The stirrer was started, and a 4–5% mixture of ozone in dry oxygen (generated in a Welsbach Corp. ozonator, Style T-23, with the voltage set at 120 and the oxygen pressure at 8 p.s.i.) was passed in through the gas inlet tube at a rate of about 500 cc./min. The yellow precipitate dissolved completely after about 2.5 hr. and, when the solution turned dark after a total of 3.25 hr., the ozonizer was turned off, but the stirring was continued and the stream of oxygen was passed through the solution for an additional 0.5 hr. Then sodium iodide (70 g., 0.47 mole) and glacial acetic acid (70 ml.) were added simultaneously all at once, and the cooling bath was removed. Stirring was continued while the mixture was allowed to warm to room temperature over a period of 0.5 hr.

Saturated aqueous sodium thiosulfate (about 250 ml.) was then added immediately after the 0.5-hr. warming period to the resulting very dark brown, iodine-containing solution until the color of the solution turned from dark brown to yellow. The solution was diluted with water (300 ml.) and extracted with ether (three 200-ml. portions). The ether extracts were washed with water (200 ml.) and then with saturated aqueous sodium bicarbonate until carbon dioxide was no longer evolved. The ether solution was then washed with saturated salt solution (two 50-ml. portions), dried over anhydrous sodium sulfate, and evaporated at aspirator pressure with a rotary evaporator. The residual oil was then evacuated further with a rotary evaporator and a vacuum pump at 60° (1mm.), leaving **2** as a light orange oil[15] (17.3 g., 89%), $n^{25}\mathrm{D}$ 1.5602. The oil obtained at this stage is nearly pure, as shown by the identity of the infrared spectrum with that of the distilled sample, except for a band at 1105 (mw) cm.$^{-1}$. This preparation has been carried out on three times the scale described, without difficulty, and in the same yield.

When subjected to ordinary vacuum distillation, *o*-nitrophenylacetaldehyde undergoes extensive decomposition, even when pure, with formation of black, tarry undistillable material. Thus, distillation of a 15.5-g. sample of the crude oil at 100–110° (0.25 mm.) gave 10.2 g. (66% recovery) of pure *o*-nitrophenylacetaldehyde as a yellow oil, $n^{25.5}\mathrm{D}$ 1.5634. Subsequent redistillations at the same pressure gave about a 70% recovery, leaving in each case a black tar as a residue in the distillation flask. Purification was best effected by molecular distillation of the crude oil in a Hickman still at 90° (5×10^{-4} mm.) until distillation stopped, which gave the product without forerun as a yellow oil (16.7 g., 86%), $n^{25.5}\mathrm{D}$ 1.5634. Alternatively, the oil can be subjected to rapid short-path (7 cm.) distillation[16] at a pot temperature up to 185° (0.05–0.02 mm.) until distillation stops. Again, there was no forerun, and the pure *o*-nitrophenylacetaldehyde was obtained as a yellow oil (15.8 g., 81%): $n^{25}\mathrm{D}$ 1.5639; reported[5] as a light yellow oil, b.p. 133–135° (5 mm.); ν 2710 (mw) (H—C=O), 3400 (w) (overtone), 1725 (s) (C=O), 1525 (s), 1350 (s) (NO_2) cm.$^{-1}$ on the oil. The n.m.r. spectrum of a 60% (w./v.) solution in deuteriochloroform contains (with areas relative to 7 protons given in parentheses; δ scale, 1 p.p.m. = 60.00 c.p.s.) a hyperfinely split triplet (1.0) with the high-field member further split into a doublet centered at 9.95 (J = ~0.5 c.p.s., aldehyde proton), an extensively split doublet (1.1) centered at 8.12 (J = 7.2 c.p.s., proton *ortho* to the nitro group), a complex multiplet (3.1) from 7.84 to 7.27 with the strongest peak at 7.59 (remaining three aromatic protons), and a hyperfinely split doublet (1.9) centered at 4.15 (J = ~0.5 c.p.s., methylene group).

[15] On several occasions yellow crystals of sulfur (0.5–0.7 g.), m.p. 116–117°, separated from the oil at this point, and were removed by suction filtration.

