

experiments utilized 0.25 in \times 6 ft columns containing 10% Carbowax 20M on Chromosorb G, DMCS treated.

Bicyclo[3.1.0]hexane (I) was prepared by the Simmons-Smith reaction on cyclopentene.¹²

trans-1,2-Dibromocyclohexane (II) was prepared by the method of Snyder and Brooks.¹³

1-Bromocyclohexene.—The method of Stevens and Valicenti was used to prepare this compound from 2,3-dibromocyclohexene.¹⁴

1,1-Dibromocyclohexane.—1-Bromocyclohexene (2.0 g) was dissolved in 40 ml of anhydrous ether in a round-bottomed flask equipped with a Dry Ice condenser and a gas-inlet tube. The flask was immersed in an ice bath, 0.1 g of FeCl₃ was added, and anhydrous hydrogen bromide was bubbled into the solution for 2 hr. The reaction mixture was washed with four 25-ml portions of water and one 25-ml portion of 10% sodium carbonate, and dried over anhydrous sodium carbonate. 1,1-Dibromocyclohexane (2.1 g) was isolated by distillation [bp 72–81° (7 mm)].¹⁵

cis-1,2-Dibromocyclohexane.—1-Bromocyclohexene (2.5 g) in 250 ml of pentane was irradiated for 1 hr in a Hanovia ultraviolet apparatus, as anhydrous hydrogen bromide was bubbled through the solution. The excess HBr was removed by washing with

water and 10% sodium carbonate, and the dried pentane solution was distilled to give 1.7 g of pure *cis*-1,2-dibromocyclohexane [bp 104–105° (9 mm)].¹⁵

3-Bromocyclohexene was prepared from cyclohexene and N-bromosuccinimide.

1,3-Dibromocyclohexanes (trans, IV; cis, V).—3-Bromocyclohexene (1.6 g) was placed in a flask containing 6 ml of 48% aqueous hydrobromic acid. The flask was stoppered, heated to 65°, and allowed to stir for 7 hr. From the organic phase, the *cis*- and *trans*-1,3-dibromocyclohexanes were obtained by preparative gas chromatography. Their nmr spectra agreed with those of Franzus and Hudson.⁷

A mixture of *cis*-1,3-, *trans*-1,3-, *cis*-1,4-, and *trans*-1,4-dibromocyclohexane was prepared from the reaction of cyclohexane-1,3-diol with PBr₃ following the method of Franzus and Hudson.⁷

Reaction of Bromine with Bicyclo[3.1.0]hexane.—The brominations were performed in a dark room under red light; the flasks were covered with aluminum foil. Bicyclo[3.1.0]hexane (1.0 g) in 10 ml of chloroform (Baker analyzed reagent grade) and bromine (0.5 g) in 10 ml of chloroform were cooled in separate flasks to –50°. The bromine solution was added slowly to the cyclopropane compounds, and the reaction mixture was then allowed to stand at –30° for about 5 min. The solvent was removed under aspirator pressure below 0°, and the residue was analyzed directly by gas chromatography. The nmr spectrum of the immediate reaction mixture did not change with time.

Registry No.—Bromine, 7726-95-6; I, 285-58-5.

Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. VI. Mediation of Alcohols in the Reduction Rearrangement of Hexamethylcyclohexadienones^{1a}

L. H. KLEMM AND D. R. TAYLOR^{1b}

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Received March 4, 1970

At 320° on alumina 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone (1) in a solvent of methanol, 1-propanol, 2-propanol, or benzene is converted into hexamethylbenzene as the main identified product (24–88 mol %). 2,3,4,4,5,6-Hexamethyl-2,5-cyclohexadienone (in methanol) gives quantitative conversion into hexamethylbenzene under the same conditions. Mechanisms of the reactions are interpreted in terms of surface processes of Meerwein-Ponndorf-Verley reduction and subsequent dienol-benzene rearrangement. Partial demethylation of 1 on the catalyst accounts directly for the formation of by-products (pentamethylbenzene and pentamethylphenol) and indirectly for the occurrence of the main reaction in benzene.

