Convenient Synthesis of Vinylcyclohexane-α-*d*

C. G. OVERBERGER, A. KATCHMAN,[1,2] AND J. E. MULVANEY

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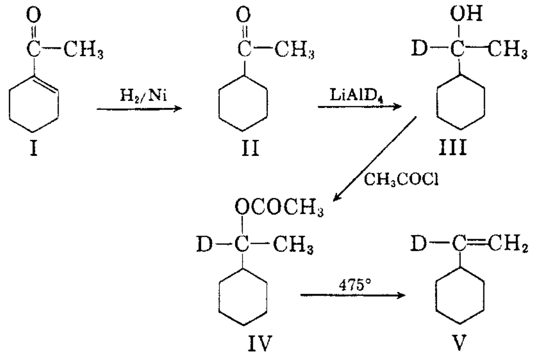
A recent note[3] on the preparation of methyl cyclohexyl ketone has prompted us to report some results we have obtained in the course of preparing the monomer vinylcyclohexane-α-*d* (V).

A convenient laboratory preparation of the deuterated vinylcyclohexane (V) utilized ketone (II) as the starting material.[4] Vinylcyclohexane has previously been reported by Van Derby and Kooyman, prepared by preparation of methyl cyclohexylcarbinol by reaction of cyclohexylmagnesium bromide and acetaldehyde, followed by acetylation and pyrolysis. The ketone (II) had also been prepared by oxidation of 1-cyclohexylethanol[5,6] and more recently by the catalytic reduction of methyl cyclohexen-3-yl ketone.[2]

The ketone (II) was readily accessible from the reduction of methyl cyclohexen-1-yl ketone[5,7] (I). Reduction was carried out in an 86% yield by hydrogenation at room temperature with Raney Nickel W-2[8] as the catalyst. Reduction with lithium aluminum deuteride gave the deuterated alcohol (III) in 91.5% yield which was smoothly acetylated to the deutero acetate (IV) in a 95.3% yield. Pyrolysis of the acetate (IV) gave the desired deuterated monomer (V) after careful fractionation (71%). Fractionations were followed by vapor phase chromatography to insure purity of the monomer. Vinylcyclohexane[4] (V. D = H) was prepared in analogous fashion using lithium aluminum hydride for the reduction of the ketone (II).



EXPERIMENTAL

Methyl cyclohexyl ketone (II). A mixture of methyl cyclohexen-1-yl ketone,[6] 17.5 g. (0.138 mol.), 75 ml. of methanol and 1 g. of W-2 Raney Nickel catalyst[7] in a rocking autoclave pressurized to 500 lbs./in.^{2} was shaken at room temperature for 20–30 min. after which no further hydrogen was absorbed. The catalyst and methanol were removed and distillation of the residual oil furnished 15.2 g. (86%), b.p. 66° (12 mm.), n_D^{26} 1.4491, of methyl cyclohexyl ketone (reported[6] b.p. 182.5–184.5° (676 mm.), $n_D^{25.9}$ 1.44955).

1-Cyclohexylethanol-1-d (III). To a solution of 3.3 g. (6.078 mol.) of lithium aluminum deuteride[9] in 300 ml. of absolute ethyl ether was added dropwise 37.9 g. (0.3 mol.) of II in 100 ml. of absolute ethyl ether. Upon completion of the addition, the mixture was refluxed for 1 hr. and then decomposed with water. The ether was removed and the residual oil was distilled yielding 35.5 g. of carbinol (91.5%), b.p. 65° (3.9 mm.), n_D^{25} 1.4632.

Anal. Calcd. for $C_8H_{15}DO$: C, 74.35; H + D, 13.26. Found: C, 74.31; H + D, 13.23, 0.891 deuterium atom/mol.[10]

1-Cyclohexylethyl-1-d acetate (IV). 1-Cyclohexylethanol-1-*d*, 33.0 g. (0.26 mol.), (III), was added dropwise to 30 g. of acetyl chloride at a rate to maintain reflux and the mixture was refluxed for 2 additional hr. Excess acetyl chloride was removed and the residual oil was distilled to yield 41.6 g. (95.3%), b.p. 67° (4.3 mm.), n_D^{25} 1.4445, of acetate.

