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ISOMERIZATION OF CYCLOOCTATETRAENE OXIDE IN THE REACTION WITH ORGANOMETALLIC REAGENTS

POSSIBLE INVOLVEMENT OF HOMOTROPYLIUM CATION INTERMEDIATE

M. OGAWA, M. SUGISHITA, M. TAKAGI and T. MATSUDA*
Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki,
Higashi-ku, Fukuoka 812, Japan

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Abstract—The reaction of cyclooctatetraene oxide (1) with several organometallic reagents and metal salts were investigated with reference to skeletal change of the ring. LAH causes ring cleavage to yield octa-2,4,6-trienal along with the formation of cycloocta-3,5-dienol. Ethylmagnesium bromide and triethylaluminum afford ethyl(cyclohepta-2,4,6-trienyl)methanol in good yields, but the addition of HMPA in the Grignard reaction results in reduction of the reactivity and formation of the isomerized cyclic trienone. A similar medium effect by HMPA or solvent is found in the reaction of 1 with ethyllithium which affords 5-ethylcycloocta-2,6-dienone (70·2%) in ether, and also in the metal salts ($MgBr_2$, LiBr, and $LiClO_4$) induced isomerization giving cycloheptatrienylcarboxyaldehydes and phenylacetaldehyde. The diverse nature of the products in the reactions is accounted for by the formation of homotropylium cation intermediates.

INTRODUCTION

Previous studies on the reaction of cyclooctatetraene oxide (**1**; 9-oxa-bicyclo[6.1.0]octa-2,4,6-triene) seem to be featured by a facile change of its 8-membered ring structure. Ganelline and Pettit[1] described that the isomerization of **1** to phenylacetaldehyde (**2**)[2] under acidic conditions proceeded via intermediate formation of cyclohepta-2,4,6-trienylcarboxyaldehyde (**3**), which subsequently rearranged to the aromatic aldehyde. Buchi and Burgess[3] reported that in the thermal rearrangement **1** afforded a mixture of three isomeric cycloheptatrienylcarboxyaldehydes at 260°, which on further heating to 400° changed to **2**. Rhodium complex was proved to be an effective catalyst in the rearrangement of **1** to **3** at a low temperature (−50°), and on warming to room temperature **3** underwent further rearrangement to **2**.[4] The treatment of **1** with lithium diethylamide constitutes an important synthetic method for preparing cycloocta-2,4,6-trienone (**4**) without suffering from such a structural change.[5] However, one of us showed that the reaction of **1** with Grignard reagents afforded isomerized addition products, alkyl or phenyl(cyclohepta-2,4,6-trienyl)methanol, in good yields.[6] The ring contraction in the Grignard reaction seems to be in sharp contrast to the behavior of **4**, since addition of several organometallic reagents, such as EtMgBr, Et_3Al, EtLi or $LiCuEt_2$, to **4** proceeded in conventional 1,2- and 1,4-manner with retention of the 8-membered ring structure (1,4-adduct) or under subsequent cleavage to 4,6,8-decatrien-3-one (1,2-adduct).[7]

In this paper, we present the reactions of **1** with typical organometallic reagents with particular reference to the relation between the ring isomerization and the organometallic reagents, and have proposed a pathway involving homotropylium cations which can account for the formation of diverse products observed in this study.

RESULTS

Reaction of **1** *with organometallic reagents.* The reaction of **1** with 2·5 equivts of LAH in ether at 30–35° produced a yellow oil composed of cycloocta-3,5-dienol and an unsaturated aldehyde. After purifications through the bisulfite adduct and two recrystallizations, the latter proved to be octa-2,4,6-trienal, m.p. 24·0–25·5°. A similar ring cleavage of **4**[8] was found to yield an isomeric product, m.p. −2·3–−3·1°. The complexity of the NMR spectra in the olefinic proton region did not mask the geometry of the three double bonds in these isomers. Nevertheless, the ring cleavage of **1** can be considered to proceed by a similar route involving intermediate formation of cycloocta-2,4,6-trienol (1,2-reduction) as was established for the cleavage reaction of **4**.[8]

Although **4** reacted with $NaBH_4$ in a similar manner, **1** was recovered unreacted in treatment with either $NaBH_4$ in methanol or $LiAlH_2(OCH_2CH_2OCH_3)_2$ in refluxing benzene.