Recently, Ramana and Pillai² reported catalysis by sodium-containing alumina of hydrogen-transfer reactions between alcohols (of three or more carbon atoms) and carbonyl compounds in a manner formally similar to the Meerwein-Ponndorf-Verley (MPV) reduction and the Oppenauer oxidation. Studies in our laboratory^{3–5} with the naphthalene ring system have also shown that methanol plus alumina serve for conversions such as (1) 1-tetralone into 1,2-dihydronaphthalene and (2) 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene and 2-oxo-1,1-dimethyl-1,2-dihydronaphthalene into 1,2-dimethylnaphthalene. It was proposed that reactions 1 and 2 (as well as conversions of naphthols to di- and polymethylnaphthalenes) proceed through a step of the MPV type, whereby hydride transfer occurs from a surface methoxide group to the carbonyl carbon atom

to produce a chemisorbed hydronaphthoxide, plus formaldehyde (or other oxidation products).^{3–6} In case 1, the transformation is completed by loss of a proton and an oxide ion from the hydronaphthoxide to the alumina surface. In case 2, an attendant process of methyl migration (neopentyl-type rearrangement) is involved.

In further study of reduction-rearrangement such as occurs in case 2 we now report reactions of 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone (1)⁷ and its cross-conjugated isomer 2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (2)⁸ with excess alcohol when passed through a bed of Houdry hard alumina (designated catalyst C,⁹ containing ~0.4% sodium ion) at 320 and 420°. For 1 at 320° (experiments 1, 3, 4) the major product was hexamethylbenzene (4), irrespective of whether methanol, 1-propanol, or 2-propanol was used as the alcohol (see Table I). This result is consistent

(1) (a) This investigation was supported by Research Grant No. CA-5969 from the National Cancer Institute, U. S. Public Health Service. For part V, see ref 5. (b) Research Assistant, 1964–1967.

(2) D. V. Ramana and C. N. Pillai, *Can. J. Chem.*, **47**, 3705 (1969).

(3) J. Shabtai, L. H. Klemm, and D. R. Taylor, *J. Org. Chem.*, **33**, 1489 (1968).

(4) L. H. Klemm, J. Shabtai, and C. E. Klopfenstein, *ibid.*, **35**, 1069 (1970).

(5) J. Shabtai, L. H. Klemm, and D. R. Taylor, *ibid.*, **35**, 1075 (1970).

(6) (a) L. H. Klemm, J. Shabtai, and D. R. Taylor, *ibid.*, **33**, 1480 (1968); (b) *ibid.*, **33**, 1494 (1968).

(7) H. Hart, P. M. Collins, and A. J. Waring, *J. Amer. Chem. Soc.*, **88**, 1005 (1966).

(8) H. Hart and D. W. Swatton, *ibid.*, **89**, 1874 (1967).

(9) This designation for the Houdry alumina catalyst was used in previous papers in this series.^{3–6}

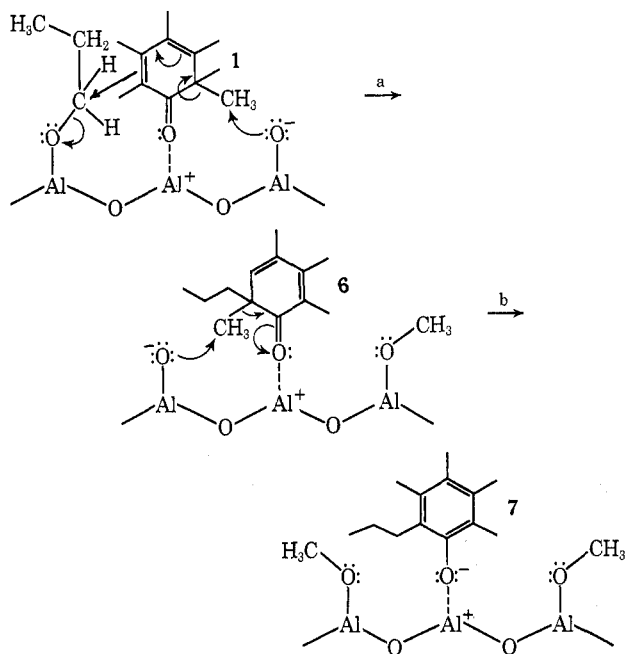
TABLE I
 ALUMINA-CATALYZED REACTIONS OF HEXAMETHYLCYCLOHEXADIENONES WITH ALCOHOLS^a

