

the ratio of 4:5:6 was 73:12:15, with platinum, 17:11:72. Both 4 and 6, and probably part of 5, are derived from the norcaradiene 2; its apparent rate of hydrogenation thus is higher than that of the cycloheptatriene 1. Isolation of 4 and 6 provides supporting evidence for the presence of the norcaradiene 2 in the equilibrium mixture although it constitutes no proof by itself since rearrangement of the cycloheptatriene 1 to the norcaradiene 2 could have taken place on the catalyst.<sup>12,13</sup>

(12) By comparison, hydrogenation of cycloheptatriene over rhodium gave only cycloheptane; less than 0.005% norcarane could have been detected. Catalytic hydrogenation of ethyl 7-cycloheptatrienecarboxylate, on the other hand, gave considerable amounts (up to 14%) of ethyl *exo*-7-norcaranecarboxylate in addition to ethyl cycloheptanecarboxylate and traces of ethyl cyclohexylacetate. The chemical shift of the protons on C-1 and C-6 in ethyl 7-cycloheptatrienecarboxylate (triplet at  $\tau$  4.63 in  $\text{CFCl}_3$ ), however, is essentially the same as the corresponding shift in cycloheptatriene ( $\tau$  4.72 in  $\text{CDCl}_3$ ); the equilibrium concentration of ethyl 7-norcaradienecarboxylate thus must be very small. Details will be described in a forthcoming publication.

(13) The adduct of bis(trifluoromethyl)carbene to benzene has recently been shown to have the cycloheptatriene structure: D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 657 (1965).

E. Ciganek

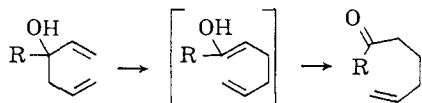
Contribution No. 1048, Central Research Department  
Experimental Station, E. I. du Pont de Nemours and Company  
Wilmington, Delaware

Received December 21, 1964

### The Thermal Vapor-Phase Rearrangement of 1,5-Hexadien-3-ol. Preparation of 5-Hexenal<sup>1</sup>

Sir:

Berson and Jones<sup>2</sup> have recently reported the rearrangement of two pairs of epimeric 3-hydroxy-1,5-hexadienes in the bicyclo series to the corresponding  $\delta,\epsilon$ -unsaturated ketones according to the scheme



and have suggested the term "oxy-Cope rearrangement" for this transformation. These communications prompt us to report our studies on the parent compound, which is devoid of the complications inherent in a bicyclic system.

We were originally interested in a facile preparation of 1,3,5-hexatriene from 1,5-hexadien-3-ol (I), readily available *via* reaction of the allyl Grignard reagent and acrolein.<sup>3</sup>

Although it has been postulated<sup>4</sup> that the dehydration of any of the six isomeric hexadienols would give hexatriene, the only previously reported attempt<sup>5</sup> at vapor-phase dehydration of I resulted in resins.

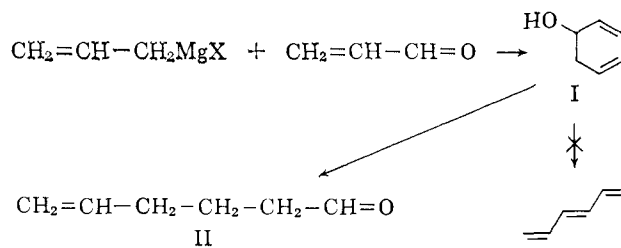
(1) From the M.S. Thesis of L. Levasseur, June 1964.

(2) J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, **86**, 5017, 5019 (1964).

(3) L. W. Butz, E. W. Butz, and A. M. Gaddis, *J. Org. Chem.*, **5**, 171 (1940).

(4) J. M. Shackelford, W. A. Michalowicz, and L. H. Schwartzman, *ibid.*, **27**, 1631 (1962).

(5) O. Kiun-Houo, *Ann. Chim.*, **13**, 175 (1940).



