

14. 1,4-Dimethylcyclohex-3-enyl Methyl Ketone

by **Wolfgang Kreiser** and **Winfried Haumesser**

Institut für Organische Chemie, Technische Universität, Braunschweig, W. Germany

and **Alan F. Thomas**

Firmenich SA, Research Laboratory, Geneva, Switzerland

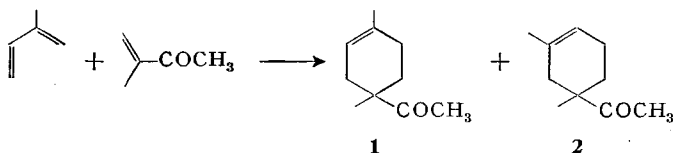
(19. XII. 73)

Summary. An improved one-step synthesis of the title compound is described, the optical activity of the natural product is confirmed, and the NMR. spectral behaviour is explained.

Recently, one of us reported [1] the isolation of 1,4-dimethyl-cyclohex-3-enyl methyl ketone (**1**) from the fruit of *Juniperus communis* L., mentioning at the same time a curious effect in the NMR. spectrum of the synthetic product, as revealed by the shift agent, Eu(fod)₃.

It was felt that this effect might be caused by the presence in the synthetic material of another isomer, e.g. 1,3-dimethylcyclohex-3-enyl methyl ketone (**2**) from which the 1,4-isomer was very difficult to separate. Indeed, the reaction between isoprene and but-3-en-2-one is known to give a 7:3 mixture of the 1,4- and 1,3-isomers of methylcyclohex-3-enyl methyl ketone [2].

We now describe a one-step synthesis of 1,4-dimethylcyclohex-3-enyl methyl ketone (**1**) using a *Lewis* acid-catalyzed *Diels-Alder* reaction, and show that the natural product is identical with this material, but not with the isomeric impurity that we have found to be present in the former synthetic material [1]. Use of a *Lewis* acid (generally aluminium chloride [3] or stannic chloride [4]) to catalyze *Diels-Alder* reactions is well-known, and the fact that such catalysts change the ratio of 1,4 to 1,3 substitution in favour of the former is also well documented [5], although experimental verification in the case we present here has not, to our knowledge, been provided. A theoretical study by *Trong Anh* [6] has now shown how both the 'thermal'



and the 'catalyzed' *Diels-Alder* reactions can be explained by the same perturbational treatment, and that the earlier supposition that the bulk of the substituent groups was responsible for the proportion of the isomers [2] [7] is erroneous [6].

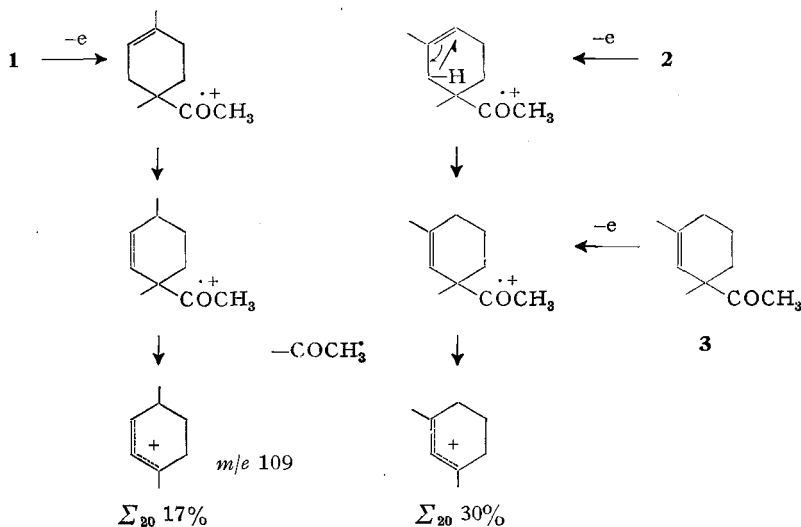
Heating isoprene and isopropenyl methyl ketone in an autoclave for 48 h at 140° results in a mixture that we believed to be a mixture of **1** and **2** on the basis of the NMR. spectrum, and from which we were able to separate a sample of 'pure' **1** in 32% overall yield by slow distillation at reflux ratio 15:1 (bp. 208–212°). The isomer (**2**) could also be equilibrated with **1** by thermal treatment. Although the ketone **1** ap-

peared to be pure gas chromatographically as obtained by this thermal treatment (as did the original synthetic material [1]), running the NMR. spectrum on an extended scale revealed that the signal of the C(1) methyl group at 1.10 ppm¹) was a 'doublet' with about 0.7 Hz between the two maxima. Addition of Eu(fod)₃ to the CDCl₃ solution of the ketone **1** increased the difference between these two maxima, and also caused doubling of the other signals in the spectrum. When the solution containing the shift agent was heated to 60°, all the 'doublets' disappeared except the 0.7 Hz difference associated with the C(1) methyl group. This implies that the disappearance of the second signals is due to thermal destruction of the complex between the shift agent and two different ketones.