Expt no.	Substrate	Reaction temp, °C	Alcohol used	Conversion, ^c %	Product selectivity, ^d %			Unidentified ^e
					Pentamethylbenzene (3)	Hexamethylbenzene (4)	Pentamethylphenol (5)	
1	1	320	MeOH	100	1.5	87.7	4.0	(8.7)
2	1	420	MeOH	100	4.0	85.5	5.8	(7.1)
3	1	320	<i>n</i> -PrOH	95	0.7	24.2	4.4	(53.3) ^f
4	1	320	<i>i</i> -PrOH	97	2.1	57.0	1.2	(14.4)
5	1	320	None ^b	94	3.6	44.1	16.0	(10.4)
6	2	320	MeOH	100	Trace	100		Trace
7	2	420	MeOH	89	Trace	67		Trace ^g

^a See Experimental Section for reaction conditions. ^b Benzene was used in place of an alcohol. ^c Conversion = 100 × mol of substrate converted/mol of substrate charged. ^d Product selectivity = 100 × mol of specific product formed/mol of substrate converted. ^e Percentage by weight of total product based on gas chromatography and the assumption of an equal factor of instrumental response/gram for each component. ^f This portion contains at least 19 components of longer retention time than 4. Spectral investigation of the mixture showed the presence of both phenolic and C_{Ar} C₃H₇ groups. ^g Acetone-insoluble products were also formed.

with the intervention of a step of the MPV type. However, the yield of 4 was higher with methanol than with 1- or 2-propanol (a favorite hydride donor in MPV reactions in solution).¹⁰ The low yield of 4 with 1-propanol (experiment 3) results from alkyl exchange between 1 and surface 1-propoxide, as evidenced by the complex mixture of products formed and the presence of C_{Ar} C₃H₇ groups therein (cf. footnote *f*, Table I). A mechanism for alkyl exchange to give an adsorbed ketone (6) or an adsorbed pentaalkylphenoxide ion (7) is depicted in Scheme I, where step a is shown as a con-

SCHEME I



certed process which involves reaction at both C-2 and C-6. Formation of 6 by a two-step process, of demethylation at C-6 to give adsorbed pentamethylphenoxide (5a) and then propylation at C-2 or C-6, is also possible. 2-Propoxide, on the other hand (experiment 4), functions as a hydride donor without effecting alkyl exchange. Probably, steric hindrance to isopropylation at a ring carbon atom already bearing a methyl substituent is too great to permit formation of

the corresponding requisite pentamethylisopropylcyclohexadienone intermediate under reaction conditions.¹¹

On the basis of the proposed surface MPV and alkyl-exchange mechanisms one might predict that 1 would be inert in the presence of a tertiary alcohol as solvent. Since tertiary alcohols dehydrate very readily under the reaction conditions used, however, this experiment was not attempted. Instead, a solution of 1 in benzene alone (believed to be inert) was passed through the reactor (experiment 5) under otherwise identical conditions.¹² Even in this absence of an attendant hydride donor, however, 1 was converted into 4 in significant yield. Accompanying the formation of 4 was a somewhat larger yield of the by-product pentamethylbenzene (3) and a markedly higher yield of the by-product pentamethylphenol (5) than occurred in experiments 1, 3, and 4. Both by-products result from monodemethylation of the substrate, as indicated in Scheme II, step a. The resultant adsorbed pentamethylphenoxide ion (5a) could abstract a proton from the catalyst surface (step d) to give 5.

Surface methoxide formed by demethylation of 1 is available for further reductive processes. Thus, it can transfer hydride to other molecules of adsorbed 1 in the MPV manner (Scheme II, step b) with the ultimate formation (step c) of 4 plus formaldehyde (as well as its oxidation products formate and/or carbon monoxide).¹³ Additionally, surface methoxide (or other alkoxide bearing an α -hydrogen atom) may cause reduction of ion 5a to 3, as indicated in Scheme III. Here it is suggested that a surface hydroxide group first transfers a proton to the ambident ion 5a (step a) to give the adsorbed tautomer of pentamethylphenol (5b). Reduction of 5b to adsorbed alkoxide 9 is again depicted as involving a surface MPV reaction (step b). Loss of a proton plus an oxide ion from 9 to the catalyst surface (step c) would then yield pentamethylbenzene (3).

