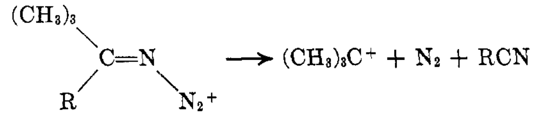
SCHEME II



shown in Scheme II. Actual isolation of **4** helps to confirm the postulated reaction path. This compound was not isolated in the production of α-camphoramic acid from the camphorquinone-3-hydrazones,[1] but it was isolated by Nagata and Takeda[6] from the Beckmann cleavage of *anti*-camphorquinone-3-oxime and proved by them to be a precursor of α-camphoramic acid, which was also isolated.

It is interesting to note that Spielman and Austin,[7] when they applied the Schmidt reaction to the α-diketone benzil, obtained benzoylphenylurea and oxanilide, interpreted as arising from normal Schmidt reactions instead of the cleavage type.

Experimental Section[8]

Several runs were made differing only in method of work-up of product. The method of product treatment given here was chosen for efficiency of analysis. A chloroform solution of hydrazoic acid was prepared by the standard method[9] using an aqueous paste of sodium azide, chloroform, and sulfuric acid. To 11.6 g (0.070 mole) of camphorquinone (**1**), mp 203.5–204.5° (prepared[10] from D-camphor), was added 49.0 ml (0.077 mole) of the hydrazoic acid solution. The resulting solution was cooled to 1°, and 23.8 ml of concentrated sulfuric acid was added, with stirring, over a period of 2 hr, the temperature being maintained between 1 and 7° by means of a cooling bath. Stirring was continued for 1 additional hr. The reaction mixture was in two layers. Subsequent distillation of the chloroform layer showed it to be devoid of product. The acid layer was carefully poured into ice-water, giving 2.3 g of white solid. The filtrate was made alkaline with sodium hydroxide and extracted with three 50-ml portions of ether. The aqueous layer was then acidified with sulfuric acid and subjected to continuous ether extraction for 8 hr. The 2.3 g of solid was then dissolved in sodium hydroxide solution, and the solution was extracted with three 50-ml portions of ether. The ether extracts from the alkaline solutions were combined, and the ether was removed by distillation, leaving 0.1 g of unidentified oil. The sodium hydroxide solution was acidified with sulfuric acid and added to the other acid solution being extracted. Ether extraction was then continued for 17 hr. A white solid was present in the flask with the ether, 7.6 g, mp 163–170°. Infrared analysis indicated this to be approximately 85% **5** and 15% **9**. Pure **5** has a specific rotation[11] of +25° in ethanol while the specific rotation of **9** is +74°. A solution of 1.50 g of the 7.6-g crop in 25.0 ml of ethanol had an observed rotation (at 25–26°) of +3.75° in a 2-dm tube. This is indicative of 88% **5** and 12% **9**. The ether was subjected to distillation until about 75 ml remained. A white solid crystallized, 2.1 g, mp 152–163°. Infrared analysis indicated this to be a 50:50 mixture of **5** and **9**. A solution of 1.50 g of the material in 25.0 ml of ethanol had an observed rotation of +5.60° in a 2-dm tube. This indicates 55% **5** and 45% **9**.

Complete removal of the ether from the remaining solution gave 1.4 g of an oil which had a strong infrared absorption at 4.4 μ. Attempts to induce the oil to crystallize were unsuccessful. The oil was then dissolved in 20 ml of ether, and the solution was first extracted with 10 ml of saturated sodium bicarbonate solution and then with 20 ml of 0.5 *M* sodium hydroxide solution. The sodium hydroxide solution was acidified with hydrochloric acid. The resulting solution was extracted with three 10-ml portions of ether giving 0.3 g of oily solid upon removal of the ether by distillation. The product when recrystallized from water gave as the second crop 0.1 g of pure α-camphornitrilic acid (**4**), mp 159.5–160°. The identity of **4** was established by infrared spectra comparison and mixture melting point with an authentic sample.[12] Acidification of the sodium bicarbonate extract gave a viscous oil which was extracted with 10 ml of petroleum ether (bp 65–110°). Evaporation of the solvent gave 0.1 g of additional **4**. While no more pure **4** was isolated, various crystallization fractions contained small amounts as indicated by infrared spectra. At no time was there any indication of the presence of β-camphornitrilic acid (**8**).

Thus, the major products were α-camphoramic acid (57%) and β-camphoramic acid (14%). They could be separated from one another by fractional crystallization from ethyl acetate giving **5**, mp 177–178.5°, and **9**, mp 178–179.5°. The identity of each was confirmed by comparison of its infrared spectrum with an authentic sample[11] and by mixture melting point determination.

Acknowledgment.—The author wishes to express appreciation to Research Corporation for a Frederick G. Cottrell Grant.

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[6] W. Nagata and K. Takeda, *J. Pharm. Soc. Japan*, **72**, 1566 (1952).