[16] A Kontes Glass Co. Bantamware short-path distillation head, no. K-28710, was used.

Some Studies of 1,3,5-Hexatriene Systems

CHARLES W. SPANGLER[1]

Department of Chemistry, Ohio Wesleyan University, Delaware, Ohio

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The preparation of pure substituted 1,3,5-hexatrienes has been accomplished recently[2,3] by utilization of a procedure[4] in which the triene is generated by means of a Hofmann elimination. Previous preparations of substituted 1,3,5-hexatrienes involved, in general, either a vapor phase catalytic dehydration over alumina or an acid-catalyzed dehydration of an appropriately substituted hexadienol. The corresponding cyclohexadiene inevitably forms as a by-product in the former procedure and can assume major proportion. The formation of these cyclohexadienes has been described by Woods and co-workers.[5,6] Woods and Viola[6] chose to look upon this reaction as an internal Diels–Alder reaction of the intermediate triene. In most cases, a temperature range can be found in which the triene is the major product of the dehydration.

Woods and Fleischacker[5] attempted the preparation of the three possible methyl-1,3,5-hexatrienes by dehydration of an appropriately substituted hexadienol by either of two procedures: (1) catalytic reaction over alumina, or (2) reaction with phosphorus pentoxide. Only the 1-methyltriene was obtained in a relatively pure state. The 2-methyl- and 3-methyl-1,3,5-hexatrienes apparently were contaminated with appreciable quantities of methylcyclohexadienes. They also found that dehydration of methylhexadienols over alumina at 500° or passage of methyl-1,3,5-hexatriene over the catalyst under the same conditions yielded methylcyclohexadienes.

We decided to reinvestigate the above system in order to elucidate the structures of the methylcyclohexadienes obtained from the pure methyl-1,3,5-hexatrienes prepared by the Hwa procedure. 1-Methyl- and 3-methyl-1,3,5-hexatriene were passed over alumina at 410–420°. The products were trapped in a Dry Ice–acetone bath and subsequently distilled. The purified products were analyzed by g.l.p.c., which indicated that the crude products were mixtures containing, in both cases, at least eight compounds. A minimum of 80% of each crude product was represented by one peak in the chromatogram. In both cases, this substance was isolated by successive collections of the appropriate peak by trapping in a Dry Ice–acetone bath. Both products were analyzed and identified as toluene by refractive index, ultraviolet spectrum, and retention time compared with an authentic sample. No appreciable quantity of methylcyclohexadiene could be found in either product. The formation of toluene as the major product can be rationalized only the basis of cyclization followed by dehydrogenation over alumina, or under the conditions in the chromatograph. This latter explanation does not seem reasonable, since cyclohexadiene does not form benzene under identical chromatographic conditions, as demonstrated with known calibrated solutions. The formation of toluene and lack of significant quantities of methylcyclohexadiene in the product differs markedly from the results reported by Woods and Fleischacker.[5]

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[1] Department of Chemistry, Northern Illinois University, DeKalb, Ill. 60115.

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The cyclization reactions over alumina were repeated utilizing pure 1,3,5-hexatriene (a mixture containing 70% *trans* isomer and 30% *cis*). All experimental procedures were identical with those involving methyl-1,3,5-hexatrienes. G.l.p.c. analysis showed only formation of 1,3-cyclohexadiene (identified by comparison to an authentic sample) plus a few minor peaks. No detectable amounts of benzene were found. These cyclizations were carried out at 200 and 300°. An interesting phenomenon was noticed by investigation of the residual 1,3,5-hexatriene peaks. At 300°, only a very small amount of *trans*-1,3,5-hexatriene survived. At 200°, the residual hexatriene was distributed equally between *cis* and *trans* isomers, both of which were in substantial quantities. Lewis and Steiner[7] have studied the cyclization of 1,3,5-hexatriene and found that the purely thermal cyclization of the *cis* isomer was practically quantitative at 120–190°. The *trans* isomer was unaffected. If the above mechanism were responsible for 1,3-cyclohexadiene formation over alumina, then one would expect the residual triene to exist primarily as the *trans* isomer. Experimentally, however, both are found in equal concentrations after passage over alumina at 200°. Two explanations are possible: (1) the *trans* isomer cyclizes more rapidly than does the *cis* over alumina, or (2) the *trans* isomer is converted to the *cis* isomer *prior* to cyclization. Examination of models of the *trans* isomer will demonstrate the inability of this isomer to attain a conformation conducive to Diels–Alder ring closure. Therefore, the author favors the latter explanation, although a complete elucidation of the cyclization reactions over alumina is beyond the scope of the present work.

