temperatures and the use of Lewis acids[17] had no effect on the distribution of the label in the products (Table I). This shows clearly that the configuration of the dienophile is retained during the cycloaddition.

The observed stereospecificity is a characteristic of a truly concerted cycloaddition rather than an ionic or radical stepwise process. Also zwitterion **19** can be excluded as an intermediate, since the rates of the cycloadditons are similar in polar and nonpolar solvents. However, the occurrence of radical **20** is in agreement with the results if one assumes that the rotation about the single bond A-B in **20** is slow compared to the C-O bond formation.[18] Simulations[19] based on an estimated experimental error of ±0.5% in the distribution of the label in the products result in a $\Delta\Delta G^{\ddagger} \approx 3.0$ kcal/mol for the two reaction paths. By setting $\Delta G^{\ddagger} = 0$ for the C-O bond formation which would indicate a concerted mechanism, $\Delta G^{\ddagger} \approx 3.0$ kcal/mol would be found for the rotation about the C-C bond A-B in **20**. This value is higher than usually accepted for barriers to rotation of free tertiary radicals, for which a $\Delta G^{\ddagger} < 1.5$ kcal/mol was estimated.[20]



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Registry No. **7**, 91404-83-0; **8**, 107115-86-6; **9**, 90-02-8; **10**, 107115-85-5; **10-17** arylene-1,3-dicarbonyl product, 107115-87-7; **11**, 769-42-6; *rac*-**12**, 107115-88-8; **13**, 2033-24-1; *rac*-**14**, 107115-89-9; **15**, 89-25-8; *rac*-**16**, 107115-90-2; **17**, 67376-72-1; **18**, 107115-91-3; $(^{13}CH_3)_2CuLi$, 15681-48-8.

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Palladium-Catalyzed Denitro-Sulfonylation and Amination of β,γ-Epoxy Nitro Compounds

Summary: β-Alkyl-β,γ-epoxy nitro compounds undergo the weak base catalyzed conversion to γ-hydroxy-α-nitro olefins followed by isomerization of the resulting double bond and the subsequent Pd(0)-catalyzed allylic substitution of the hydroxy allylic nitro intermediates by $PhSO_2Na$ and piperidine in a single-pot to afford hydroxy sulfones and amines, respectively.

Sir: We have recently revealed a general synthetic method to prepare allylic nitro compounds by *N,N*-dimethylethylenediamine-catalyzed condensation of primary nitroalkanes with various ketones.[1] This procedure in combination with Pd(0)[2] or Lewis acid[3] mediated allylic substitution of allylic nitro compounds by nucleophiles offers a new synthetic route to take carbonyl compounds

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