The reaction of **1** with ethyllithium in ether produced a mixture consisting of 5-ethyl-2,6-cyclooctadien-1-one (**5**, 70·2%), **4** (6·0%) and a trace of an unidentified component. After purification by column chromatography, the ethyl ketone absorbed two equivalents of hydrogen over Pd–$BaSO_4$. The resultant saturated ketone was different from the authentic 3-ethylcyclooctanone derived from the product in the reaction of **4** with $LiCuEt_2$.[7] The spectral data of **5** [1670 cm^{-1} ($\nu_{C=O}$) and λ_{max}; 230 nm, $\epsilon = 6700$ (*cf* 2,6-cyclooctadienone: λ_{max}; 227 nm, $\epsilon = 7200$)] supported the presence of α,β-unsaturated carbonyl moiety. The palladium chloride complex of **5** was obtained on treatment with Pd(PhCN)$_2$Cl$_2$ in benzene. Its IR spectrum did not contradict the 1,5-cyclooctadiene structure, but the limited solubility of the chloride complex in conventional solvents for NMR measurement and the facile decomposition observed on the attempted preparation of the acetate complex prevented further analysis of the structure. NMR spectra of **5** in the presence of Eu(dpm)$_3$ in three concentrations (CDCl$_3$) were explained reasonably by assuming that the Et group was located at the most remote position (C-5) from the CO group. Table 1 shows the dependence of the products on solvent and on the addition of HMPA in the reaction. In petroleum ether the proportion of the base induced isomerization (**4**, 24·4%) increased considerably with decrease in **5** (15%), and the formation of a small amount of ethyl(cyclohepta-2,4,6-trienyl)methanol (**6a**, 1·2%). Addition of one or two equivalents of HMPA to the reaction system resulted in the reduction of the reactivity as evidenced by the recovery of a considerable amount of the starting material (45·9%), and the only product isolated was **4** (17·9%).

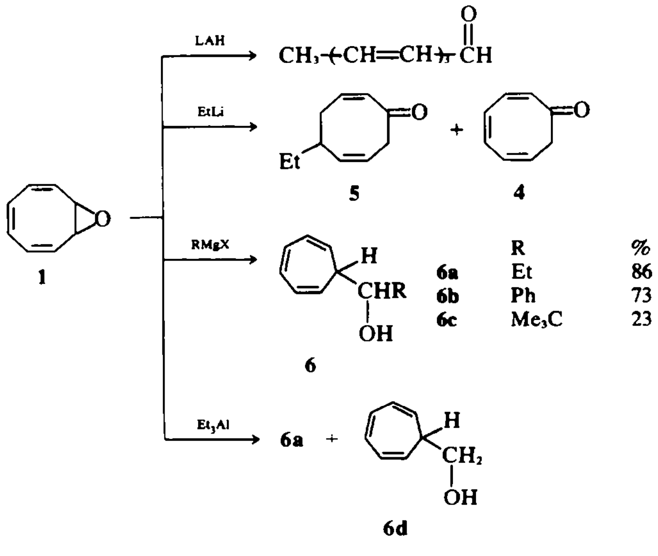
The reaction of **1** with lithium diethylcopper in ether under various conditions resulted in the formation of polymeric material, and none of the characterizable product could be isolated.

It has been found[6] that the reaction of **1** with ethyl-, phenyl-, and t-butylmagnesium bromides afford alkyl or phenyl(cyclohepta-2,4,6-trienyl)methanols (**6**) in yields of 83, 73, and 23%, respectively. A small amount of β-t-butylstyrene was accompanied by the main product (**6c**) in the reaction with t-butylmagnesium bromide. When two equivalents of HMPA was added in the reaction of **1** with ethylmagnesium bromide in ether, a considerable amount of the starting material was recovered (65·6%) and a mixture of **4** (10%) and **6a** (11%) was obtained.

The reaction of **1** with triethylaluminum in *n*-hexane proceeded with ring contraction to give **6a** (71%) and a small amount of the reduction product (**6d**, 2·5%).

