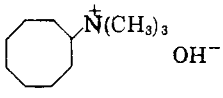
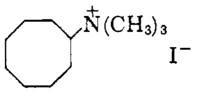
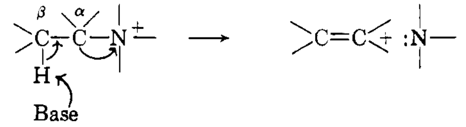
cycloöctyltrimethylammonium hydroxide (III) and treatment of cyclooctyltrimethylammonium iodide (IV) with potassium amide in liquid ammonia yield predominately *trans*-cyclooctene.[4,5] Wittig and Polster[4] concluded that *cis*-cyclooctene comes from α'-β-elimination of the amine function in compounds I and II (and possibly III and IV), whereas *trans*-cyclooctene arises mainly, if not entirely, from pure β-elimination generalized by Equation 2.



III

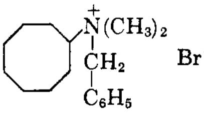


IV



(2)

If the interpretation depicted in Equation 1 is correct, and if Wittig and Polster's rationalization is valid, the action of sodium amide in liquid ammonia on cyclooctylbenzyldimethylammonium bromide (V) would be expected to afford *cis*-cyclooctene. We have carried out this reaction and have obtained *cis*-cyclooctene which infrared analysis indicates is free of the *trans*-isomer.



V

Therefore, two complementary low temperature methods of forming olefins from quaternary ammonium halides appear to be available: treatment of alkyltrimethylammonium halides with potassium amide in liquid ammonia (the Wittig-Polster procedure), which produces olefins by *trans*-β-elimination (Equation 2); and treatment of alkylbenzyldimethylammonium halides with sodium amide in liquid ammonia, which yields olefins by the *cis*-α'-β-process (Equation 1).

EXPERIMENTAL[6]

Cyclooctylbenzyldimethylammonium Bromide. (V). A benzene solution containing 2.64 g. of cyclooctyldimethylamine[5] and 5.56 g. of benzyl bromide was stirred and refluxed for 19 hr. The white solid which formed was separated by filtration, washed with benzene, and dried in a vacuum desiccator. Cyclooctylbenzyldimethylammonium bromide (5.02 g.), m.p. 184–186°, was obtained in 90% yield.

Anal. Calcd. for $C_{17}H_{28}NBr$: C, 62.58; H, 8.59; N, 4.29. Found: C, 62.79, H, 8.73; N, 4.07.

cis-Cyclooctene. Bromide V (4.8 g.) was added during 10 min. to 100 ml. of liquid ammonia containing 0.022 mole of sodium amide. The mixture was stirred for 3 hr.; then 1.8 g. of ammonium chloride followed by 75 ml. of ether was added. The Dry Ice condenser was replaced by a water condenser and the ammonia was allowed to evaporate overnight. Water was added to the residue and the two resulting liquid phases were separated. The ethereal solution, after being washed with 10% hydrochloric acid solution, water, 5% sodium bicarbonate solution, and water, was dried over magnesium sulfate. Distillation through a semimicro column yielded 0.87 g. (54%) of *cis*-cyclooctene, b.p. 62–63° (47 mm.), $n_D^{19.5}$ 1.4685. The infrared spectrum was the same as a published spectrum and the absence of bands at 11.8 and 12.6 μ indicated that *trans*-cyclooctene was not present.[5]

From the aqueous acid solution, benzyldimethylamine, identified by its infrared spectrum, was isolated in 65% yield by adding an excess of 20% potassium hydroxide solution, extracting the liberated amine with ether, and distilling.

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[6] Melting points and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer with a sodium chloride prism.

Preparation of Dipivaloylmethane

Karl R. Kopecky, Derek Nonhebel, Gene Morris, and
George S. Hammond

Received October 13, 1961

As a consequence of our interest in metal chelates derived from sterically hindered β-diketones we have frequently needed to prepare large batches of 2,2,6,6-tetramethylheptan-3,5-dione (dipivaloylmethane). The method of Adams and Hauser[1] does not give high yields when used for the synthesis of sterically hindered β-diketones so a variety of modifications have been investigated. These have included the use of lithium amide as the condensing agent followed by isolation of the lithium chelate by extraction of the reaction mixture with ether and the use of phenyl pivalate rather than ethyl pivalate as the substrate in the condensation with pinacolone. Combination of the two variations has given yields as high as 85%. The method is not reported in detail, however, since isolation of lithium dipivaloylmethide is tedious because of the large volume of ether required. The procedure which we have found most practical for preparation of large batches involves formation of the sodium enolate of pinacolone in dimethoxyethane solution by reaction of the ketone with sodium hydride. The enolate is acylated *in situ* with methyl or ethyl pivalate. Yields in the 60–70% range are very easily obtained. The method should be general for the preparation of hindered diketones.

EXPERIMENTAL

Methyl pivalate (90 g.) and 72 g. of sodium hydride dispersed in mineral oil (52% hydride by weight) were added to 1 l. of dimethoxyethane in a 2-l. flask. The mixture was

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[1] J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).

stirred with an efficient mechanical stirrer and brought to the reflux temperature. Pinacolone (80 g., dried over magnesium sulfate and distilled) in 100 ml. of dimethoxyethane was added from a dropping funnel over a 2-hr. period. Gas evolution (96% of the theoretical amount) ceased about 20 min. after addition was completed. Concentrated hydrochloric acid (180 ml.) was added as rapidly as possible to the mixture. Just before addition was complete the suspension became clear and a fine white precipitate formed. The mixture was then cooled and poured into 2 l. of water. Five hundred milliliters of pentane was added and the organic layer was separated and washed with five 500-ml. portions of water dried over magnesium sulfate and concentrated by distillation. The concentrate was fractionated by distillation through a 10-in. Vigreux column at 36 mm. A forerun of 80 ml., b.p. 60–100°, was discarded. The product was collected at 100–102°. Yield, 85 g., 63%. Recovery by this procedure is not maximum since both the forerun and the pot residue contain dipivaloylmethane.