In conjunction with the above work, it was decided that some estimation of the energy differences between *cis*- and *trans*-1,3,5-hexatriene was desirable. Hwa, *et al.*,[4] reported that *cis*-1,3,5-hexatriene could be converted in entirety to *trans*-1,3,5-hexatriene by treatment with a catalytic quantity of iodine in ether. In repeating this work, however, it was found that under various conditions and temperatures *cis*-1,3,5-hexatriene does survive in quantities large enough to be determined accurately by g.l.p.c. techniques. It was hoped that this approach would yield a reasonable approximation of thermodynamic equilibrium between the two isomers, rather than complete isomerization as reported.

Under controlled conditions, the 1,3,5-hexatriene isomers were equilibrated with a catalytic amount of iodine dissolved in ether. The reaction was followed by g.l.p.c. until the ratio of the two isomers, determined by measuring the areas under the respective chromatographic peaks, was constant. A free-energy difference was then calculated. Ideally, a wide temperature range should be employed. Data collected at 0 and 5° were consistent with one another, but, at higher temperatures (25 and 50°), polymerization was a serious side reaction and the results were inconclusive. Equilibrations below 0° were hampered by the freezing of *trans*-1,3,5-hexatriene. Laboring under these handicaps, the results compare favorably with predicted ΔF values[8] for the *cis* to *trans* conversion (Table I).

TABLE I

cis–trans-1,3,5-HEXATRIENE EQUILIBRATION

Temp., °C.	K (*trans*/*cis*)	ΔF, kcal./mole	ΔF_{298}, kcal./mole
0	3.97	−0.75	−0.73[a]
5	2.97	−0.60	

[a] Calculated value.[8]

The order of magnitude seems to indicate that the system is a classical example of *cis–trans* isomerism and that the *trans* form is the more stable. If polymerization is still an important reaction, then the value at 0° should be the more reliable. There is reason to believe that the polymerization rates are very different for the two isomers. A crude estimation of ΔH based on the above for the conversion of *cis* → *trans* yields a value of −0.9 kcal. (calcd.[9] $\Delta H_{298} = -1.0$ kcal./mole). It is hoped that in the future, accurate heats of combustion or hydrogenation will yield better values for the above thermodynamic values. However, these results are the first quantitative indication that *trans*-1,3,5-hexatriene is more stable than *cis*-1,3,5-hexatriene, a result that most workers in the field have qualitatively observed for the past 4 years.

Experimental Section

Gas–liquid partition chromatography was performed with an Aerograph instrument, Model 90-P3, with a 10-ft. β,β'-oxydipropionitrile-on-Chromosorb column. The chromatographic areas were measured by at least two different procedures which usually agreed within 0.5–1%. K values were considered constant if they did not vary more than 1% over several hours. Ultraviolet spectra were obtained with Bausch and Lomb Model 505 spectrophotometer. All thermolytic reactions were performed with a 1 ft. long, 1 in. o.d. Pyrex column packed with Matheson Coleman and Bell activated alumina (8–14 mesh). Thermolysis temperatures were measured at column inlet and outlet and the differential was maintained at less than 10°.