Anal. Calcd. for $C_{10}H_{17}DO_2$: C, 70.13; H + D, 11.18. Found: C, 70.29; H + D, 11.28; 0.942 deuterium atom/mol.[9]

Vinylcyclohexane-α-d (V). 1-Cyclohexylethyl-1-*d* acetate, 34.5 g. (0.20 mol.), (IV), was pyrolyzed[11] by dropping the liquid at a rate of 8–12 drops per min. through a 12″ tube packed with Pyrex glass Raschig rings at 475° under a nitrogen atmosphere. The pyrolyzate was washed with aqueous sodium bicarbonate and water and dried over anhydrous sodium sulfate. Distillation in a seventy-five plate concentric tube column yielded 17.8 g. (80%), boiling at 127–129°, n_D^{25} 1.4459, of crude olefin. Careful distillation yielded 12.7 g. (71%), boiling at 127.5–128°, n_D^{25} 1.4441, of vinylcyclohexane-α-*d*. The product was pure as determined by vapor phase chromatography. It absorbed strongly at 11.0 μ in the infrared which indicated that it was a terminal olefin.

Anal. Calcd. for $C_8H_{13}D$: C, 86.40; H + D, 13.60. Found: C, 86.13; H + D, 13.62; 0.889 deuterium atom/mol.[10]

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, N. Y.

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[1] Present address: General Electric Research Laboratory, Schenectady, N. Y.

[2] Hooker Chemical Company, Post Doctoral Fellowship, 1957–59.

[3] W. K. Johnson, *J. Org. Chem.*, **24**, 864 (1959).

[4] J. R. Van Derby and E. C. Kooyman, *Rec. trav. Chem.*, **71**, 837 (1952).

[5] O. Wallach, *Ann.*, **360**, 26 (1908).

[6] S. van Woerden, *Rec. trav. Chem.*, **45**, 124 (1926).

[7] J. H. Saunders, *Org. Syntheses*, **Coll. Vol. III**, 22 (1955).

[8] R. Mozingo, *Org. Syntheses*, **Coll. Vol. III**, 181 (1955).

[9] Purchased from Metal Hydrides, Inc., Beverly, Mass.

[10] Deuterium analyses were performed by Professor D. B. Denney of Rutgers, the State University of New Jersey, by means of a mass spectrograph.

[11] C. G. Overberger and D. Tanner, *J. Am. Chem. Soc.*, **77**, 369 (1955).

Preparation and Properties of 1-Phenyl-4-methyl-2-penten-1-one

KURT KULKA, ROBERT J. EISERLE, JAMES A. ROGERS, JR.,
AND FRED W. RICHTER

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The recent availability of isobutyraldehyde in commercial quantities through the oxo process[1]

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[1] H. J. Hagemeyer and G. C. DeCroes, *The Chemistry of Isobutyraldehyde and its Derivatives*, Tennessee Eastman Co., Kingsport, Tenn., 3 (1953).

prompted us to prepare a sample of isobutylideneacetophenone for investigation of its organoleptic properties. The reaction of isobutyraldehyde with acetophenone under alkaline conditions yielded a small amount of unreacted acetophenone, a liquid boiling at 130° at 8 mm. and, as the main product, a solid. The latter, white, odorless crystals, melted at 144.5–145° after repeated recrystallizations from a methanol-benzene mixture.

The liquid was not the aldol since water was not produced upon heating in the presence of iodine or oxalic acid, but the starting material was recovered. A carbon-hydrogen ratio determination of the liquid and the solid compounds gave identical results. Consequently, we investigated the possibility that the solid and the liquid reaction products were geometrical isomers, or that the double bond in the side chain of either compound was out of conjugation with the carbonyl group.

