

under these conditions. The controlled hydrolysis of the enol ether with deuterium chloride in diglyme also gave VI free of C-4 deuterium.

Turning to direct sources of the neutral enol, cholest-5-en-3-one (II) was allowed to conjugate for 5 min. in diglyme-deuterium chloride-deuterium oxide solution<sup>11</sup> yielding the  $\Delta^4$ -3-one (VI) containing only 1.06 atoms<sup>8</sup> of deuterium. The main C-D band in the infrared appeared at 2136 cm.<sup>-1</sup> while no more than 0.05-0.1 atom of deuterium was present at C-4.<sup>12</sup> An experiment terminated after 70% conjugation gave recovered II completely free of deuterium. If acid conjugation of the  $\Delta^5$ -3-one proceeds *via* the  $\Delta^{3,5}$ -enol, which would appear to be the most likely path, then protonation of the enol, in contrast to the anion, occurs preferentially at C-6.

The deuterium incorporation pattern of the  $\Delta^4$ -3-ketone in the presence of acid was also investigated. Although  $\Delta^{2,4}$ , as well as  $\Delta^{3,5}$ -enol formation is possible the more stable  $\Delta^{3,5}$ -enol (V) is the kinetically favored product in acid medium.<sup>13</sup> Thus cholest-4-en-3-one (IV) was treated with diglyme-deuterium chloride-deuterium oxide in the same concentrations<sup>11</sup> utilized to conjugate II. A reaction terminated after 7 hr. led to the incorporation of 1.5 atoms<sup>8</sup> of deuterium into the steroid with only 0.05-0.1 atom located at C-4<sup>12</sup> while 24 hr. exchange incorporated 2.4 atoms<sup>8</sup> with only 0.2 atom at C-4.<sup>12</sup> The 7-hr. product was shown to be almost completely deuterated at C-6 $\beta$  by the intensity and appearance of the 2136 cm.<sup>-1</sup> C-D band, by the shift of the C-4 proton out-of-plane deformation band<sup>14</sup> from 867 to 854 cm.<sup>-1</sup> and by the marked narrowing<sup>15</sup> of the C-4 proton peak in the n.m.r. spectrum. The deuterium chloride catalyzed exchange of another  $\Delta^4$ -3-ketone, testosterone, in methanol-*d*<sub>4</sub>, was followed by rapid scanning of the n.m.r. spectrum. After 7 hr. the C-4 proton had undergone little exchange although C-2 and C-6 proton exchange was extensive. A sample which after two hours had incorporated 3.2 atoms<sup>16</sup> (apart from O-D) of deuterium showed only about 0.05 atom<sup>12</sup> of C-4 deuterium. The greater specificity in his case appears to be solvent, rather than substrate-dependent.

These experiments almost certainly indicate preferential protonation of the enol at the  $\gamma$ -position (C-6)<sup>17</sup> in analogy to protonation of the  $\Delta^{3,5}$ -enol ether and to bromination of the enol.<sup>13</sup> When the enol has dissociated to the enolate anion, the highest negative charge density on carbon is at the C-4 position<sup>8</sup> and proton-

ation<sup>8</sup> and alkylation<sup>18</sup> should occur at that position.<sup>19</sup> Product stability is unimportant in the latter case since there is little bond formation in the transition state<sup>19</sup> while protonation of the neutral enol must involve a greater degree of bond formation with some development of ketonic character. Under these conditions C-6 protonation with formation of the more stable  $\Delta^4$ -3-ketone will be favored. The results reported herein strongly suggest that the anion protonates directly on carbon rather than on oxygen since formation of the neutral enol in acid medium leads to C-6 and not to C-4 deuteration.

(13) Cf. ref. 2.

(19) See ref. 13 for a discussion of the protonation of non-enolic mesomeric carbanions.

