

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, LABORATORIES OF THE MOUNT SINAI HOSPITAL]

The Partial Reduction of an Enyne System by Lithium Aluminum Hydride

By J. D. CHANLEY AND HARRY SOBOTKA

We have found that lithium aluminum hydride¹ is effective as a selective reducing agent for the triple bond in the enyne system of 1-(1'-cyclohexenyl)-1-butyne-3-ol (I); the dienol, trisnor- β -ionone (II) was obtained in 70% yield. In contrast, catalytic hydrogenation of this triple bond failed to yield more than spectroscopically detectable traces of the dienol. When the catalytic hydrogenation was interrupted upon absorption of 1 mole of hydrogen, a mixture of saturated or mono-unsaturated reaction products together with unchanged starting material was found.

Rearrangement, during reduction, of the carbon skeleton or allylic shift of the hydroxyl group was excluded, since complete hydrogenation yielded 1-cyclohexyl-3-butanol (III) and the oxidation of the latter led to the known 1-cyclohexyl-3-butanone (IV). By oxidation according to Oppenauer the alcohol II was, furthermore, converted to the corresponding ketone, 1-(1'-cyclohexenyl)-1-buten-2-one (V), the trisnor analog of β -ionone. After the preparation of this paper, two publications by Heilbron and co-workers^{2a,b} have appeared, which describe the preparation of the enynol (I)^{2a} by the same method as employed by us, but of the dienone (V)^{2b} by two other methods; the physical constants of our compounds and their derivatives agree with those given by Heilbron, *et al.*

The synthesis of trisnor- β -ionone permits the comparative examination of the ultraviolet absorption spectra of this group. Table I gives the absorption maxima and the molecular extinction coefficients for the dienone, its derivatives and precursors, and the same data for the corresponding enynes.³

TABLE I

ABSORPTION SPECTRA OF CYCLOHEXENYL ETHYLENES AND ACETYLENES

R	C ₆ H ₉ CH=CHR		C ₆ H ₉ C≡CR	
	λ_{\max} , m μ	ϵ_{\max}	λ_{\max} , m μ	ϵ_{\max}
-H	230 ⁷	8,500	223 ⁴	10,400
-CHOH·CH ₃	233.5	24,300	227.5	12,500
-CO·CH ₃	280	26,700	274 ⁴	9,500
-C[·NNHCONH ₂]CH ₃	290	45,000	285 ⁴	14,500
-C[·NNHC ₆ H ₄ (NO ₂) ₂]CH ₃	390	30,000	372 ⁵	27,800

The λ_{\max} of these dienes is regularly 5-7 m μ higher than that of the analogous enynes. As was to be foreseen on the basis of numerous examples adduced by Heilbron and co-workers⁴ the

(1) Nystrom and Brown, *THIS JOURNAL*, **69**, 1179, 2548 (1947); **70**, 491 (1948).

(2) (a) Heilbron, Jones, Lewis, Richardson and Weedon, *J. Chem. Soc.*, 742 (1949); (b) Heilbron, Jones, Richardson and Sondheimer, *ibid.*, 737 (1949).

(3) Sobotka and Chanley, *THIS JOURNAL*, **70**, 3914 (1948).

(4) Heilbron, *et al.*, *J. Chem. Soc.*, **77**, 84 (1945); Heilbron, *et al.*, *ibid.*, 54 (1946); Haynes and Heilbron, *ibid.*, 1585 (1947); Jones and McCombie, *ibid.*, 26 (1943).

extinction was about twice as strong. A comparable difference in λ_{\max} of 8 m μ has also been observed for the pair β -ionone and dehydro- β -ionone.⁵ This difference in λ_{\max} between the spectra of dienes and enynes is not found in open chain compounds⁴ such as 2,4-pentadien-1-ol and 2-penten-4-yn-1-ol or 3,5-hexadien-2-ol and 3-hexen-5-yn-2-ol; however, the extinction coefficients in these cases are twice as high in the dienes, compared to the enynes.

Experimental

All reactions were carried out under nitrogen. The ultraviolet absorption spectra were obtained with a Beckman spectrophotometer Model DU in 95% ethanol solutions. All melting points were corrected. The microanalyses were performed by Elek Microanalytical Laboratories, Los Angeles 16, Calif.