The structure of the liquid isomer was proven by its reduction products which were previously reported in the literature. Thus catalytic hydrogenation with Raney nickel in methanol solution at 50 p.s.i. yielded 1-phenyl-4-methyl-pentan-1-one and 1-phenyl-4-methylpentan-1-ol. By potassium borohydride reduction and also by Meerwein, Ponndorf-Verley reduction the unsaturated alcohol 1-phenyl-4-methyl-2-penten-1-ol was obtained. This alcohol was reduced by catalytic hydrogenation with Raney nickel in methanol solution at 50 p.s.i. to 1-phenyl-4-methylpentane. As these compounds were previously obtained by more complicated synthesis such as Grignard reactions, the above reductions are novel and simple ways for their preparation.

Attempted reduction of the solid compound at 50 p.s.i. in various solvent systems, with various catalysts including Raney nickel, Adams platinum oxide and palladium on charcoal were unsuccessful. Bromination in carbon tetrachloride and in hexane solution did not proceed satisfactorily. Hydrogen bromide was given off and resins were formed. The absence of a double bond in the solid compound became obvious and suggested the possibility that it was a dimer having the uncommon cyclobutane structure similar to that in truxillic acid which is formed by the dimerization of cinnamic acid. Molecular weight determinations of the liquid as well as the solid reaction products by a modified Rast method gave evidence that the liquid was the monomer and the solid a dimer of 1-phenyl-4-methyl-2-penten-1-one.

Prior to this paper, the crystalline dimer was erroneously defined as the monomer by Thoms and Kahre[2]; the actual monomer was not reported.

It was of interest to prepare these compounds by other syntheses. Isobutyraldehyde was treated with malonic acid in pyridine solution using piperidine as the catalyst to obtain 4-methyl-2-pentenoic acid which was converted to its acid chloride. The acid chloride was treated with benzene in a Friedel-Crafts synthesis to give mainly the liquid monomer and a small amount of the solid dimer. Knoevenagel reaction of benzoylacetic acid with isobutyraldehyde in pyridine solution, using piperidine as the catalyst, gave only the liquid monomer after decarboxylation.

Depolymerization of the dimer to the monomer was accomplished by vacuum distillation in the presence of a catalytic amount of sodium acetate. Dimerization of the liquid monomer was carried out under identical conditions as in the previously described condensation, *i.e.*, in methanol solution using potassium hydroxide as the catalyst. It was further observed that the liquid on standing in a stoppered brown bottle over a prolonged period of time was partly dimerized.

The degree of reactivity of these two compounds is best demonstrated by the fact that it took 480 hr. for the solid and only 24 hr. for the liquid to react completely with hydroxylamine hydrochloride at room temperature. Molecular weight determinations of these two oximes by a modified Rast method showed the first to be the oxime of a dimer and the latter to be the oxime of the monomer.

The next higher member of this series of branched-chain, unsaturated ketones (1-phenyl-5-methyl-2-hexen-1-one) was obtained from the reaction of acetophenone with isovaleraldehyde under identical (alkaline) conditions. In this reaction only the liquid monomer was formed.

Infrared curves of 1-phenyl-4-methyl-2-penten-1-one (monomer and dimer) were run on a Perkin-Elmer Model 21 spectrophotometer with sodium chloride prism. The liquid ketone gave the normal spectrum for a conjugated unsaturated actophenone except for a splitting of the monosubstituted phenyl peak in the 750 cm.$^{-1}$ range. The recrystallized solid ketone melted film run on a hot stage cell showed aromatic carbon-carbon double bond and carbonyl stretching bands and monosubstituted phenyl ring peaks. It lacked aliphatic carbon-carbon double bond stretching peaks, indicating saturation of the *trans* double bond. A medium intensity peak at 880 cm.$^{-1}$ can be assigned to the cyclobutane ring which according to Reid and Sack[3] is the expected range for 1,2,3,4-tetrasubstituted cyclobutane compounds.