Isomerization of **1** *with metal salts.* The results in the preceding section clearly show that the nature of the product in the reactions with the typical organometallic reagents is dependent on the metal and also on the reaction medium. Ring contraction of cyclic epoxide in the reaction with Grignard reagent has been accounted for by the action of magnesium halide in the reaction system.[9] Rickborn and Gerkin[10] observed the similar epoxide–carbonyl rearrangement effected by LiBr and LiClO$_4$. In order to examine the function of the metal salts which are possibly present in the current reaction systems, **1** was treated with MgBr$_2$, LiBr or LiClO$_4$ under various conditions. The reaction of **1** with an equivalent amount of MgBr$_2$ in ether resulted in the formation of a large amount of polymeric material and only the product identified was **2** (4%). In the presence of a catalytic amount of the salt an increased yield of **2** (76%) was obtained.[6] Variation of the reaction medium gave rise to a significant change in the product. Thus, in THF a mixture of **2** (10·8%) and **3*** (10·2%) was obtained with an equivalent amount of MgBr$_2$. A further increase of the latter compound (29%) was realized by using an equivalent amount of MgBr$_2$–2HMPA in refluxing benzene.

The reaction of **1** with LiBr or LiClO$_4$ was carried out by heating in benzene under reflux in the presence of HMPA in order to obtain a solution. The results listed in Table 2 indicate that in the absence of any effective nucleophile, such as Et$^-$ or Et$_2$N$^-$, the lithium salts also bring about the ring contraction to **3** or even to **2**, and their



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*After purification by column chromatography, this aldehyde (2,4-dinitrophenylhydrazone: m.p. 189–191°, dec) showed a single peak on GLC analysis. However, its NMR spectrum suggested the presence of other isomers probably due to the liability of the cycloheptatrienyl system to the double bond isomerization. The same was true for the 7-membered ring aldehyde obtained in the isomerization by LiBr or LiClO$_4$.

Table 1. Reaction of **1** with ethyllithium[a]

1 (mmol)	EtLi mmol (mol/l)[b]	HMPA (mmol)	Solvent	Time (min)	Product yield %[c]			
					5	**6a**	**4**	unknown
8	10 (0·28)	—	Et_2O	60	70·2	0	6·0	trace
8	10 (0·24)	—	Light petroleum	60	15·0	1·2	24·4	1·5
8	10 (0·24)	11	Light petroleum	90	—	—	17·9 (recover oxide 45·9%)	—
8	10 (0·24)	22	Light petroleum	60	—	—	21·0 (recover oxide 42·8%)	—

[a] All reactions were carried out under reflux.
[b] The concentration was determined by acid-titration.
[c] The yield was calculated on the basis of GLC analysis.

Table 2. Isomerization of **1** with metal salts[a]

1 (mmol)	Metal salts (mmol)	HMPA (mmol)	Solvent	Time (min)	Product yield %[b]		
					2	**3**	unknown
4	$MgBr_2$ 5	—	Et_2O	90	4·0	—	6·1
4	$MgBr_2$ 5	10	Benzene	60	0·5	29·0	3·8
4	$MgBr_2$ 5	—	THF	60	10·8	10·2	2·7
4	LiBr 5	10	Benzene	360	trace	37·9	—
4	LiBr 5	5	Benzene	360	9·2	28·3	—
4	LiI 5	10	Benzene	180	trace	10·0	—
4	$LiClO_4$ 5	10	Benzene	40	75·0	—	—

[a] All reactions were carried out under reflux.
[b] Other product was polymeric material.

ratio is dependent on the amount of HMPA and also on the anion.

Aluminum methoxide in methanol and magnesium methoxide in THF were proved ineffective to the rearrangement of **1**.