From this, and the fact that the semicarbazone of pure **1** (see below) showed no splitting in its NMR. spectrum, it becomes clear that the thermal *Diels-Alder* product **1** actually must be a mixture.

Further support for these results was provided by examination of the mass spectra of the two ketones. Using a capillary column (UCON, 40 m)²) programmed from 50° to 160° at 2°/min, it was possible to resolve the peak corresponding to the 'pure' ketone into two components. Coupling a similar column with a mass spectrometer, and measuring the mass spectra during the elution of these substances enabled mass spectra of the two ketones, now presumed to be **1** and **2**, to be measured. These turned out to be very different, in particular as concerns the percentage of the total ionization above *m/e* 30 (Σ_{30}) for which the fragment at *m/e* 109 (*M*-COCH₃) is responsible. Loss of an acetyl radical will be most favourable after a shift of the double bond. This is known to occur with ease in the mass spectrometer, but it is reasonable to suppose that it would occur more readily in the case of the 1,3-isomer (**2**), where the resulting

Scheme



¹) NMR. spectra were measured in CDCl₃ with Me₄Si as internal standard at 0 ppm.

²) Supplied by H. & G. Jaeggi, Laboratorium für Gas-Chromatographie, 9043 Trogen, Switzerland.

double bond is still trisubstituted, than in the case of the 1,4-isomer. Moreover, the ion resulting from loss of acetyl from **2** will be more stable than the ion arising from loss of acetyl from **1** (see *scheme*). It was found that the compound with slightly shorter retention time on UCON had $\Sigma_{30} = 30$, the longer retention time corresponding to a compound having $\Sigma_{30} = 18$, and it is therefore concluded that the mass spectrum of the latter (Fig. 1) corresponds to the 1,4-isomer, that of the former (Fig. 2) corresponding to the 1,3-isomer **2**. Examination of the natural products on the same UCON column yielded a single peak, and mass spectra taken at different points throughout this peak corresponded only to that of the substance presumed to be the 1,4-isomer **1**, the major product of the thermal *Diels-Alder* reaction.

As expected, the mass spectrum of 1,3-dimethylcyclohex-2-enyl methyl ketone (**3**)³ had an even high percentage of the total ionization ($\Sigma_{30} = 38$) for the fragment at m/e 109.

