

sure. The calculated amount of hydrogen was taken up in a few minutes, with the evolution of appreciable amounts of heat. The catalyst was removed by filtration, the batches were combined, and distilled through a column until the b. p. reached 70°. Some low-boiling petroleum ether was added, causing separation of a lower layer, which was removed, and the solution dried. The solvent was removed and the residue distilled, which yielded the following fractions:

I	II	III
3.4 g.	b. p. 100–136°	n_D^{20} 1.4213
29.0	136–141°	1.4220
16.0	141–146°	1.4240

The analytical sample had the properties: b. p. 138–138.5°; n_D^{20} 1.4201; d_4^{20} 0.8958.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.03; H, 10.42. Found: C, 62.00; H, 10.39.

1,4-Dimethoxybutane has n_D^{16} 1.4031⁵; Johnson² reports n_D^{20} 1.4220 for (*trans*) 1,4-dimethoxy-2-butene. The percentage composition calculated by this author for this compound (C, 63.2; H, 8.8) is somewhat in error.

1,4-Dimethoxy-3-chloro-2-butanol.—A 0.68 molar solution of hypochlorous acid was prepared by passing chlorine

(5) Dionneau, *ann. chim.*, [9] 3, 259 (1915).

into a solution of 95 g. of sodium bicarbonate in 1140 cc. of water.⁶ One hundred-cc. portions of this solution were added with stirring to 72.9 g. of 1,4-dimethoxy-2-butene while cooling with ice, a total of 1080 cc. (theoretical 930 cc.) of the hypochlorous acid solution being added. After the addition was complete, the solution was stirred for one-half hour in the ice-bath, then for three and one-half hours at room temperature, and allowed to stand overnight. At this point, a potassium iodide test showed practically no oxidizing power in the solution, and it was saturated with sodium chloride, extracted three times with ether and the residue from the ether extract distilled. A total of 69.0 g. was collected as product in several fractions, b. p. 92–98.5° (8 mm.) most of it boiling at 96–98.5°; the analytical sample had the following properties: b. p. 97–97.5° (8 mm.), n_D^{20} 1.4542.

Anal. Calcd. for $C_6H_{10}ClO_3$: C, 42.74; H, 7.77. Found: C, 42.32; H, 7.41.

(6) Wohl and Schweitzer, *Ber.*, 40, 94 (1907).

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COMMUNICATIONS TO THE EDITOR

THE CRYSTAL STRUCTURES OF AMMONIUM AND POTASSIUM MOLYBDOTELLURATES

Sir:

A structural study is now being made in this Laboratory of heteropoly ions of the general type $[XMo_6O_{24}]^{-n}$, in which the charge n depends on the metalloid X. The investigation is centered on the salts ammonium and potassium molybdotellurate, $(NH_4)_6TeMo_6O_{24} \cdot 7H_2O$ and $K_6TeMo_6O_{24} \cdot 7H_2O$, which have been described morphologically by Donnay and Mélon¹ as orthorhombic, homeomorphous and probably isostructural. A preliminary X-ray lattice study was reported by the writer to the Crystallographic Society in March 1947.² A more complete diffraction study since then has shown that the two salts are not isostructural, but possess entirely different and unrelated (though similar) symmetries. The final unit cell and space group data are as follows:

$(NH_4)_6TeMo_6O_{24} \cdot 7H_2O$, orthorhombic *mmm*; $a_0 = 14.62 \text{ \AA}$, $b_0 = 14.91$, $c_0 = 14.26$; space group *Pnaa* = C_{2h}^2 ; 4 formulas (as above) per cell, density calcd. 2.82, found (Donnay and Mélon) 2.78.
 $K_6TeMo_6O_{24} \cdot 7H_2O$, orthorhombic *mmm*; $a_0 = 14.30 \text{ \AA}$, $b_0 = 14.95$, $c_0 = 14.26$; space group *Pbca* = C_{2h}^{15} ; 4 formulas per cell, density calcd. 3.15, found (Donnay and Mélon) 3.05.