DISCUSSION

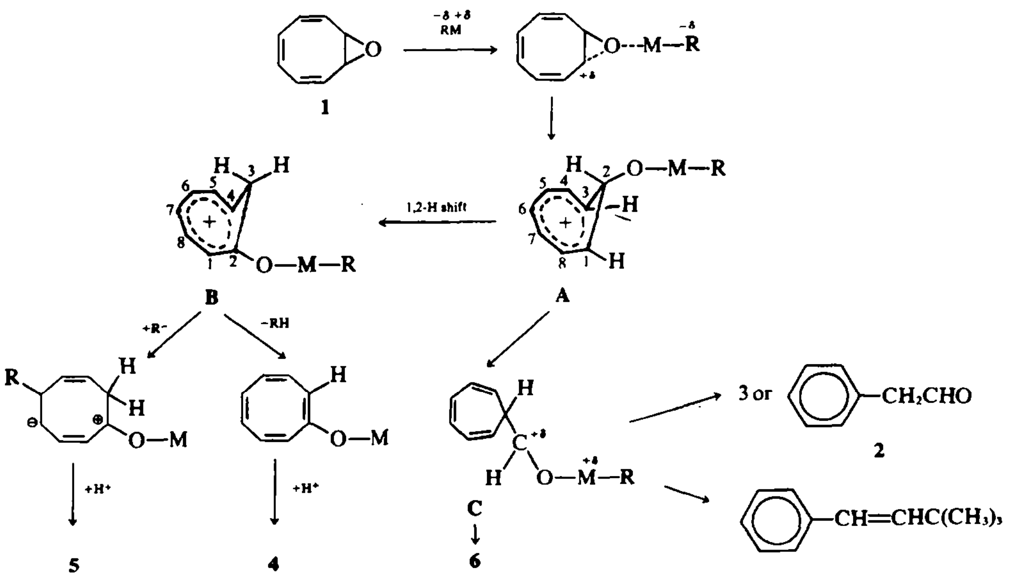
Previous papers have revealed that the addition of organometallic reagents to an α,β-unsaturated epoxide proceeded not only in 1,2- and 1,4-manner, but also are accompanied by other side reactions, such as the isomerization to a carbonyl compound.[11] The diverse nature of the products in the reactions of **1** with the organometallic reagents can be understood not only as a manifestation of such behavior of unsaturated epoxide in general, but also as due to the special structure of **1** imposed by three conjugated double bonds in a 8-membered ring. The reaction of **1** with LAH is only the case where **1** reacts in a similar manner to **4**. Although an ambiguity remains in the route yielding the different cleaved product from that of **4**, the cleavage is considered to proceed directly without forming such a cationic intermediate as discussed below, presumably because of the powerful nucleophilic activity and less "effective bulk"[12] of the reagent. On the other hand, the use of other reagents brought about the markedly different results between **1** and **4**. Nevertheless, examination of the effect of medium in the reactions with ethyllithium and ethylmagnesium bromide and also the behavior of **1** with metal salts with or without added HMPA strongly suggested that the pathways leading to 8-, 7-membered ring product or aromatic compounds are mutually related to one another and that they may involve a common intermediate playing an important role in the key steps.

Winstein *et al.*[13] reported that the treatment of **4** with super acid afforded a homotropylium cation, which collapsed slowly to protonated acetophenone. The rearrangement of **1** to **2** under acidic conditions has been explained by the formation of a cation having a cyclohepta-2,4,6-trienyl group.[1] With these facts in mind, we propose Scheme 1 to account for the present results in the reactions of **1**.

The initial step would be the coordination of electrophilic metal center of the organometallic reagents or metal cation itself of the metal salts to the epoxy oxygen. The coordination then induces the cleavage of the epoxy ring of **1** to give a carbonium ion. The 6π-electron system in the ring must contribute to stabilize the carbonium ion forming a homotropylium cation **A**. If a hydrogen at the α-carbon (C-2, located at the apex) shifts to the neighboring carbon (C-3 or C-1), another homotropylium cation **B** might result. The latter cation can be considered *a priori* more stable than the initial one, since the electron-donating oxygen at C-2 in **B** can provide an additional stabilizing effect to the homotropylium system, as was discussed by Winstein *et al.*[13] However, in the present epoxy ring cleavage promoted by an electrophilic metal moiety, the coordination of metal to the oxygen in the intermediate cations would affect considerably the stabilizing effect of the oxygen in such a manner that the more acidic the participating metal, the less effective would be the electron donation by the oxygen. In other words, the nature of the metal and the nucleophilic part of the reagent may control whether the subsequent reaction proceeds directly from **A** or through **B**. The Lewis acidity of the organometallic reagents can be arranged as follows, $R_3Al > RMgX > RLi$. Thus, in the reaction with either Grignard reagent or triethylaluminum the unstable cation **A** is thought to undergo further isomerization to the more stable cationic species (**C**) possessing the cycloheptatrienyl ring through 1,2-alkyl shift, and the following nucleophilic attack results in the formation of the alkyl or phenyl(cyclohepta-2,4,6-trienyl)methanol. Although an intermediate cationic species of the type **C** is considered to rearrange readily to an aromatic compound under acidic conditions,[14,15] there is much evidence[1a,16] supporting the expectation that a product bearing a cycloheptatrienyl group can be obtained if the reaction is carried out in the presence of a nucleophile capable of trapping the intermediate cation. Decrease of electrophilicity of the cation ($Li^+ < Mg^{++} \ll H^+$) bound to the oxygen in **C** would also function in favor of the formation of the 7-membered ring product. This idea is in line with the present results that in the absence of any effective nucleophile (with $MgBr_2$ in ether or THF) or in the case that the nucleophilic attack is suppressed by steric factors (with t-butylmagnesium bromide), the cation **C** is liable to rearrange further to give the aromatic products.