When we passed the vapors of I through a 25-cm. column filled with 8–20 mesh alumina, maintained at 300° in a nitrogen atmosphere, we were able to detect minute traces of hexatriene in the product by means of its characteristic ultraviolet spectrum. Vapor phase chromatography indicated two main constituents in that fraction of the product boiling above 80°, one of which was shown to be surviving I. The second component, II, appeared to be an unsaturated aldehyde. When the dehydration attempt was repeated at 400°, none of I appeared to survive. Subsequent trials indicated that alumina was not necessary for the reaction<sup>6</sup>; indeed, a column packed with glass wool gave the same percentage of II in the higher boiling fraction and much less low boiling material. Under optimum conditions for the transformation of I  $\rightarrow$  II (distillation of I through a 50-cm. column packed with 3-mm. Pyrex helices and maintained at 380°) 92% of the product fraction boiling above 80° consisted of II. This corresponds to an over-all yield of 57% based on I.

The structure of the rearrangement product II is based on the following evidence. Molecular weight determinations and carbon-hydrogen analyses of the compound and its 2,4-dinitrophenylhydrazone were consistent with the formula  $\text{C}_6\text{H}_{10}\text{O}$ . The compound reduced Tollens' reagent and gave positive Schiff and Baeyer tests. The infrared spectrum exhibited a strong carbonyl band (in  $\text{cm}^{-1}$ ) at 1735, an aldehydic C-H band at 2700, and bands consistent with an isolated terminal vinyl group at 915, 995, 1300, 1420, 1650, and 3075. The ultraviolet spectrum consisted only of end absorption in the 220–230  $\mu$  region, no further maxima in the region below 280  $\mu$ , and only a small ill-defined peak ( $\epsilon < 10$ ) at about 290  $\mu$ . Further chemical structure proof seemed essential since our other physical constants<sup>8</sup> were not in sufficient agreement with the two reported preparations<sup>9,10</sup> of 5-hexenal. We were particularly concerned with the unambiguous determination of the linearity of the carbon chain and the position of unsaturation. Consequently, the compound was found to absorb 102% of the amount of hydrogen (over Pd-C) calculated for the saturation of one double bond, and the 2,4-dinitrophenylhydrazone derivative of the hydrogenation product showed no melting point depression on admixture with an authentic sample of the same derivative

(6) We initially experienced some difficulty with vapor phase chromatography of the hexadienol. Peaks due to formation of the rearrangement product appeared in the chromatograms of highly purified hexadienol if the injection port or column temperatures exceeded 200° and particularly if 10-ft. rather than 2-ft. columns were used.

(7) As ascertained by vapor phase chromatography and confirmed by quantitative 2,4-dinitrophenylhydrazone precipitation.

(8) B.p. 120–121°, lit.<sup>9</sup> b.p. 118–118.5°;  $n_D^{20}$  1.395, lit.<sup>9</sup>  $n_D^{20}$  1.4109; m.p. of 2,4-dinitrophenylhydrazone 101–101.5°, lit. 93–94°,  $96^\circ$ .<sup>10</sup>

(9) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953);

(10) R. R. Burford, F. R. Hewgill, and P. R. Jeffries, *J. Chem. Soc.*, 2937 (1957).

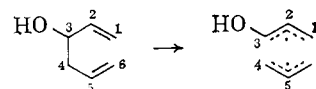
of *n*-caproaldehyde. Oxidation of the suspected hexenal with permanganate in acetone according to the method of Nunn<sup>11</sup> afforded glutaric acid, thereby unequivocally establishing the structure of the rearrangement product as 5-hexenal.

As we were mainly interested in the utilization of the rearrangement for the syntheses of  $\Delta^5$ -unsaturated carbonyl compounds on a preparative scale, we did not fully investigate the nature of the low-boiling fraction. The relative amount of this fraction increased with increasing temperatures and also appeared to be a function of the column packing. Thus, alumina gave the largest amount of low-boiling components, possibly due to acid-catalyzed cracking reactions. Acrolein was always present in small amounts, as could be readily ascertained by its characteristic odor, its v.p.c. retention time, and its 2,4-dinitrophenylhydrazone.

Berson and Jones<sup>2</sup> have suggested the occurrence of several competing reactions which the diradical intermediate may undergo, among which are single inversion, double inversion, and hydrogen transfer.<sup>12</sup> In our system both single inversion (by C-1-C-4 bond formation) and double inversion (by C-1-C-6 bond formation) would give rise to the same end product. Single

(11) J. R. Nunn, *J. Chem. Soc.*, 313 (1952).

