

packed in two layers of twelve above and twelve below the plane of the hexagon, so that the tellurium and molybdenum atoms are octahedrally coordinated.

The detailed structures of both the ammonium and potassium salts are now under analysis, and will be described in full in a forthcoming paper.

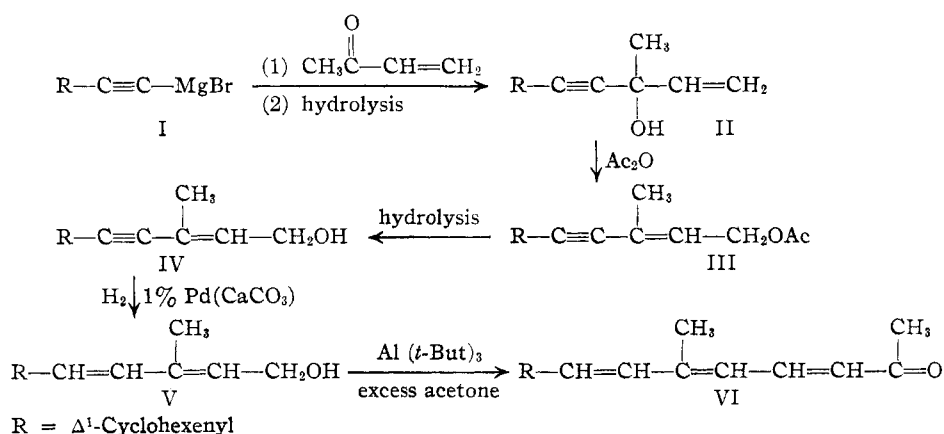
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THE SYNTHESIS OF 1-[CYCLOHEXEN-1'-YL]-3-METHYL-1,3,5-OCTATRIEN-7-ONE (C₁₅ KETONE)¹

Sir:

Using the new approach to vitamin A synthesis,² we wish to report an alternative route which makes possible the synthesis of vitamin A and its analogs. The C₁₅ ketone (VI) was thus synthesized by the following series of reactions:



The carbinol (II) was obtained in yields of 45–50%; b. p. 45–48° (10⁻⁴ mm.); *n*_D²⁵ 1.5135; *d*₄²⁵ 0.964; λ_{max.} (alcohol), 231 mμ, log ε_{mol.} 4.36.

Anal. Calcd. for C₁₂H₁₆O: C, 81.8; H, 9.13; A. H. (Zer.), 1.0; unsaturation, 4.0 $\overline{\text{m}}^{\text{u}}$. Found: C, 81.23, 81.60; H, 9.20, 8.99; A. H. (Zer.), 0.99; unsaturation, 4.08 $\overline{\text{m}}^{\text{u}}$.

When the carbinol (II) was refluxed with acetic anhydride, the acetate (III) was obtained in 58–60% yields; b. p. 69–70° (10⁻⁴ mm.); *n*_D²⁵ 1.5267; *d*₄²⁵ 0.9938; λ_{max.} (alcohol), 266.5 mμ, log ε_{mol.} 4.33.

Anal. Calcd. for C₁₂H₁₈O: C, 77.2; H, 8.33; unsaturation, 4.0 $\overline{\text{m}}^{\text{u}}$; saponification equivalent, 218. Found: C, 77.03; H, 8.51; unsaturation, 4.21 $\overline{\text{m}}^{\text{u}}$; saponification equivalent, 216.

The carbinol (IV) was obtained in good yields by the saponification in nitrogen of the acetate (III); b. p. 61–64° (10⁻⁴ mm.); *n*_D²⁵ 1.5530; *d*₄²⁵ 0.983; λ_{max.} (alcohol), 266.5 mμ, log ε_{mol.} 4.22.

(1) Paper X on the synthesis of products related to vitamin A.

(2) Milas and Harrington, *THIS JOURNAL*, **69**, 2247 (1947).

Anal. Calcd. for C₁₂H₁₆O: C, 81.80; H, 9.13; A. H. (Zer.), 1.0; unsaturation, 4.0 $\overline{\text{m}}^{\text{u}}$. Found: C, 81.51; H, 9.14; A. H. (Zer.), 0.9; unsaturation, 4.19 $\overline{\text{m}}^{\text{u}}$.

The carbinol (V) was obtained either by selective hydrogenation of (IV) or of (II) followed by allylic rearrangement. It boiled at 55–57° (10⁻⁴–10⁻⁵ mm.); *n*_D²⁵ 1.5268; *d*₄²⁵ 0.961; λ_{max.} (alcohol), 267 mμ, log ε_{mol.} 4.30.

Anal. Calcd. for C₁₂H₁₈O: C, 80.80; H, 10.18; A. H. (Zer.), 1.0; unsaturation, 3.0 $\overline{\text{m}}^{\text{u}}$. Found: C, 80.78; H, 10.48; A. H. (Zer.), 0.95; unsaturation, 3.16 $\overline{\text{m}}^{\text{u}}$.

The C₁₅ ketone (crude) was obtained by the method previously described² in 90% yield; *n*_D²⁵ 1.5765; A. H. (Zer.), 0.6. The mixture of the ketone and its aldol precursor was further dehydrated in toluene either with iodine or with *p*-toluenesulfonic acid; b. p. 75–85° (10⁻⁴ mm.); *n*_D²⁵ 1.5960; λ_{max.} (alcohol), 333 mμ; log ε_{mol.} 4.28.

Anal. Calcd. for C₁₅H₂₀O: C, 83.30; H, 9.31; unsaturation, 4.0 $\overline{\text{m}}^{\text{u}}$. Found: C, 83.38; H, 9.27; unsaturation, 4.0 $\overline{\text{m}}^{\text{u}}$.

The C₁₅ ketone formed a light yellow semi-carbazone which discolors on standing in air; m. p. 162–164° (dec.).

All of the compounds (II to V inclusive) were also prepared with the methyl group in position two of the ring by Tome³ and those with methyl groups in both two and six positions of the cyclohexene ring by other members of our group.

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(5) B.S. Thesis, M. I. T., June, 1945.

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