The addition of HMPA in the reaction of ethylmagnesium bromide is expected to cause a considerable change in the coordination of magnesium to the oxygen because of the stronger dative power of HMPA to the metal. The present results have shown that the decreased coordination functions in two ways, one in depressing the epoxy ring cleavage giving a considerable recovery of the starting material, and the other in allowing the rearrangement from **A** to **B** leading to the formation of **4**.

When lithium reagents with less Lewis acidity take part in the reaction, the stabilization by the oxygen could strongly assist the rearrangement to the cation **B**, which then proceeds either to the addition to form **5** or proton abstraction by a base (for example, Et_2N^-) to give **4**. In the reaction with ethyllithium the adduct **5** is always accompanied by **4**, and is replaced completely by the latter under the conditions where the nucleophilic activity of the reagent is suppressed by the presence of HMPA. Moreover, none of the products which might form by other modes of addition was detected. It is worthy to mention here that **4**, one of the reaction products from **1**, was found to react with the organometallic reagents,



Scheme 1

RMgX, R_3Al or RLi, through direct attack of the nucleophile either to carbonyl carbon (1,2-addition) or unsaturated β-carbon (1,4-addition).[7] On the other hand, it is generally accepted[9] that the reaction of an epoxy compound with these reagents proceeds via the initial opening of the epoxy ring to give an electron-deficient species and the subsequent attack of the nucleophile to the cationic center adjacent to the carbon bound to oxygen. Thus, it is hardly conceivable that the ketone **4** also reacts via the same cationic species as proposed for **1** (Scheme 1) under the present reaction conditions, though the homotropylium ion **B** is found to form from **4** under such a special condition as in super acid.

The transannular nucleophilic attack (1,6-addition) to yield **5** seems unusual. The previous studies concerning with nucleophilic attack to homotropylium cation, though beihg scanty, seems to be featured by significant stereospecificity in the position of the attachment. Huisgen *et al.*[17] has reported a high degree of stereospecificity in collapse of the 8-chlorohomotropylium cations with chloride to *trans*-7,8-dichlorocycloocta-1,3,5-triene. The Diels-Alder addition of N-phenylazodicarbonylimide to cyclooctatetraene to yield the abnormal 1,4-adduct retaining the 8-membered ring is explained in terms of a transannular attack in the initially formed homotropylium cation.[18] The addition of chlorosulfonylisocyanate to *anti*-9-methylbicyclo-[6.1.0]nonatriene or the related compounds reported by Paquett *et al.*[19] is also considered as another example of a uniquely stereocontrolled reaction due to the intermediacy of homotropylium cation (1,3-bishomotropylium ions). In this connection, it should be noted that the circumambulatory rearrangement in homotropylium cation[20] is found to be a much slower process ($\Delta F^{\neq} > 27$ kcal/mol) than that in the bicyclo[3.1.0]hex-3-enyl system ($\Delta F^{\neq} = 15$ kcal/mol). In view of these facts, the specific formation of **5** from **1** could be taken as a manifestation of the reaction pathway involving the homotropylium cation (**B**).