Thus the spectrum and previously reported experimental findings indicate the structure of our solid to be either of the two structures following:

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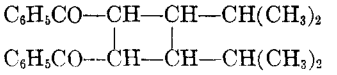
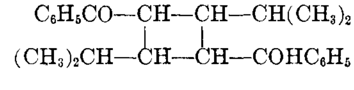
[2] H. Thoms and H. Kahre, *Arch. Pharm.*, **263**, 251 (1925).

[3] E. B. Reid and M. Sack, *J. Am. Chem. Soc.*, **73**, 1985 (1951).



$$\begin{array}{l} C_6H_5CO\text{—}CH\text{—}CH\text{—}CH(CH_3)_2 \\ \qquad\qquad\ \ |\qquad\ | \\ C_6H_5CO\text{—}CH\text{—}CH\text{—}CH(CH_3)_2 \end{array}$$



$$\begin{array}{l} \qquad\qquad C_6H_5CO\text{—}CH\text{—}CH\text{—}CH(CH_3)_2 \\ \qquad\qquad\qquad\qquad\ \ |\qquad\ | \\ (CH_3)_2CH\text{—}CH\text{—}CH\text{—}COHC_6H_5 \end{array}$$

EXPERIMENTAL

All boiling points and melting points are uncorrected.

Dimer of 1-phenyl-4-methyl-2-penten-1-one (I). During 1.5 hr. at a temperature of 50°, 72.1 g. isobutyraldehyde was added to a well agitated solution of 120.7 g. acetophenone, 17 g. potassium hydroxide (reagent grade), 125 ml. methanol, and 125 ml. water. On continuing agitation at 48–50° a white solid formed. After 3.5 hr. the reaction mass was cooled to room temperature neutralized with acetic acid, and filtered on a Buchner funnel. The separated solid was washed with 100 ml. methanol and dried; it weighed 107 g. (61% yield). After 3 recrystallizations from a mixture of 70% methanol and 30% benzene, it gave a constant melting point of 144.5–145°, the dimer of 1-phenyl-4-methyl-2-penten-1-one (I). The liquid organic filtrate combined with the above methanol was fractionated through a 40-cm. Vigreux column yielding 10.5 g. unreacted acetophenone and 38 g. of a liquid boiling 133–134° at 8 mm. n_D^{20}: 1.5385, which on redistillation boiled at 130° at 8 mm. n_D^{20}: 1.5385. This liquid was identified as the *monomer of 1-phenyl-4-methyl-2-penten-1-one* (II). The distillation residue (12.2 g.) after recrystallization from a methanol-benzene mixture was found to be identical with I having a melting point of: 144.5–145°.

Anal. Calcd. for I: $C_{24}H_{18}O_2$: C, 82.2; H, 8.1. Found: C, 81.6; H, 7.8.

Anal. Calcd. for II: $C_{12}H_{14}O$: C, 82.2; H, 8.1. Found: C, 83; H, 7.86.

Molecular weight determination of I. The modified Rast procedure described by Becker[4] for the semimicro molecular weight determination was applied in principle. When the solution of the organic compound in camphor, prepared as advised by Becker, was used, erroneous and nonreproducible results were obtained, probably due to partial depolymerization of the dimer. The compound to be analyzed was, therefore, thoroughly mixed with the camphor. As five consecutive experiments gave almost identical results, we consider this abbreviation of the procedure to give sufficiently accurate results. Calculated molecular weight: 348, Found: 344 (average).

Determination of the carbonyl content of I *and* II *using hydroxylamine hydrochloride.* The method described by Guenther[5] was employed: Thus 0.5421 g. of I was treated at room temperature with 35 ml. of 0.5*N* hydroxylamine hydrochloride solution, and the liberated hydrochloric acid titrated with 0.5*N* sodium hydroxide solution. The following ketone contents were obtained: After 24 hr.: 32.3%; after 384 hr.: 93.3% and after 480 hr.: 99.9%. In the same way 0.5384 g. of II was treated as I, but gave after 24 hr. a ketone content of 98.2%.