Cyclization of Methyl-1,3,5-hexatrienes.—Methyl-1,3,5-hexatriene[3] (15 g., 0.16 mole) was added dropwise through a pressure-equalizing addition funnel to the packed thermolysis column maintained at a temperature of 410–420°. The alumina had been previously dried by heating the column at 300° under vacuum for 1 hr. A pressure of 20–25 mm. was maintained in the system to facilitate rapid removal of the product from the column. The product was trapped in a flask immersed in a Dry Ice–acetone bath. The product was separated manually from a small quantity of water and dried with anhydrous magnesium sulfate. After filtration, the clear yellow product was distilled at reduced pressure and the entire volatile fraction was collected. A small polymeric residue remained. The product was analyzed by g.l.p.c. with a β,β'-oxydipropionitrile column at 70°, and the main peak was trapped in Dry Ice–acetone. At least 1 ml. of product was collected for both the 1-methyl- and 3-methyl-1,3,5-hexatriene series. For the 1-methyl product, $n^{25}\mathrm{D}$ 1.4923 and $\lambda_{\max}$ 261 mμ ($\epsilon_{\max}$ 224) were compared with those of toluene, $n^{20}\mathrm{D}$ 1.4969,[10] $\lambda_{\max}$ 261 mμ ($\epsilon_{\max}$ 225).[11] Retention times for the product and toluene were identical. Similarly, for the 3-methyl product, the following were obtained: $n^{25}\mathrm{D}$ 1.4931, $\lambda_{\max}$ 261 mμ ($\epsilon_{\max}$ 225). Retention times were also identical for this product and toluene. Yields of toluene from 1-methyl- and 3-methyl-1,3,5-hexatriene were, respectively, 77 and 78%.

Cyclization of 1,3,5-Hexatriene.—A procedure similar to that utilized for studying the cyclization of the methylhexatrienes was employed with 1,3,5-hexatriene. A mixture of 70% *trans*-

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and 30% *cis*-1,3,5-hexatrnene (5 g.) was added dropwise to the alumina column and the product was collected and isolated as above (*ca.* 80% recovery). G.l.p.c. analysis of the product was conducted at 35 and 50°. No benzene was detected. 1,3-Cyclohexadiene was identified by comparison with an authentic sample. With an alumina column temperature of 300°, only *trans*-1,3,5-hexatriene and 1,3-cyclohexadiene were found. With a column temperature of 200°, *cis*- and *trans*-1,3,5-hexatriene were found in equal amounts, as well as 1,3-cyclohexadiene. In both cases, the amounts of 1,3-cyclohexadiene formed corresponded to the loss of 1,3,5-hexatriene (total area under peaks).

Equilibration of *cis*- and *trans*-1,3,5-Hexatriene.—To samples of freshly distilled 1,3,5-hexatriene (chromatographically pure 70% *trans*, 30% *cis* mixture), a few drops of a saturated iodine–ether solution were added. The resulting samples were equilibrated at 0, 5, 25, 30, and 50° (±0.5°). These were analyzed by g.l.p.c. at various times until the observed *K* values (obtained by measuring the areas under the *cis* and *trans* peaks) were constant. At the higher temperatures, polymer formation was evident before *K* became constant. These runs were discarded for calculation purposes.

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The Syntheses of (±)-β-Bisabolene and 2-*p*-Tolyl-6-methylhepta-1,5-diene

A. MANJARREZ AND A. GUZMÁN

Contribution No. 180 from the Instituto de Química de la Universidad Nacional Autónoma de México, México 20, D. F., México

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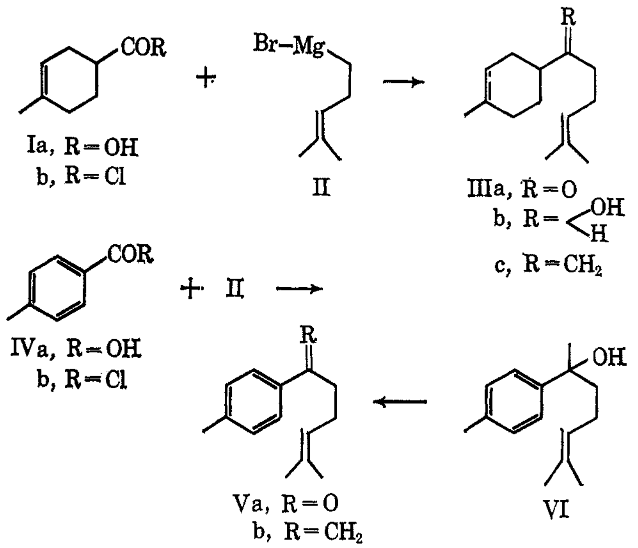
The sesquiterpene hydrocarbon β-bisabolene (IIIc, $C_{15}H_{24}$) has been recently found in nature.[1-4] Navés has prepared it from lanceol,[5] and bisabolene trihydrochloride has been synthesized by Ruzicka and Liguori.[6]