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### THE STRUCTURES OF THE CROCONATE IONS

Sir:

Recently, interest has been revived in the poly-keto cyclic acids, rhodizonic acid, croconic acid, squaric acid and related compounds.<sup>1</sup> In this connection a report of the structures of one of the members of the series seems appropriate.

The crystal structures of the mono- and diammonium salts of croconic acid have been determined by single crystal X-ray diffraction methods. Both salts crystallize with monoclinic cells: for  $(\text{NH}_4)_2\text{C}_5\text{O}_5$ ,  $a = 7.45$  Å.,  $b = 13.32$  Å.,  $c = 3.56$  Å.,  $\beta = 97^\circ$ ,  $Z = 2$ , space group = Cm; for  $(\text{NH}_4)\text{HC}_5\text{O}_5$ ,  $a = 7.71$  Å.,  $b = 10.50$  Å.,  $c = 7.82$  Å.,  $\beta = 102^\circ$ ,  $Z = 4$ , space group = P2<sub>1</sub>/c. Weissenberg films,  $(hk0)$ - $(hk2)$  and  $(0kl)$ - $(5kl)$ , were obtained at 80° K. for the diammonium salt. Weissenberg films,  $(h0l)$ - $(h7l)$ , and precession films,  $(0kl)$ - $(3kl)$ ,  $(hk0)$ - $(hk3)$ , were made at room temperature for the monohydrogen salt. Intensities were obtained by the visual method.

**Structure of Diammonium Croconate.**—Systematic absences indicated either space group C2 or Cn1. Trial structures for both space groups were obtained from the assumed planar arrangement of the croconate ion and the short  $c$  dimension of the cell. Only the structure in Cm refined by least-squares methods to a low discrepancy factor. Approximate positions of the H atoms were obtained from a two dimensional electron density difference map and assumed N-H distances. Inclusion of the H atoms brought the discrepancy factor,  $R$ , to 10.6% at the present stage of refinement (individual isotropic temperature factors).

The structure consists of  $\text{NH}_4^+$  ions arranged in columns parallel to the  $c$ -axis at the corners of a roughly hexagonal net. The croconate ions, tilted 13° from the  $ab$  plane, are stacked above one another in the hexagonal column shaped cavities. The croconate ion is planar; the largest deviation of any atom in the ion from the least-square plane is 0.024 Å. The bond distances and estimated standard deviations for these distances are given in Fig. 1. The nitrogen-oxygen distances range from 2.80 to 3.10 Å.; the smallest intermolecular oxygen-oxygen distance is 2.79 Å. The carbon ring is a perfect pentagon within the precision of the determination.

**Structure of Ammonium Hydrogen Croconate.**—The structure was first obtained from rubidium hydrogen croconate crystals, which are isomorphous, by a

(1) K. Yamada, N. Mizuno and Y. Hirata, *Bull. Chem. Soc. Japan*, **31**, 543 (1958); M. Washino, K. Yamada and Y. Kurita, *ibid.*, **31**, 552 (1958); S. Cohen, J. R. Lacher and J. D. Park, *J. Am. Chem. Soc.*, **81**, 3480 (1959); **84**, 2919 (1962); R. West, H. Y. Niu, D. L. Powell and M. V. Evans, *ibid.*, **82**, 6204 (1960).

(11) Fifty milligrams of steroid, 0.5 ml. of 0.5 N DCl, 5 ml. of diglyme.

(12) The amount of C-4 deuterium was determined by integration of the area of the C-4 proton peak in the n.m.r. spectrum and of the 2260 cm.<sup>-1</sup> C-D band in the infrared.

(13) This assumption which is supported by the observed (unpublished data, this Laboratory) acid-catalyzed monobromination of the  $\Delta^4$ -3-ketone at C-6 and by the preferential formation of  $\Delta^{3,5}$ -enol ethers and -enol acetates is in accord with Hammond's postulate: G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955). In the presence of strong acid the transition state for enol formation should resemble the enol more than ketone and thus favor direct formation of the more stable  $\Delta^{3,5}$ -enol. See also H. J. Ringold and A. Turner, *Chem. Ind. (London)*, 211 (1962).