Dioxime of I. The dioxime was prepared according to a procedure described by Vavon and Anziani:[6] Thus 8.9 g. of I, 10 g. hydroxylamine hydrochloride, 70 g. ethanol, 30 g. water, and 3.6 g. sodium hydroxide (reagent grade) were refluxed for 24 hr. The solution was poured into 100 ml. water, the precipitated crystals collected on a Buchner funnel, and recrystallized 4 times from 80% ethanol to a constant m.p. of 184–185°.

Anal. Calcd. for $C_{24}H_{30}N_2O_2$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.13; H, 8.06; N, 7.39.

Oxime of II. The above procedure was followed with the exception that the solution was permitted to stand at room temperature (25–30°) for 24 hr. The oxime, recrystallized 4 times from 80% ethanol, had an m.p. of 57°.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.12; H, 8.02; N, 7.41.

Depolymerization of I *to* II. A mixture of 50 g. of I and 1.5 g. anhydrous sodium acetate (reagent grade) was heated in a vacuum of 8 mm. At 185° the mixture became completely liquid, and the depolymerization was considered complete. On distillation without a column, 41 g. were collected, boiling from 130–135° at 8 mm. n_D^{20}: 1.5392. On redistillation through a 40-cm. Vigreux column, the ketone (II) boiled at 130° at 8 mm.; n_D^{20}: 1.5385.

Dimerization of II *to* I. At a temperature of 50°, 70 g. of I was agitated for 45 min. with a solution of 6 g. potassium hydroxide in 70 g. methanol and 70 g. water. The solid was collected on a Buchner funnel and recrystallized twice from methanol. The resulting white crystals had an m.p. of 143–144°. A mixed melting point with the original ketone (I) showed no depression.

Research Laboratories of
Fritzsche Brothers, Inc.
Port Authority Bldg.
76 Ninth Ave.
New York 11, N. Y.

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[4] E. I. Becker, *Chemist Analyst*, **40,** 80 (1951).

[5] E. Guenther, *The Essential Oils*, Vol. I, D. Van Nostrand Co., N. Y., 1948, p. 286.

[6] G. Vavon and P. Anziani, *Bull. soc. chim.*, **5,** 2026 (1937).

Synthesis of 2-Phenyltriphenylene and 2,6,10-Trimethyltriphenylene

D. David Lawson and Charles M. Buess

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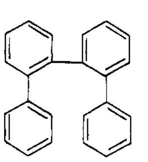
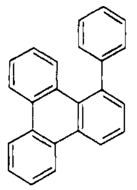
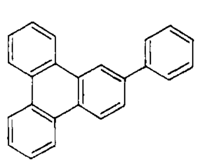
Hansch and Geiger[1] recently prepared a phenyltriphenylene by cyclodehydrogenation of 2,2'-diphenylbiphenyl (I). Although 1-phenyltriphenylene (II) might be expected from this reaction, the authors considered rearrangement to the 2-isomer (III) very likely. In the course of related work in this laboratory, 2-phenyltriphenylene was prepared by an unequivocal method, an adaptation of the Rapson synthesis as improved by Barker, Emmerson, and Periam.[2] The sample was compared with one kindly supplied by Dr. Corwin Hansch and the physical properties including infrared spectra were found to be identical. The melting point of a mixture sample was not depressed. It may therefore be concluded that the phenyl group does migrate under the cyclodehydrogenation conditions employed in ref. 1.



I



II



III

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[1] C. Hansch and C. F. Geiger, *J. Org. Chem.*, **23,** 477 (1958).

[2] C. C. Barker, R. G. Emmerson and J. D. Periam, *J. Chem. Soc.*, 1077 (1958).