The sesquiterpenoid hydrocarbon 2-*p*-tolyl-6-methylhepta-1,5-diene (Vb, $C_{15}H_{20}$), which has not been found in nature, is the 1-dehydro derivative of the major component in the natural sesquiterpene mixture known as α-curcumene and, so far as we are aware, has not been prepared.

We have obtained both compounds in accordance with Scheme I. The acid chloride of 4-methyl-1-carboxy-Δ^3-cyclohexene (Ib) was coupled with the Grignard reagent from 1-bromo-4-methyl-Δ^3-pentene (II) yielding 2-methyl-6-keto-6-(4′-methyl-$\Delta^{3'}$-cyclohexenyl)-Δ^2-hexene (IIIa). The acid Ia reported by Meldrum and Perkin[7] was prepared by the hydrolysis of the ester obtained by condensation of isoprene and methyl acrylate.[8] The bromo compound II was obtained from α-acetylbutyrolactone according to Julia, *et al.*[9]

SCHEME I



The keto compound IIIa (characterized as its alcohol) was treated with triphenylmethylphosphonium bromide[10] to yield the desired (±)-β-bisabolene (IIIc).

2-*p*-Tolyl-6-methylhepta-1,5-diene (Vb) was prepared in a similar manner by coupling the same Grignard reagent (II) with *p*-toluic acid chloride and treating the 2-methyl-6-keto-6-(*p*-tolyl)-Δ^2-hexene (Va) obtained with triphenylmethylphosphonium bromide, affording an oil that showed infrared and n.m.r. spectra consistent with structure Vb. The same compound (Vb) is obtained when 2-*p*-tolyl-6-methylhept-5-en-2-ol (VI)[11] is dehydrated by means of oxalic acid. It is, therefore, not surprising that the elimination leads predominantly to the 1-olefin, that is, the less-hindered one.[12,13]

Experimental Section[14]

2-Methyl-6-keto-6-(4′-methyl-$\Delta^{3'}$-cyclohexenyl)-Δ^2-hexene (IIIa).—The bromo compound II (45 g.) was slowly added, at room temperature, with stirring to Mg turnings (6.71 g.) in anhydrous ether (200 ml.). When the reaction was completed (45 min.), the organomagnesium compound was slowly added to a mixture of the acid chloride Ib (49 g.), cuprous chloride (200 mg.), and anhydrous ether (60 ml.). Stirring was prolonged overnight and a 5 *N* solution of H_2SO_4 (400 ml.) was then added. After the usual extraction procedure, 73 g. of an oily product was obtained. Fractional distillation afforded a fraction (53 g.): b.p. 123–125° (2 mm.); d^{25}_4 0.920; n^{25}D 1.4869; ν_{max} 2860, 1710, 1375, 910 cm.$^{-1}$; n.m.r. 1.65, 1.8–2.5, 5.0, 5.35.

Reduction of 5 g. of the ketone with 1 g. of $NaBH_4$ in methanol afforded 4 g. of 2-methyl-6-hydroxy-6-(4′-methyl-$\Delta^{3'}$-cyclohexenyl)-Δ^2-hexene (IIIb): b.p. 100–104° (0.25 mm.); d^{25} 0.951; n^{25}D 1.4910; ν_{max} 3040, 2900, 1375 cm.$^{-1}$; n.m.r. 1.6, 3.4, 5.15, 5.35.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61; O, 7.68. Found: C, 80.30; H, 11.48; O, 8.01.

(±)-β-Bisabolene (IIIc).—To a suspension of triphenylmethylphosphonium bromide (7.72 g.) in anhydrous ether (100

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