DL-1-(1'-Cyclohexenyl)-1-butyne-3-ol (I).—To an ice-cold suspension of 0.65 mole of the Grignard compound of 1-ethynylcyclohexene³ in one liter of dry ether, 28.6 g. (0.65 mole) acetaldehyde was added during a period of two and one-half hours. The reaction mixture was stirred for additional three hours at room temperature, decomposed with saturated ammonium chloride solution and worked up in the usual manner; yield of carbinol (I): 62 g. (59%), b. p. 99-100° at 3 mm. (distilled and stored in the presence of hydroquinone).

Anal. Calcd. for C₁₀H₁₄O: C, 79.95; H, 9.39. Found: C, 79.84; H, 9.42.

DL-1-(1'-Cyclohexenyl)-1-buten-3-ol (II).—Twelve grams of the preceding compound (I) (0.08 mole) in 100 ml. of absolute ether was added over a period of one-half hour to a solution of 1.87 g. (0.05 mole) of lithium aluminum hydride in 250 ml. of absolute ether. A voluminous precipitation occurred; the mixture was then refluxed and stirred for three hours, the precipitate having dissolved at the end of the first hour. After decomposition with water and dilute sulfuric acid, the product was isolated in the customary manner; yield, 8.5 g. (70%); b. p. 98-100° at 3-4 mm. The presence of traces of hydroquinone during distillation is vital for the prevention of polymerization.

Anal. Calcd. for C₁₀H₁₆O: C, 78.80; H, 10.58. Found: C, 78.92; H, 10.53.

On careful redistillation the physical constants obtained for the two carbinols are:

	Enynol (I)	Dienol (II)
B. p. at 2 mm., °C.	93.5-94
B. p. at 1.5 mm., °C.	90
n_D^{25}	1.5197	1.5220
d_4^{25}	0.9740	0.9572
MR found	46.84	48.52
MR calcd.	45.25	46.78
Exaltation	1.59	1.74
λ_{\max} , m μ	227.5	233.5
ϵ_{\max}	12,500	24,300
$\lambda_{\text{infl.}}$, m μ	229

The slight increase rather than diminution of the refractive index and of the exaltation of the molecular refraction upon partial reduction is peculiar.^{4,6}

(5) Sobotka and Chanley, *THIS JOURNAL*, **71**, 4136 (1949).

(6) Isler, Huber, Ronco and Kofler, *Helv. Chim. Acta*, **30**, 1911 (1947); *Festschrift f. E. Borell*, p. 31 (Basle, 1946).

The shift of λ_{\max} by 6 $m\mu$ toward higher wave lengths in the diene is analogous to the difference between λ_{\max} of cyclohexenylacetylene³ (223 $m\mu$) and that of cyclohexenylethylene⁷ (230 $m\mu$), a pair which shows, however, no appreciable difference in extinction.

DL-1-Cyclohexyl-3-butanol (III).—Two grams (0.013 mole) of the dienol (II) was hydrogenated completely over 100 mg. of platinum oxide in 100 ml. of ethanol. Hydrogen uptake at 26° and 750 mm.: calculated for two double bonds, 662 ml.; found (corrected for uptake by the catalyst), 622 ml. The saturated product was obtained in the theoretical yield and boiled at 84° at 4 mm.; n_D^{20} 1.4670. Oxidation by sodium hypiodite according to Shriner and Fuson⁸ yielded iodoform.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.91; H, 12.91. Found: C, 77.26; H, 12.57.

1-Cyclohexyl-3-butanone (IV).—A solution of 1.1 g. of cyclohexylbutanol (III) in 10 ml. of glacial acetic acid and 0.82 g. of chromic anhydride was heated gently on the steam-bath for thirty minutes and permitted to stand overnight. The mixture, poured into 50 ml. of water, was extracted with petroleum ether, which was then washed and dried. The residue was evaporatively distilled at 16 mm. and 50° bath temperature; yield, 0.85 g. (76%); n_D^{20} 1.4590; reported⁹ n_D^{20} 1.4586.

The semicarbazone of IV, recrystallized from aqueous methanol, melted at 166–168°; reported⁹ m. p. 163°.

The 2,4-dinitrophenylhydrazone of IV, recrystallized from methanol, melted at 106°; reported⁹ m. p. 106°.