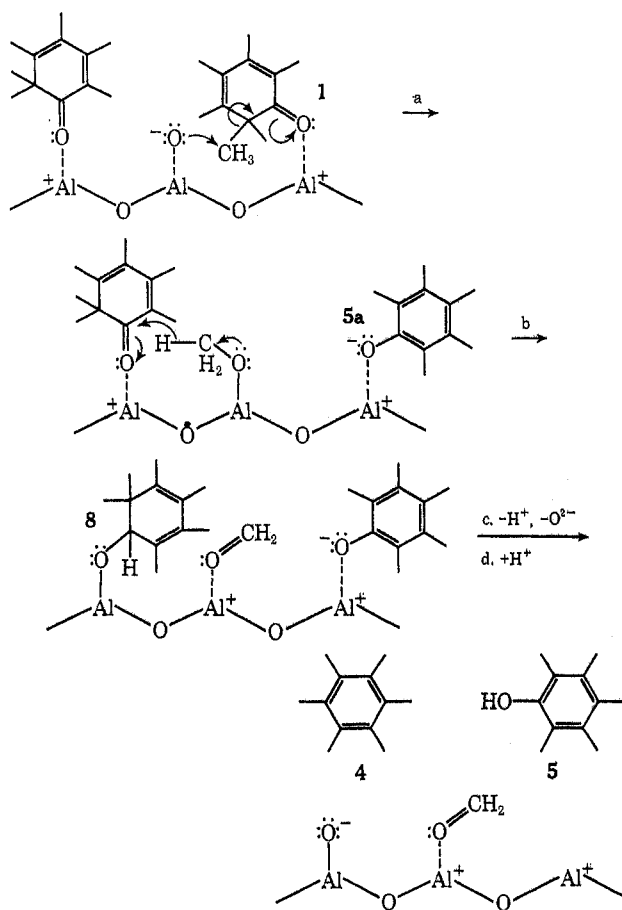
(11) Indirect evidence from this laboratory indicates that phenol will dialkylate at C-2 with 1-propanol but will only monoalkylate at C-2 with 2-propanol: L. H. Klemm and D. R. Taylor, unpublished results.

(12) It should be noted that apparent activity of the catalyst may vary depending on the solvent used, since the catalytic surface will be in a steady-state condition (involving adsorbed substrates) during the reaction proper. It is presumed that benzene will not be dissociatively chemisorbed (as has been postulated in the case of alcohols).^{5,6}

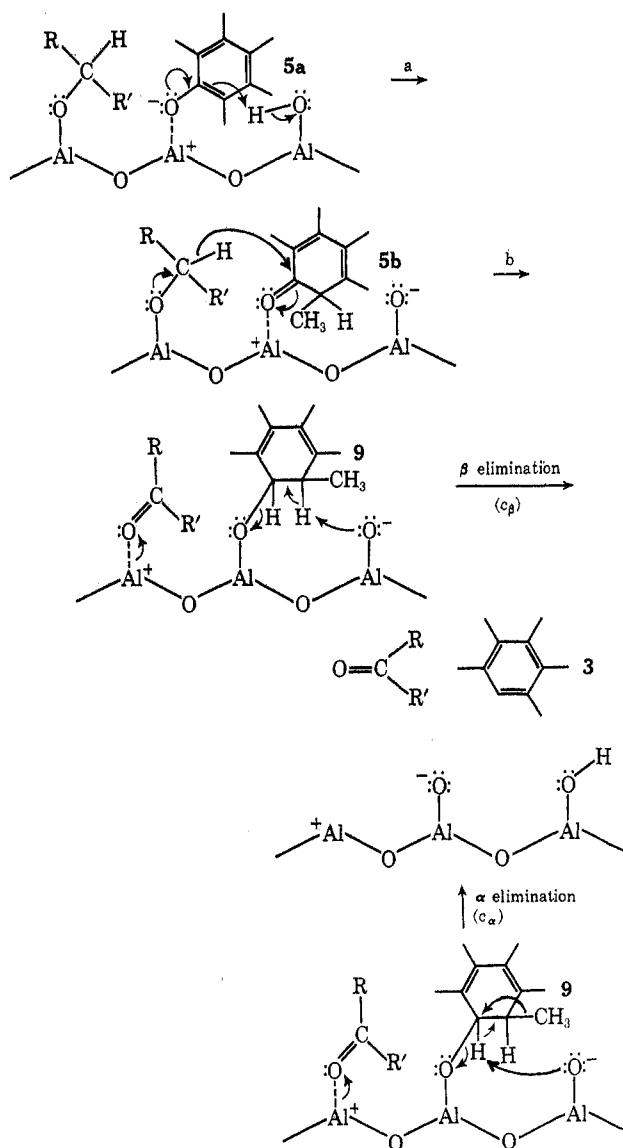
(13) A material balance for formation of 3, 4, and 5 from 1 (in experiment 5) shows that more oxygen atoms are released than could be converted into water and carbon monoxide by the methyl groups released. Although an experimental determination of the fate of the "excess oxygen" has not been made, it seems plausible that it may be present in carbon dioxide or in the unidentified products.