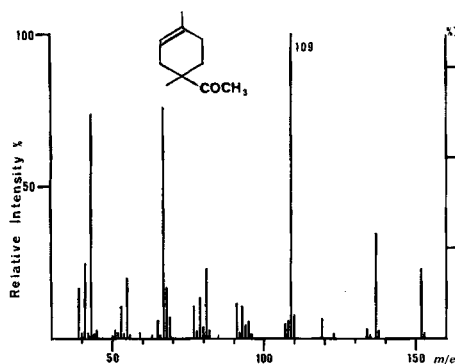


Fig. 1. Mass spectrum of 1,4-Dimethylcyclohex-3-enyl Methyl Ketone

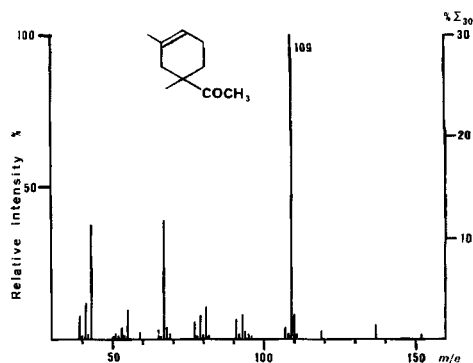


Fig. 2. Mass spectrum of 1,3-Dimethylcyclohex-3-enyl Methyl Ketone

When isoprene was allowed to react with isopropenyl methyl ketone in benzene in the presence of stannic chloride at 0° for 13/4 h, a 70% yield of a single substance, presumably **1**, was obtained. This was easily purified by bulb distillation, and contained less than 4% of another isomer. Material prepared in this way yielded a semicarbazone, mp. 150–153° (lit., recorded on mixture of **1** and **2** semicarbazones, mp. 146–148° [1]) and a 2,4-dinitrophenylhydrazone m.p. 128–130°. The ketone was readily resolved through its menthylhydrazone [8] (less soluble isomer, m.p. 157–159°, $[\alpha]_{578}^{25} = -58.0^\circ$, $[\alpha]_{546}^{25} = -66.4^\circ$, $[\alpha]_{436}^{25} = -113^\circ$, $[\alpha]_{405}^{25} = -135^\circ$, $[\alpha]_{364}^{25} = -178^\circ$ (21.1 mg/2ml dioxan), decomposed to the ketone having $[\alpha]_{578}^{25} = -1.58^\circ$, $[\alpha]_{546}^{25} = -1.84^\circ$, $[\alpha]_{436}^{25} = -2.79^\circ$, $[\alpha]_{405}^{25} = -3.17^\circ$, $[\alpha]_{364}^{25} = -3.56^\circ$ (63.0 mg/2 ml dioxan)), and thus corresponded to the optical activity of the compound isolated from *J. communis* [1].

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³) The synthesis of ketone **3** will be described elsewhere by the Braunschweig authors.

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15. Metall- π -Komplexe des 2,5-Diphenyl-1-silacyclopentadiens

von Walter Fink

Monsanto Research S.A., Eggbühlstrasse 36, 8050 Zürich

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Summary. The preparation of 2,5-diphenyl-1-silacyclopentadienes and their reaction with iron carbonyls and π -cyclopentadienyl-dicarbonylcobalt yielding metal- π -silole complexes is described. Mass spectral data indicate the existence of an 'aromatic' silacyclopentadienyl species.

Tetraphenylsilole¹⁾ sind gegenüber Metallcarbonylen sehr reaktionsträge. Erst unter energiereichen Bedingungen (180–200°) setzen sie sich mit Fe(CO)₅ zu Tricarbonyl(2,3,4,5-tetraphenylsilol)eisen Komplexen um [1]; mit anderen Metallcarbonylen reagiert dieses Ringsystem nicht [2]. Reaktiver und daher geeigneter als diolefinische, cyclische Liganden in Metall- π -Komplexen sind 2,5-Diphenylsilole. Darüber wird nachfolgend berichtet.

Zur Darstellung von 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadien (**1a**) (durch Bromierung von 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentanol mit N-Bromsuccinimid zu *trans*-2,5-Dibrom-1,1-dimethyl-2,5-diphenyl-1-silacyclopentanol und dessen Dehydrobromierung mit Kaliumacetat) wurde die bekannte Vorschrift [3] modifiziert; sie ist für grössere Ansätze ungeeignet²⁾. 1-Methyl-1,2,5-triphenyl-1-silacyclopenta-

¹⁾ Für das Ringsystem der Silacyclopentadiene wird in der Literatur häufig die Bezeichnung «Silol» verwendet (vgl. [3]).

²⁾ Bei Ansätzen von über 0,2 Mol (bezogen auf Silacyclopentanol) liefert die Bromierung durch Zutropfen des Silacyclopentanol zu einer siedenden Suspension von N-Bromsuccinimid in CCl₄ nur eine geringe Ausbeute (<10%) an *trans*-2,5-Dibrom-1,1-dimethyl-2,5-diphenyl-1-silacyclopentanol. Es überwiegt die Reaktion zu 2,3,5-Tribrom-1,1-dimethyl-2,5-diphenyl-1-silacyclopentanol [Smp. 143°, aus Cyclohexan. NMR. (CCl₄)³⁾: δ = 0,11 (s, 3H, Si-CH₃); 0,26 (s, 3H, Si-CH₃); 2,9–3,8 (m, 2H, -CH₂); 5,1–5,35 (m, 1H, -CH); 7,1–7,5 (m, 10H, -C₆H₅). C₁₈H₁₉Br₃Si (503,2) Ber. C 42,97 H 3,81 Br 47,64% Gef. 42,81 H 3,81 Br 47,74%]

und 2,3,4,5-Tetrabrom-1,1-dimethyl-2,5-diphenyl-1-silacyclopentanol, deren Dehydrobromierung nicht zu **1a** führt.

³⁾ In den ¹H-NMR. Spectren (60 MHz) sind die Daten wie folgt angegeben: δ = chem. Verschiebung in ppm (Multiplizität, Anzahl der Protonen, Zuordnung). Die δ -Werte sind auf Tetramethylsilan (δ = 0) bezogen.