[7] M. A. Spielman and F. L. Austin, *J. Am. Chem. Soc.*, **59**, 2658 (1937).

[8] Melting points are corrected. Optical rotation measurements were made with a Rudolph Routine polarimeter. Infrared spectra were determined on a Perkin-Elmer 137B spectrophotometer. The quantitative spectra were run using the KBr pellet method. The Beer's law plots using absorbance at 8.06 μ for **5** and 7.88 μ for **9** were excellent, but there was some slight overlapping with mixtures of the two. The polarimetric analysis was considered more accurate, and those are the figures used in the final yield calculations.

[9] H. Wolff, *Org. Reactions*, **3**, 327 (1946).

[10] W. C. Evans, J. M. Ridgion, and J. L. Simonsen, *J. Chem. Soc.*, 137 (1934).

[11] M. Delépine and M. Badoche, *Ann. Chim.*, **17**, 171 (1942).

[12] S. Hoogewerff and W. H. van Dorp, *Rec. Trav. Chim.*, **14**, 262 (1895).

The Catalytic Isomerization of 4-Vinylcyclohexene to Bicyclo[3.2.1]oct-2-ene

PAUL R. STAPP

The Research Division, Phillips Petroleum Company,
Bartlesville, Oklahoma

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Previously reported syntheses of bicyclo[3.2.1]oct-2-ene include a four-step synthesis from cyclopentadiene,[1] phosphoric acid dehydration of 2-hydroxymethylbicyclo[2.2.1]heptane,[2] ferric chloride catalyzed isomerization of bicyclo[2.2.2]oct-2-ene,[3] and isomerization of 4-vinylcyclohexene with massive quantities of alkylaluminum compounds.[4] We wish to report a new and convenient method for catalytic isomerization of 4-vinylcyclohexene to bicyclo[3.2.1]oct-2-ene.

Catalysts prepared from lithium aluminum hydride and anhydrous cerous chloride, magnesium chloride, or strontium chloride in benzene diluent were found to effect cyclization of 4-vinylcyclohexene at temperatures of 200–250°. In a typical preparation, 20 mmoles each of lithium aluminum hydride and anhydrous cerous chloride were magnetically stirred overnight in 200 ml of benzene at room temperature under nitrogen; the resulting suspension was then heated with 250 g of 4-vinylcyclohexene in a stirred autoclave at 230°. Work-up and distillation gave recovery of 64% of the materials as C_8 compounds, along with considerable high-boiling residue. Gas chromatographic analysis of the C_8 mixture showed that there were four com-

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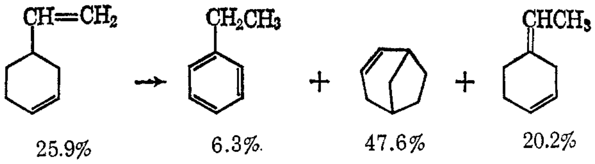
[1] K. Alder, H. Krieger, and H. Weiss, *Chem. Ber.*, **88**, 144 (1955).

[2] H. Krieger, *Suomen Kemistilehti*, **35B**, 136 (1962); *Chem. Abstr.*, **58**, 5535 (1963); J. Knotnerus and H. Schilling, *Rec. Trav. Chim.*, **83**, 1185 (1964).

[3] A. F. Bickel, J. Knotnerus, E. C. Kooyman, and G. C. Vegter, *Tetrahedron*, **9**, 230 (1960).

[4] J. Casanova, French Patent 1,351,716 (1964).

pounds present, two of which were identified as unreacted 4-vinylcyclohexene and ethylbenzene by comparison of their retention times with those of authentic samples. Hydrogenation of the four-component mixture gave only two compounds, ethylcyclohexane and bicyclo[3.2.1]octane, identified by comparison of retention times and mass spectra with those of an authentic sample.[5] The percentage of bicyclo[3.2.1]octane in the saturated hydrocarbon mixture was nearly identical with the percentage of the major constituent (*i.e.*, the bicyclic olefin) in the precursor olefins and indicated that the fourth compound was a 4-vinylcyclohexene position isomer which had been reduced to ethylcyclohexane. Pure samples of the bicyclic olefin and this 4-vinylcyclohexene isomer were isolated by preparative gas chromatography; the isomer was identified as 4-ethylidenecyclohexene by comparison of its retention time and infrared spectrum with those of an authentic sample.[6] Confirmation of the position of the double bond in the bicyclic olefin was afforded by examination of its nmr spectrum. The spectrum showed two vinyl protons (not equivalent), three α protons, and seven other protons in complete agreement with the structure of bicyclo[3.2.1]oct-2-ene. Thus, it appeared that the following reactions of 4-vinylcyclohexene had occurred; the percentage of each compound in the C_8 mixture is indicated.