The reasoning based on the variation of the coordinative strength of metal can be applied to explain the results obtained in the metal salt promoted rearrangement of **1**. Thus, more acidic magnesium bromide tends to yield the most stable final product, phenylacetaldehyde (**2**), while $MgBr_2$–2HMPA affords cycloheptatrienylcarboxyaldehydes (**3**) due to the decrease in Lewis acidity on complexation with HMPA. The formation of the 7- and 6-membered ring (aromatic) aldehydes can be understood by the increased ionic character of the lithium salts and the absence of effective nucleophile (or base).

EXPERIMENTAL

Materials. Cyclooctatetraene oxide **1** was prepared by epoxydation of cyclooctatetraene with monoperphthalic acid. Triethylaluminum was a commercial product (Ethyl Corporation, N.Y.). Commercial hexamethylphosphortriamide (HMPA) was distilled prior to use. Manipulation of the soln of air- and water-sensitive reagents, triethylaluminum and ethyllithium, was done in a dry N_2 box. All reactions were carried out under N_2.

Reaction of **1** *with lithium aluminumhydride.* LAH (3·4 g, 88 mmol) in ether (80 ml) was placed in a 500 ml flask equipped with reflux condenser, thermometer and magnetic stirrer. A soln of **1** (17 g, 142 mmol) in ether (80 ml) was added to the mixture at 30–35° during 20 min under stirring and then heated under reflux for 1 hr. The mixture was cooled and hydrolysed by addition of NH_4Cl aq. The water layer was extracted with ether, and the combined ethereal soln was washed once with water, dried and concentrated. The residue was distilled to yield light yellow liquid, 10 g (58%), b.p. 75–85°/6·5 mmHg. Hydrogenation of a small portion of the product over Raney Ni afforded a mixture of n-octanol (34%) and cyclo-octanol (66%). The crude product was treated with sat $NaHSO_3$ aq. The oily residue was taken up in ether and washed with water. Distillation of the ethereal extract gave cycloocta-3,5-dienol, which was confirmed by comparison with an authentic sample obtained by LAH reduction of cycloocta-1,3-dien-5,6-epoxide. The bisulfite adduct (white needles) was hydrolysed by the treatment with 30% K_2CO_3 aq. Distillation after work-up yielded light yellow liquid, b.p. 80·0–81·0°/6·5 mmHg, which crystallized as yellow needles, m.p. 24·0–25·5° (twice recrystallizations from n-hexane); UV(EtOH): λ_{max} 318 nm, log $\epsilon = 4{\cdot}53$. IR(neat): ν_{CH}(CHO) 2720 cm^{-1}, $\nu_{C=O}$ 1675 cm^{-1}, $\nu_{C=C}$ 1615 cm^{-1}, δ_{CH}(cis) 718 cm^{-1}. 2,4-Dinitrophenylhydrazone; m.p. 188–189°, semicarbazone; m.p. 216° (dec). Hydrogenation of the product in EtOH over Raney Ni absorbed 4 molar equivts of H_2 to give n-octanol.

Reaction of **1** *with ethyllithium.* A soln of **1** (960 mg, 8 mmol) in ether (10 ml) was placed in a 200 ml flask equipped with reflux condenser, thermometer and magnetic stirrer under N_2, and cooled to 0°. A filtered ethereal EtLi (11 mmol, 0·28 M/l, 40 ml) was added to the soln, and the mixture was refluxed for 1 hr. The mixture was cooled and hydrolysed by addition of sat NH_4Cl aq. Distillation after work-up gave a faint yellow liquid, 890 mg, b.p. 70–72°/1 mmHg. The product containing a small amount of **4** (6·0%, by GLC) was purified by column chromatography (silicagel, light petroleum : ether = 9·1); UV(MeOH): λ_{max} 230 nm, $\epsilon = 6700$, *cf* cycloocta-2,6-dienone:[21] λ_{max} 227 nm, $\epsilon = 7200$; IR(neat): $\nu_{C=O}$ 1670 cm^{-1}, $\nu_{C=C}$ 1635, 1600 cm^{-1}; NMR(CCl_4): δ, 0·98(t, 3H), 1·92(q. 2H), 2·24(m, 2H), 3·06(m, 2H), 3·58(m, 1H), 5·55(m, 2H), 5·90(m, 2H). (Found: C, 79·72; H, 9·49. Calc. for $C_{10}H_{14}O$: C, 79·95; H, 9·39%). Hydrogenation of the product (262 mg) absorbed two molar equivts of H_2 (80 ml) to yield 5-ethylcyclooctanone. The treatment of **5** (100 mg) in benzene with $Pd(PhCN)_2Cl_2$ (186 mg) afforded a yellow powder, 107 mg, m.p. 163° (dec); IR(Nujol): $\nu_{C=O}$ 1710 cm^{-1}, $\nu_{C=C}$ 1510 cm^{-1}, *cf* cycloocta-1,5-dienedichloropalladium;[22] $\nu_{C=C}$ 1500 cm^{-1}. (Found: C, 36·67; H, 4·31. Calc. for $C_{10}H_{14}OPdCl_2$: C, 36·75; H, 4·49%). The chloride complex (50 mg) was added to silver acetate (55 mg) in acetone (10 ml), and the ppt (AgCl) was filtered off. On concentration the clear filtrate obtained was colored and formed a brown viscous material.