Trisnor- β -ionone (V).—A mixture of 1.8 g. (0.118 mole) of trisnor- β -ionol (II) and 4.55 g. of aluminum *t*-butoxide in 90 ml. of dry acetone plus 135 ml. of dry benzene were refluxed under nitrogen for forty-eight hours. After decomposition with 150 ml. of 2 *N* sulfuric acid, the reaction product was worked up in the customary manner. According to the spectral data, the crude distillate (1.5 g.) of b. p. 92–95° at 4 mm. consisted of five-sixth ketone and the rest starting material. The ketone was converted into the semicarbazone. After one recrystallization from ethanol, decomposition according to Heilbron⁹ and subsequent evaporative distillation at 47° bath temperature and 12 mm. pressure yielded 0.77 g. (43% yield) of the

(7) Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940).

(8) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1940, p. 53–54.

(9) Heilbron, E. R. H. Jones and Richardson, *J. Chem. Soc.*, 287 (1949).

pure ketone; n_D^{20} 1.5500, λ_{\max} 280 $m\mu$, ϵ_{\max} 26,700. The secondary maximum at 234 $m\mu$, due to the presence of the dienol in the crude product was not completely eliminated.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.57; H, 9.55.

The semicarbazone, melting after two recrystallizations at 201–203° (dec.), had a λ_{\max} of 290 $m\mu$, ϵ_{\max} 45,000; it turns yellow on exposure to light.

Anal. Calcd. for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.58; H, 8.13; N, 19.78.

The 2,4-dinitrophenylhydrazone, recrystallized three times from absolute ethanol, consisted of garnet-red crystals melting at 199–200° (dec.); λ_{\max} 390 $m\mu$, ϵ_{\max} 30,000.

The 4-phenylsemicarbazone, buff-colored platelets recrystallized from ethanol, m. p. 199–200° (dec.).

Catalytic Reduction of the Enynol I.—Various attempts to reduce selectively the triple bond of I with hydrogen over a 0.3% palladium-calcium carbonate catalyst in ethyl acetate yielded mixtures which were subjected to fractional distillation. The lowest boiling fractions, comprising less than 20% of the reduction product, showed, in typical runs, λ_{\max} between 231 and 233.5 $m\mu$ with ϵ_{\max} from 4000 to 6600 and n_D^{20} of 1.4960, supposedly a mixture of one-fourth or less (5% of the total yield) of dienol with three-fourths non-conjugated carbinol of low refractive index (either compound III or trisnor-dihydroionol). The higher fractions, comprising the bulk of the mixture, converged toward λ_{\max} 229 $m\mu$ with ϵ_{\max} up to 11,600 and n_D^{20} 1.5086, with starting material predominating. Similar results were obtained with Raney nickel in ethyl acetate, whereas no reduction at all was achieved with copper-zinc in alcohol.

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Summary

Lithium aluminum hydride serves for the partial hydrogenation of the triple bond to a double bond in cyclohexenylbutynol. The resulting trisnor- β -ionol was oxidized to trisnor- β -ionone. The ultraviolet absorption spectra of cyclohexenyl ethylenes and acetylenes are discussed.

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Grignard Reactions. XX.¹ Effect of Cuprous Chloride on the Reaction of *t*-Butylmagnesium Chloride and Trimethylacetyl Chloride

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In a continuation of the study of the reaction between acid halides and Grignard reagents we have now found conditions which make it possible to obtain consistently high yields of a highly branched ketone from a reaction which heretofore has given mainly reduction products. In earlier attempts to prepare hexamethylacetone from *t*-butyl Grignard reagent and trimethylacetyl chloride² no ketone was formed using a one-to-one ratio of the Grignard reagent and the acid

chloride. With a five-to-one ratio of reagents and using reverse addition at -10° , there was obtained a 32% yield. We have now shown that through the use of cuprous chloride with a one to one ratio of reactants, yields of 70 to 80% hexamethylacetone are readily obtained.

The role of cuprous chloride in such reactions was suggested when an 87% yield of 2,4,4-trimethyl-3-hexanone was obtained by treating *t*-amylmagnesium chloride and isobutyryl chloride in a copper reactor.³ Previously, only 10 to

(1) For Paper XIX see Stehman, Cook and Whitmore, *This Journal*, **71**, 1509 (1949).

(2) Whitmore, *Rec. trav. chim.*, **57**, 562 (1938).

(3) In the original note¹ this compound was erroneously reported as 2,4,4-trimethyl-3-pentanone.