The structure problem was attacked by the preparation of Patterson maps for the ammonium

(1) J. D. H. Donnay and J. Mélon, *Proc. Nat. Acad. Sci.*, 20, 327–335 (1934).

(2) H. T. Evans, Jr., *Am. Min.*, 32, 687 (1947).

salt projected on the three pinacoid faces, using diffraction intensities visually estimated from Weissenberg photographs. These maps showed sharp peaks revealing the positions of the tellurium and molybdenum atoms. Although these maps were greatly simplified by the presence of the heavy tellurium atom at a symmetry center, an ambiguity still remained which allowed the possibility of three different models. This ambiguity is represented by an indeterminacy of sign of the parameters of one of the three kinds of molybdenum atoms in the structure. Calculation of the structure factors for a certain class of reflections in each of the series $(hk0)$, $(0kl)$ and $(h0l)$ which is sensitive to this change of sign, shows that a reasonable check of observed and calculated intensities is obtained with only one of the three possible models. The correct parameters for the tellurium and molybdenum atoms in the ammonium crystals, and probably also the potassium crystals (with x and z interchanged), are

	x	y	z
Te	0	0	0
Mo _I	0	0.228	0
Mo _{II}	0.113	0.121	-0.168
Mo _{III}	0.113	-0.121	-0.168

The model accepted here is one originally proposed hypothetically by Anderson.³ In it, the molybdenum atoms lie in a hexagon about the tellurium atom at the center (Te–Mo and Mo–Mo distances 3.42 Å.); the oxygen atoms lie close-

(3) J. S. Anderson, *Nature*, 140, 850 (1937).

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.

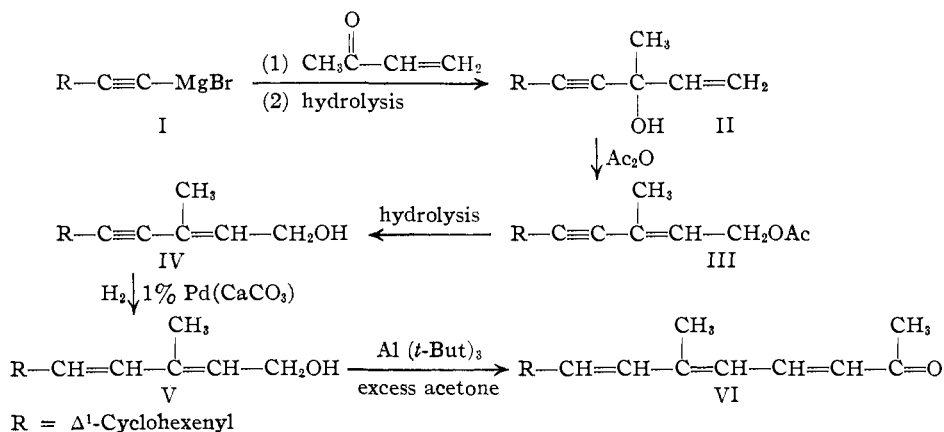
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THE SYNTHESIS OF 1-(CYCLOHEXEN-1'-YL)-3-METHYL-1,3,5-OCTATRIEN-7-ONE (C₁₅ KETONE)¹

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 $\overline{\text{f}}$. Found: C, 81.23, 81.60; H, 9.20, 8.99; A. H. (Zer.), 0.99; unsaturation, 4.08 $\overline{\text{f}}$.

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 $\overline{\text{f}}$; saponification equivalent, 218. Found: C, 77.03; H, 8.51; unsaturation, 4.21 $\overline{\text{f}}$; 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 0.933; 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 $\overline{\text{f}}$. Found: C, 81.51; H, 9.14; A. H. (Zer.), 0.9; unsaturation, 4.19 $\overline{\text{f}}$.

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 $\overline{\text{f}}$. Found: C, 80.78; H, 10.48; A. H. (Zer.), 0.95; unsaturation, 3.16 $\overline{\text{f}}$.

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 $\overline{\text{f}}$. Found: C, 83.38; H, 9.27; unsaturation, 4.0 $\overline{\text{f}}$.

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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RECEIVED FEBRUARY 4, 1948

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