Reaction of **1** *with triethylaluminum.* A soln of **1** (2·40 g, 20 mmol) in n-hexane (20 ml) was cooled to −37° under N_2 (using the same apparatus described above). A soln of 3·4 ml (25 mmol) of triethylaluminum in n-hexane (8 ml) was added during 15 min under stirring. The mixture was allowed to warm to 30° in a period of *ca* 1 hr, and then stirred at 50° for 1 hr. The resultant mixture was cooled (0°) and hydrolysed by addition of wet ether (50 ml) and then 2 ml of water, and filtered. The ppt was washed with three 30 ml portions of ether. The combined organic layer was washed twice with water and dried. Concentration and distillation of the soln yielded a faint yellow liquid, 2·1 g, b.p. 79·0–80°/2 mmHg. The two components in the distillate were separated by preparative gas chromatography. The principal product (**6a**, 71% based on **1**) was coincided with the authentic sample obtained by the similar reaction of **1** with EtMgBr.[6] The minor constituent (**6d**) showed the following spectral data, which does not conflict with the structure of cyclohepta-2,4,6-trienyl-methanol; IR(neat): ν_{OH} 3320 cm^{-1}, $\nu_{C=C}$ 1625, 1605 cm^{-1}, δ_{CH}(C=C) 750, 715, 690 cm^{-1};

NMR(CCl_4): δ, 1·97(m, 1H), 3·21(s, 1H), 3·80(d, 2H), 5·23(m, 2H), 6·12(m, 2H), 6·55(m, 2H).

Effect of the addition of HMPA. The following general procedure was used to see the effect of HMPA on the products in the reactions of **1** with EtLi and EtMgBr. An EtMgBr soln prepared from Mg in 10 ml ether and a calculated amount (10·0 mmol) of EtLi soln (in light petroleum or diethylether) were used for the reaction. To the EtLi soln (0·24 M/l) one or two equivts of HMPA (1·97 g, 11 mmol or 3·94 g, 22 mmol, respectively) in 5 ml of solvent was added, and the mixture was refluxed under stirring for 30 min. A soln of **1** (0·96 g; 8·0 mmol) in 10 ml of solvent was added to the mixture at 5°. After stirring for 30 min, the mixture was heated under reflux with stirring for 1·5 hr and then hydrolysed. The water layer was extracted with three 20 ml portions of ether. The combined organic layer was dried, concentrated and distilled. The ratio of the components (**4**, **5** and **6a**) in the distillate was determined by gas chromatography on 3 mm × 2 m 10% Silicon SE 30 column. The results were tabulated in Table 1.