In this particular reaction using cerous chloride as the metal halide component, the 4-vinylcyclohexene conversion was 85%; substitution of magnesium chloride or strontium chloride gave similar results with somewhat lower conversions. Changing the cerous chloride/lithium aluminum hydride catalyst ratio to 1:2 increased the conversion to 98% at 230°, while lithium aluminum hydride alone gave only a 9% conversion to the same products. Cerous chloride/calcium hydride and titanium tetrachloride/lithium aluminum hydride combinations were ineffective catalysts for the cyclization reaction.

A brief investigation into purification of the bicyclic olefin showed that simple atmospheric pressure fractionation through a 3/4 in. × 24 in. column packed with 1/4-in. Penn State protruded stainless steel packing readily afforded product purities of 80–88% with the principal contaminant being ethylbenzene.

Experimental Section

Materials.—Phillips Petroleum Co. pure grade 4-vinylcyclohexene was dried and stored over indicating mole sieves under nitrogen in capped beverage bottles and was transferred with a hypodermic syringe. Reagent grade benzene was dried, stored, and transferred similarly. Anhydrous metal halides and lithium aluminum hydride were commercial materials, stored, weighed, and transferred in a nitrogen-filled glove box.

Isomerization of 4-Vinylcyclohexene to Bicyclo[3.2.1]oct-2-ene.—A typical preparation is given. In the glove box, 0.76 g (20 mmoles) of lithium aluminum hydride and 4.92 g (20 mmoles) of anhydrous cerous chloride were weighed into an 8-oz beverage bottle. A magnetic stirring bar was introduced and the bottle was sealed using a neoprene liner and a perforated cap. The bottle was removed from the drybox, 200 ml of dry benzene was introduced with a syringe, and the mixture was stirred overnight on a magnetic stirrer. The resulting catalyst suspension was introduced into a stirred autoclave (flushed with and maintained under a dry nitrogen atmosphere), 250 g of 4-vinylcyclohexene was introduced, and the autoclave was sealed, pressure tested with dry nitrogen, and stirred and heated at 230° for 6 hr. After cooling, the autoclave was vented and opened, and the resulting mixture was filtered. After being washed thoroughly with water and being dried over anhydrous magnesium sulfate, the benzene and C_8 materials were distilled through a short column to a head temperature of 150°. The resulting distillate was analyzed on an F & M Model 720 gas chromatograph equipped with a 25-ft 20% Dow Corning-200 silicone oil on Chromosorb P column operated isothermally at 150°. The order of elution from the column was benzene, 4-vinylcyclohexene, ethylbenzene, bicyclo[3.2.1]oct-2-ene, and 4-ethylidenecyclohexene.

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[5] J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936).

[6] Dr. E. T. Kittleman, unpublished results.

A Reinvestigation of the Reduction of 9-Carboethoxybicyclo[6.1.0]nona-2,4,6-triene

TERRY L. BURKOTH

Department of Chemistry, Stanford University, Stanford, California

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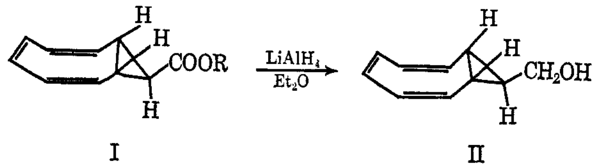
Akiyoshi and Matsuda[1] and Phillips[2] isolated and characterized 9-carboethoxybicyclo[6.1.0]nona-2,4,6-triene (I, R = CH_2CH_3) as the addition product of carboethoxycarbene and cyclooctatetraene. Although his experimental work and conclusions were in exact agreement with the Japanese workers, Phillips found it necessary to postulate an interaction of the ester and triene chromophores in I to rationalize the absorption of the adduct at lower than the expected wavelength[3] in the ultraviolet. Evidence to support this postulation was provided by a shift from the λ_{max} of 245 mμ of the ester to 263 mμ in the corresponding alcohol upon lithium aluminum hydride reduction "in the usual fashion." The alcohol was purified by distillation and characterized as II on the basis of analysis, quantitative hydrogenation, and analysis of a crystalline derivative formed by Diels–Alder reaction with N-(*p*-bromophenyl)maleimide.



Two pieces of information subsequently appeared in the chemical literature which cast a shadow of doubt on the reduction results of Phillips. Firstly, a facile, thermal, valence-bond isomerization of the parent bicyclo[6.1.0]nona-2,4,6-triene system (III) to the *cis*-bicyclo[4.3.0]nona-2,4,7-triene (IV) was reported by Vogel[4] (and in the case of I (R = CH_2CH_3) by Bangert

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[1] S. Akiyoshi and T. Matsuda, *J. Am. Chem. Soc.*, **77**, 2476 (1955).

[2] D. D. Phillips, *ibid.*, **77**, 5179 (1955).

[3] A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, *ibid.*, **74**, 4867 (1952), as cited.[2]

[4] E. Vogel and H. Kiefer, *Angew. Chem.*, **73**, 548 (1961); E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, 673 (1963).