(10) A. L. Wilds, *Org. React.*, **2**, 178 (1944). H. Plieninger and G. Keilich [*Chem. Ber.*, **91**, 1891 (1958)] found that cyclohexadienones were readily converted into cyclohexadienols in this manner.

SCHEME II



SCHEME III



Step c in Scheme III may be envisioned as occurring by α , β , or γ elimination. β elimination has been suggested previously⁵ in the methanol-alumina conversion of 1-tetralone to 1,2-dihydronaphthalene. It is particularly attractive here because it has an overall simplicity as a concerted process, it involves the formation of a pseudocyclic eight-membered transition state (expected to be preferred on an alumina surface),⁵ and it should be facilitated by *cis* geometry in **9** (which would allow *trans* elimination). If, as seems reasonable, steps a and b in Scheme III involve attack of H⁺ and H⁻, respectively, from the catalyst surface onto flatwise adsorbed substrate, **9** would, indeed, be the *cis* isomer. γ elimination (not shown in Scheme III) has been proposed previously⁴ for conversion of adsorbed 2,2-dimethyl-1,2-dihydro-1-arenoxides to 1,2-dimethylarenes (cf. **8** \rightarrow **4**, Scheme II, step c). Neither β nor γ elimination would be expected to give methyl migration in the conversion of **9** to **3**. On the other hand, α elimination (whether concerted or not) could result in methyl migration, as shown in Scheme III, step c _{α} .

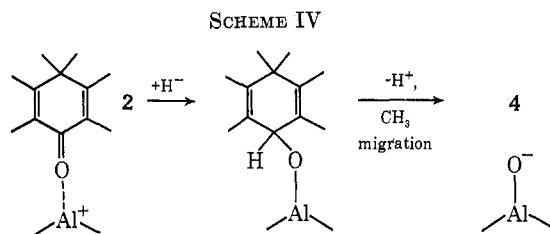
Experiments reported here do not allow an evaluation of the relative extents of α , β , and γ elimination in the pentamethylphenol system. However, the presence of 19% of the 1 isomer in the monomethylnaphthalene fraction from reaction of 1-naphthol with methanol at 350° over Houdry alumina^{6a} is consistent with the occurrence of some α elimination under closely similar conditions. In the same series of experiments,^{6a} the composition of this fraction attained 47% of 1-methylnaphthalene for a more acidic alumina and a reaction temperature of 420°. On the other hand,

only small amounts (<10%) of 2 isomer were found in the monomethylnaphthalene fraction from reaction of 2-naphthol with methanol in the presence of alumina catalysts of various acidities⁴ at temperatures up to 420°. A reduction-elimination mechanism of the type shown in Scheme III is also suggested for the direct deoxygenation (*via* an adsorbed keto form) of 1- and 2-naphthols to naphthalene.^{6a}

Reaction of 2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (**2**) with methanol in the presence of catalyst C at 320° (experiment 6) gave quantitative formation of hexamethylbenzene (**4**). Failure to detect any pentamethylphenol or more than a trace of pentamethylbenzene in the total product implies that neither demethylation of **2** to adsorbed pentamethylphenoxide ion nor rearrangement (*e.g.*, by concerted demethylation at C-4 and methylation at C-2) of **2** to **1** occurs as an intermediate process.¹⁴ Moreover, methylation at C-2 without attendant demethylation at C-4 seems highly unlikely. In fact, a concerted intramolecular migration of the methyl group from C-4 to C-1 in a surface

(14) In fact R. F. Childs, *J. Chem. Soc. D*, 946 (1969), found that **1** rearranges to **2** under strongly acidic conditions.

dienol-benzene rearrangement¹⁵ may be implicated (Scheme IV).



