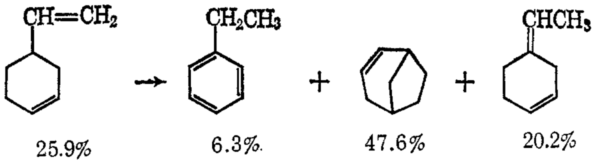
pounds present, two of which were identified as unreacted 4-vinylcyclohexene and ethylbenzene by comparison of their retention times with those of authentic samples. Hydrogenation of the four-component mixture gave only two compounds, ethylcyclohexane and bicyclo[3.2.1]octane, identified by comparison 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.

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

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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.

I II

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

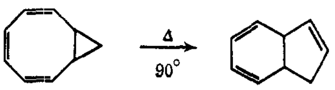
[6] Dr. E. T. Kittleman, unpublished results.

[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).

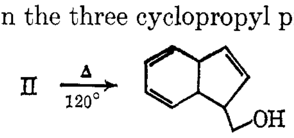


III IV

and Boekelheide[5]). Secondly, an assignment of the stereochemistry of I (as shown) on the basis of nuclear magnetic resonance (nmr) coupling constants by Bangert and Boekelheide[5] appeared to preclude, by reason of molecular geometry, the interaction postulated by Phillips. The present reinvestigation of the reduction of I (as the pure acid, R = H) justified the doubt and provided another example of the above valence-bond isomerization.

The pure acid I (R = H) was obtained by alkaline hydrolysis as described by Akiyoshi and Matsuda[1] (mp 162–163° uncor). This acid was reduced directly with lithium aluminum hydride in ethyl ether at room temperature to yield a single alcohol (by thin layer chromatography, tlc) which differed from that of Phillips by exhibiting $\lambda_{\max}$ 246 mμ (ϵ 3400). The position of the ultraviolet absorption maximum, consistent with those of all reported bicyclo[6.1.0]nonatrienes,[1,2,4-6] and the simple, expected nmr spectrum identify the structure and stereochemistry[7] of this alcohol as II. The nmr spectrum in carbon tetrachloride (tetramethylsilane as internal standard) contained, in addition to one proton which exchanged upon D_2O addition, a singlet at δ 5.94 (4 H), a broadened singlet at 5.81 (2 H), a doublet at 3.55 (J = 6.5 cps) (2 H), a doublet at 1.33 (J = 5.5 cps) (2H), and an unsymmetrical five-line multiplet centered at 0.65 (1 H). Heating of this alcohol either as a neat liquid or in a solution gave the alcohol characterized by Phillips, $\lambda_{\max}$ 263 mμ.

In one such thermolysis the [6.1.0] alcohol was prepared as an nmr sample in pentafluorobromobenzene,[8] degassed, and sealed under argon. The nmr spectrum, unchanged from that in carbon tetrachloride except for the observation of three distinct vinyl absorptions, was recorded and then the sample was heated at 120° in approximation of conditions of its isolation by Phillips. In 20 min >95% of the starting alcohol was observed to have rearranged.[9] The nmr spectral change, best expressed only qualitatively owing to lack of an internal reference, involved an increase in complexity and broadening of the vinyl absorption (6 H), a shift of one upfield proton to the region of those two on carbon bearing oxygen, and a shift of the two remaining upfield protons to the region δ 2.5–3.0. This spectrum is consistent with the rearrangement II → V, wherein the three cyclopropyl protons are converted to two allylic methine protons and one proton both doubly allylic and methine. Proof of the identity of this resulting alcohol (VI) with that obtained by Phillips was found in preparation, from this nmr sample, of the adduct with N-(p-bromophenyl)maleimide,[10] mp 199–200° (lit. mp 198–201°). A mixture melting point with authentic material[11] was not depressed and the infrared spectra (KBr) were superimposable.



V

Experimental Section

Reduction of 9-Carboxybicyclo[6.1.0]nona-2,4,6-triene.—To a magnetically stirred suspension of 100 mg (2 mmoles) of lithium aluminum hydride in 10 ml of sodium-dried ether at room temperature was added dropwise under nitrogen a solution of 50 mg (0.31 mmoles) of the acid I (R = H) in 5 ml of sodium-dried ether. The addition took ~15 min and the resulting suspension was stirred at room temperature for an additional 2 hr. At this time, the excess lithium aluminum hydride was decomposed cautiously and with ice cooling by adding 1 ml of a saturated aqueous solution of sodium potassium tartrate. An additional 10 ml of ether was added to permit easy stirring for 10 min more, at which time the mixture was filtered on sintered glass with light suction and concentrated under water vacuum at room temperature to provide 35 mg of 9-hydroxymethylbicyclo[6.1.0]nona-2,4,6-triene (II). An additional 11 mg of II could be obtained by acidification of the aluminum salts of the filter cake with 10% sulfuric acid and extraction with three 10-ml portions of ether and 5 ml of saturated sodium bicarbonate, brief drying over magnesium sulfate, filtration, and concentration. The combined product, 46 mg (100% theoretically) of a slightly yellow oil,[12] was dissolved in carbon tetrachloride and again concentrated to remove traces of ether. Samples thus prepared provided the physical data in the discussion. Thermal instability plus the anticipation of only isomeric impurities discouraged preparation of a sample for analysis.

Acknowledgment.—The author thanks Dr. E. E. van Tamelen for valuable discussions and Stanford University for a predoctoral research assistantship. This research was supported by U. S. Army Grant DA-31-124-ARO-D-285.

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(5) K. F. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, **86**, 905 (1964).

(6) A. C. Cope, P. T. Moore, and W. R. Moore, *ibid.*, **80**, 5505 (1958).

(7) See ref 5 above and especially ref 7 therein.

(8) Chosen for its high boiling point (137°), which facilitated degassing as well as the thermolysis experiment, and its availability (Imperial Smelting Corp. Ltd., London).

(9) It is noteworthy that, in an identical experiment in the case of the methyl ester I (R = CH_3), the time required to attain the same degree of rearrangement was ~13 hr. This amounts to a crude rate difference of a factor of 40 and explains isolation of the correct ester by early workers and isolation of only the rearranged alcohol without a clue to the rearrangement involved.

(10) To our knowledge this simple compound has not been reported in the literature. It was prepared without incident by the general method of M. Cava, *et al.*, *Org. Syn.*, **41**, 93 (1961). The product, pale yellow crystals, mp 122–123°, had as its major absorptions in the infrared 5.80, 6.70, 7.15 (s), 7.23, 8.7, and 12.0 μ, that is, essentially the spectrum of the known N-phenylmaleimide. The nmr spectrum in chloroform-d displayed an A_2B_2 pattern centered at δ 7.43 (4H) and a singlet at 6.83 (2 H).

(11) The author is grateful for a sample of the authentic N-(p-bromophenyl)maleimide adduct kindly provided by Dr. Phillips.

(12) This oil crystallized upon standing for several days at −20°. A sample was recrystallized from pentane to a constant melting point of 60–61°.

Catalytic Decomposition of Tetrachlorodiazocyclopentadiene. Formation of Spirocyclic Olefins

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The reaction of 1,2,3,4-tetrachlorodiazocyclopentadiene (1) in several acetylenes has been examined as part of a continuing study on this extraordinarily

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(1) Allied Chemical Corp. Research Fellow, 1963–1966.