(12) Hydrogen transfer in our system leads to the formation of the observed acrolein. We did not attempt to isolate or identify any other three-carbon species such as allene or methylacetylene.



inversion by C-6-C-3 bond formation re-forms the starting material.

A cyclic four-membered transition state, as required by either single-inversion pathway, seems unlikely to us on steric grounds. However, in the internal Diels-Alder cyclization of hexatriene to cyclohexadiene, a reaction which appears extremely similar to the one discussed here, the formation of a secondary product has been reported.<sup>13</sup> Since the nature of the minor product was not established a vinylcyclobutene structure remains a possibility.

In the rearrangement of simple 1,5-hexadiene-3-ols, the utilization of a nonsymmetrical radical intermediate, produced by substitution at C-4 or C-6, should permit a differentiation among these different mechanistic possibilities. We are currently engaged in a study to establish the scope of the reaction, intended as a general method for the preparation of 5,6-unsaturated carbonyl compounds.

(13) G. F. Woods and A. Viola, *J. Am. Chem. Soc.*, 78, 4380 (1956).

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Received January 4, 1965

## Book Reviews

**Preparative Inorganic Reactions. Volume 1.** By WILLIAM L. JOLLY, Department of Chemistry, University of California, Berkeley, Calif. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. ix + 271 pp. 16 × 24 cm. Price, \$9.00.

The progress in the ten areas of preparative inorganic chemical research in concise, well-written form has been collected into the first volume of this new series. General preparative procedures for each topic are discussed in some detail and are followed by specific synthetic details illustrating these methods. The aim "to develop in inorganic chemists the same 'chemical intuition' which has been the foundation of the great synthetic achievements in organic chemistry," falls short. Occasionally references to mechanistic ideas have been made and most of the authors have correlated the reaction conditions for the synthetic procedures they are discussing; yet, the over-emphasis on what to do or what has been done, instead of on how or why something happens, may cause readers to feel that much of the synthetic inorganic chemistry presented herein is more art than science.

The reviews begin with very general topics; namely, coordination polymers by John C. Bailar, Jr., and optically active coordination compounds by Stanley Kirschner. Although both are well written, the reviewer was disturbed to find no mention in the first chapter of the interesting silicon phthalocyanine polymers, which have Si-O-Si-O-type linkages, and to read about racemic compounds and racemic mixtures in Chapter 2 for two pages before they are defined. The latter chapter gets bogged down at times in a concern over dissymmetry as separate from asymmetry so why not call all optically active compounds  $S_n$ -less compounds, since the definitive tests for potential optical activity is the lack of any  $S_n$  symmetry elements.

Also, the formulas on pages 46 and 48 should be multiplied by 100% rather than by 100.

Reaction principles for metal derivatives of unsaturated  $\beta$ -ketoamines and the corresponding aldamines have been well organized by Dean F. Martin in Chapter 3. (Even though n.m.r. evidence to the contrary has been known for several years, the ketimine nomenclature has been used in this volume.) The tabulations of the note-worthy chapters which follow on metal carbonyls by Jack C. Hileman and on halide and oxyhalide complexes of the titanium, vanadium, and chromium subgroups by G. W. A. Fowles should serve as guides for contributors to future volumes of this series. For completeness Professor Fowles could have included the  $W_2Br_9^{3-}$ , the  $Mo_8X_8^{4+}$ , and  $W_8X_8^{4+}$  complexes, since all have been known for many years. Fewer illustrations of commercial equipment in the carbonyl chapter might have lowered the price of this book and would not have been missed. Numerous typographical errors also were noted in this otherwise superb chapter.

The volume is rounded out by chapters on anhydrous metal nitrates, halogen and halogenoid derivatives of silanes, saline hydrides, sulfur-nitrogen-fluorine compounds, and hypohalites and compounds containing the -OX group. These chapters have been written by C. C. Addison, N. Logan, Alan G. DacDiarmid, Charles E. Messer, Oskar Glemser, and Stanley M. Williamson, respectively. Tabulation of most of the boring one- and two-sentence paragraphs in Chapter 7 and donation of Chapter 9 to *Inorganic Syntheses* (since the chapter is a preface and six detailed syntheses in the style of that series) would have improved the latter part of the volume considerably. Alternatively, the latter chapter could have included other sulfur-nitrogen-halogen compounds. The editor's use of random-sized areas of inorganic chemistry is probably the most disappointing aspect of this new series.