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Vinylcyclohexane from 4-Vinylcyclohexene-1

LYNN H. SLAUGH AND EUGENE F. MAGOON

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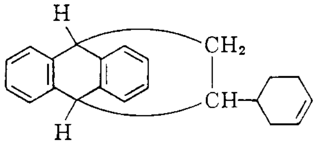
Because vinylcyclohexane has received considerable attention in recent polymerization studies,[1] we are prompted to report a new convenient synthesis of this monomer, which we believe offers several advantages over those previously reported.[2–4]

Since 4-vinylcyclohexene-1 is readily obtainable from the thermal dimerization of 1,3-butadiene, it is a convenient starting material. It is difficult to hydrogenate 4-vinylcyclohexene-1 to vinylcyclohexane[5]; however, it may be indirectly converted *via* the following three steps: (1) The Diels-Alder addition of the former to anthracene, (2) hydrogenation of the adduct, (3) pyrolysis of the hydrogenated adduct.

There is a marked difference in reactivity of the two double bonds in 4-vinylcyclohexene-1 toward anthracene as is shown by the exclusive addition of the vinyl double bond to form adduct I in high yields.



I

This is consistent with previously reported[6] additions of 4-vinylcyclohexene-1 to butadiene and cyclopentadiene, in which the vinyl group, rather than the ring double bond, added to the diene.

Hydrogenation of I followed by pyrolysis gave high yields of vinylcyclohexane and recovered anthracene, indicating a selective reduction of the "cyclohexene" double bond. Mass spectrometric and gas chromatographic analyses failed to show impurities in the vinylcyclohexane, while the infrared and NMR spectra were those to be expected. Specifically, it was shown that ethylidenecyclohexane, ethylcyclohexenes, and vinylcyclohexenes were not present as impurities.

EXPERIMENTAL

Diels-Alder addition of 4-vinylcyclohexene-1 to anthracene. Anthracene (300 g., 1.7 moles), 4-vinylcyclohexene-1 (1000 g., 9.2 moles), and toluene (800 ml.) were shaken in a 3-l. stainless steel autoclave at 225° for 16 hr. The pressure during the experiment did not exceed 150 p.s.i.g. After removal of most of the excess 4-vinylcyclohexene-1 and toluene *via* vacuum distillation the crystalline residue was filtered and washed with toluene, yielding 413 g. (85% yield basis anthracene used) of I. A second crop, 71 g. (14.6%) of less pure, semicrystalline product was obtained by removing the remaining solvent from the filtrate. Gas chromatographic analyses of the liquid removed by distillation indicated a 100% recovery of the unchanged 4-vinylcyclohexene-1, while ultraviolet analysis indicated $< 0.1\%$ unconverted anthracene in the solid adduct which melted at 164–165° (uncorr.) (from benzene) and 176–178° (uncorr.) [from bis(2-methoxyethyl) ether].

Anal. Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74; mol. wt., 286; bromine no., 56. Found: C, 92.39; H, 7.75; mol. wt. (ebul. benzene), 280; bromine No., 57.

Only a slightly lower yield of pure adduct was obtained when the toluene was omitted in a similar experiment. Shorter reaction times gave incomplete conversions of anthracene.

Hydrogenation of the anthracene adduct. Adduct I (150 g.) in isopropyl alcohol (300 ml.) with Raney nickel (∽5 g.) was hydrogenated to completion within 1–2 hr. at 125°, and 500 p.s.i.g. of hydrogen. The yield of white crystalline solid, separated from the catalyst by extraction with acetone, was 98%. Toluene, benzene, and bis(2-methoxyethyl) ether were also good solvents for the hydrogenation. The product, m.p. 163° (uncorr.), was free of anthracene as shown by its ultraviolet spectrum.

Anal. Calcd. for $C_{22}H_{24}$: C, 91.61; H, 8.39; mol. wt., 288. Found: C, 91.72; H, 8.34; mol. wt. (ebul. benzene), ∽280.

Attempts to hydrogenate the molten adduct I, in the absence of a solvent, over copper–chromite catalyst at 120–180° were not successful.

Pyrolysis of the hydrogenated adduct. Pyrolysis (330–390°)

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(1) See for example, T. W. Campbell and A. C. Haven, Jr., *J. Appl. Poly. Sci.*, **1**, 73 (1959); C. G. Overberger and J. E. Mulvaney, *J. Am. Chem. Soc.*, **81**, 4697 (1959).

(2) R. Ya. Levina and N. W. Mezentsova, *Org. Khim.*, **7**, 241 (1950).

(3) J. R. van der Bij and E. C. Kooyman, *Rec. trav. chim.*, **71**, 837 (1952).

(4) N. A. Rozanov and Belikov, *J. Russ. Phys. Chem. Soc.*, **61**, 2309 (1929); *Chem. Abstr.*, **24**, 3766.

(5) Direct hydrogenation of 4-vinylcyclohexene-1 over a nickel catalyst gives ethylcyclohexene in good yields. O. C. W. Allenby, U. S. Patent **2,576,743**, November 27, 1951.

(6) K. Alder and H. F. Rickert, *Ber.*, **71**, 373 (1938).