Isomerization of **1** *with metal salts.* The metal salt, LiBr, $LiClO_4$ or anhyds $MgBr_2$, 5 mmol each, was brought into soln in benzene (15 ml) with 5 mmol or 10 mmol of HMPA, or in THF (20 ml) in a 100 ml flask under N_2, respectively. A solution of **1** (480 mg, 4 mmol) in the same solvent was added to the soln at 0°, and then refluxed for 40 min. The mixture was cooled and washed twice with sat NH_4Cl aq. The water layer was extracted with three 20 ml portions of ether. The combined soln was dried and distilled. The ratio of **2** and **3** was determined by gas chromatography on 3 mm × 2 m 10% Silicon SE 30 column. The distillate, 360 mg (75%), b.p. 68–73°/9 mmHg, obtained from the treatment with $LiClO_4$–HMPA proved to be **2** by comparison with an authentic sample. Cycloheptatrienylcarboxyaldehydes were isolated from the product obtained with LiBr-2 HMPA by column chromatography (silica-gel, light petroleum ether:ether = 10:1); IR(neat): ν_{CH}(CHO) 2820, 2720 cm^{-1}, $\nu_{C=O}$ 1690 cm^{-1}, $\nu_{C=C}$ 1610 cm^{-1}. Treatment of the aldehyde with 2,4-dinitrophenylhydrazine in MeOH containing a trace of HCl gave the 2,4-dinitrophenylhydrazone, m.p. 189–191° (dec), violet-red prisms. Hydrogenation of the aldehyde (165 mg) over 5% Pd–$BaCO_3$ in MeOH absorbed 3·3 equivts of H_2. The saturated aldehyde gave cycloheptylcarboxyaldehyde 2,4-dinitrophenyl-hydrazone, yellow needles, m.p. 133–134° (133–134°).[3]

REFERENCES

[1] C. R. Ganellin and R. Pettit, *Chem. Ber.* **90**, 2951 (1957); C. R. Ganellin and R. Pettit, *J. Chem. Soc.* 576 (1958)
[2] W. Reppe, O. Schlichting, K. Klager and T. Teopel, *Liebigs Ann.* **560**, 1 (1948)
[3] G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.* **84**, 3104 (1962)
[4] R. Grigg, R. Hayes and A. Sweeney, *Chem. Commun.* 1248 (1971)
[5] A. C. Cope and B. D. Tiffany, *J. Am. Chem. Soc.* **73**, 4158 (1951)
[6] T. Matsuda and M. Sugishita, *Bull. Chem. Soc. Japan* **40**, 174 (1967)
[7] M. Ogawa, M. Takagi and T. Matsuda, *Tetrahedron* **29**, 3813 (1973)
[8] M. Kröner, *Chem. Ber.* **100**, 3172 (1967)
[9] N. G. Gaylord and E. J. Becker, *Chem. Revs.* **49**, 413 (1951)
[10] B. Rickborn and R. M. Gerkin, *J. Am. Chem. Soc.* **93**, 1693 (1971)
[11] R. J. Anderson, *Ibid.* **92**, 4978 (1970); R. Rickborn, *Ibid.* **93**, 3046 (1971)
[12] J. D. Morrison and H. S. Mosher, *Asymmetric Organic Reactions* p. 123. Prentice-Hall, Engelwood Cliffs, New Jersey (1971)
[13] M. Brookhard, M. Ogliaruso and S. Winstein, *J. Am. Chem. Soc.* **89**, 1965 (1967)
[14] A. C. Cope, N. A. Nelson and D. S. Smith, *Ibid.* **76**, 1100 (1954)
[15] W. von E. Doering and L. H. Knox, *Ibid.* **79**, 352 (1957)
[16] C. R. Ganellin and R. Pettit, *Ibid.* **79**, 1767 (1957)
[17] G. Bocke, W. Hechtl, H. Huber and R. Huisgen, *Ibid.* **89**, 3344, 3345 (1967)
[18] R. Huisgen, W. E. Konz and U. Schnegg, *Angew. Chem.* **84**, 765 (1972)
[19] L. A. Paquett, M. J. Broadhurst, Chee-man Lee and J. Clardy, *J. Am. Chem. Soc.* **94**, 630 (1972); L. A. Paquett and M. J. Broadhurst, *Ibid.* **94**, 632 (1972)
[20] J. A. Berson and J. A. Jenkins, *Ibid.* **94**, 8907 (1972)
[21] T. S. Cantrell and S. Solomon, *Ibid.* **92**, 4656 (1970)
[22] P. J. Hedra and D. B. Powell, *Spectrochimica Acta* **17**, 913 (1961)