Increasing the reaction temperature from 320 to 420° for 1 in the presence of methanol gave little change in the yield of 4 but did increase the extent of demethylation (experiments 1 and 2). On the other hand, a similar change in reaction temperature for 2 (experiments 6 and 7) produced a much lower yield of 4, without accompanying appearance of demethylation products 3 and 5. Since unidentified chromatographic peaks were not observed in the regular range, it is presumed that 2 undergoes extensive decomposition at the higher temperature.

It is noteworthy that cases of demethylation have been found in hydroaromatic ketones of the naphthalene series, as well as in the presently reported benzene series. Thus, 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene (analogous to 1) underwent limited conversion to 2-methylnaphthalene at 350–420° in the presence of alumina-methanol, while the isomeric compound 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene (analogous to 2) gave no monomethylated products under similar conditions. At 275° reduction-rearrangement occurred with 1,1-dimethyl-2-oxo-1,2-dihydronaphthalene without attendant demethylation.⁴ Investigation of this compound at higher temperatures was not made. With catalyst C⁹ and methanol at 325–420°, monomethylated compounds constituted 52–82 mol % of the total identi-

fied product from 2,2-dimethyl-1-tetralone.⁵ With more acidic alumina (catalyst A), however, monomethylated products were less prevalent (3–6 mol %), probably because of a much more facile rearrangement on this catalyst. Catalyst A, likewise, gave 4–7 mol % monodemethylated product (presumed to be 1,3,6-trimethylnaphthalene) from 2,2,4,7-tetramethyl-1-tetralone.⁵ It is thus apparent that (at least for the second methyl group) the methylation-demethylation process is reversible at C-2 in the temperature range of 320–420° for the 1-naphthol, the 1-tetralone, and the phenol systems, but it is not reversible at C-4 under these conditions. It is suggested that the general mechanism shown in step a, Scheme II (and its reverse), applies to these cases. For the 1-oxo-2,2-dimethyl-1,2-dihydro systems involved, demethylation and MPV reduction (plus skeletal rearrangement) are competing reactions. Demethylation is fostered by using basic alumina catalysts and low (or zero) ratios of methanol to substrate in the influent.

Experimental Section

The apparatus and procedure were similar to those reported earlier.⁶ In each experiment a solution of 1 g of substrate (1⁷ or 2⁸) in the appropriate alcohol [molar ratio, alcohol:substrate (40:1)] or (for experiment 5 only) in benzene (15 ml) was added at a rate of 15 drops/min in a stream of dry nitrogen gas (41 ml/min) to a vertically mounted, externally heated 53 cm × 2.7 cm (o.d.) Pyrex reactor tube, packed to a height of 28 cm with 45 g of fresh Houdry HA-100 alumina (cylindrically extruded 0.125-in. pellets, containing ~0.4% sodium ion, pre-activated *in situ* by passing 25 ml of solvent and a slow stream of nitrogen through the reactor at the reaction temperature). After completion of the reaction proper the catalyst was flushed (hot) with 25 ml of solvent, allowed to cool, and extracted with boiling acetone. Combined effluents and washings were evaporated to remove solvents and extracted with ether. The ether extract was washed with water, dried, and evaporated. The residue was analyzed by gas chromatography (by comparison with authentic samples) using columns of 10% DC-550 silicone fluid on Chromosorb W (8 ft × 0.375 in. at 160–200°) and of Bentone 34-silicone on Chromosorb (to separate hexamethylbenzene and 1, not resolved on the former column).

Registry No.—1, 3854-96-4; 2, 14790-04-6.

(15) H. Plieninger and G. Keilich, *Angew. Chem.*, **68**, 618 (1956). For mechanistic characteristics of this reaction in the 2-allyl-2-methyl-2,4-cyclohexadien-1-ol and 4-allyl-4-methyl-2,5-cyclohexadien-1-ol systems, see H. J. Hansen, B. Sutter, and H. Schmid, *Helv. Chim. Acta*, **51**, 828 (1968).