(14) The out-of-plane deformation band of the C-4 proton occurs (KBr pellet) at 867 cm.<sup>-1</sup> in cholest-4-en-3-one. A 6 $\beta$ -deuterio substituent shifts this peak to 854 cm.<sup>-1</sup> while extensive deuteration leads to a doublet at 854 and 840 cm.<sup>-1</sup>.

(15) It has been demonstrated (T. A. Wittstruck, S. K. Malhotra and H. J. Ringold, *J. Am. Chem. Soc.*, in press.) that substitution of deuterium, halogen or methyl at the 6 $\beta$ - but not 6 $\alpha$ - position reduces the width of the C-4 proton peak in the n.m.r. by removal of long-range coupling with the 6 $\beta$ -proton.

(16) Determined by integration of the area of the methylenic protons (C-2 and C-6) in the n.m.r. We wish to thank Mr. Tom Wittstruck for the n.m.r. spectra which were obtained with a Varian 4300 spectrometer.

(17) An alternate but highly unlikely explanation may be posed for the virtual absence of deuterium at C-4: preferential deuteration of the enol occurs at C-4 yielding the 4-deuterio- $\Delta^4$ -3-one which then undergoes isomerization by addition of D<sup>+</sup> at C-6 followed by stereospecific loss of the C-4 deuterium atom despite an adverse isotope effect.

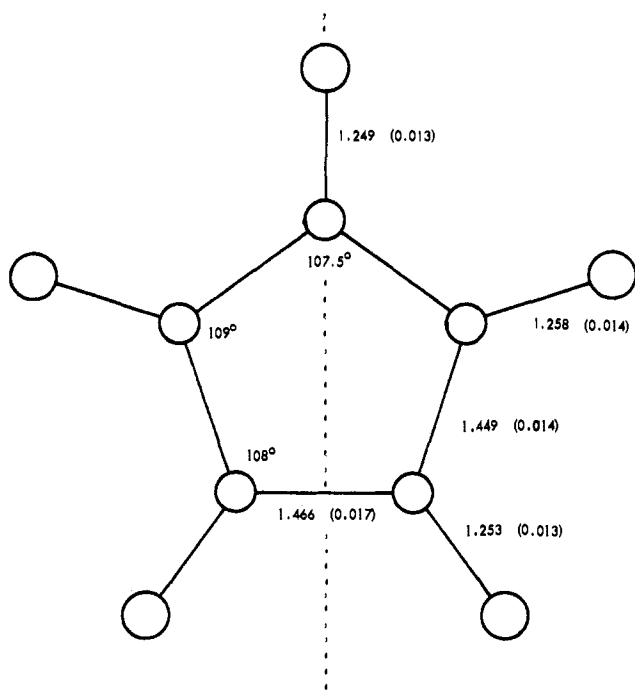


Fig. 1.—Vertical dotted line refers to a mirror plane. Distances are given in Ångstroms; standard deviations are in parentheses.

vidual isotropic temperature factors, H atoms not included).

The croconate ions are connected by hydrogen bonds into chains which lie in planes parallel to the  $(10\bar{1})$  planes. The croconate ions are nearly planar, the greatest deviation from the least-squares plane being 0.12 Å.; the average deviation is 0.05 Å. The bond distances and estimated standard deviations for these distances are given in Fig. 2. It would be expected that the monohydrogen croconate ion would have a mirror plane passing through the C-O-H bond, perpendicular to the plane of the ion. This symmetry apparently is partly destroyed by the strong hydrogen bond to only one of the adjacent oxygen atoms. The double bond is thus partly localized between the two carbon atoms whose attached oxygen atoms are involved in the hydrogen bond formation. Further refinement of this structure using low temperature intensity data undoubtedly will increase the reliability of these distances.

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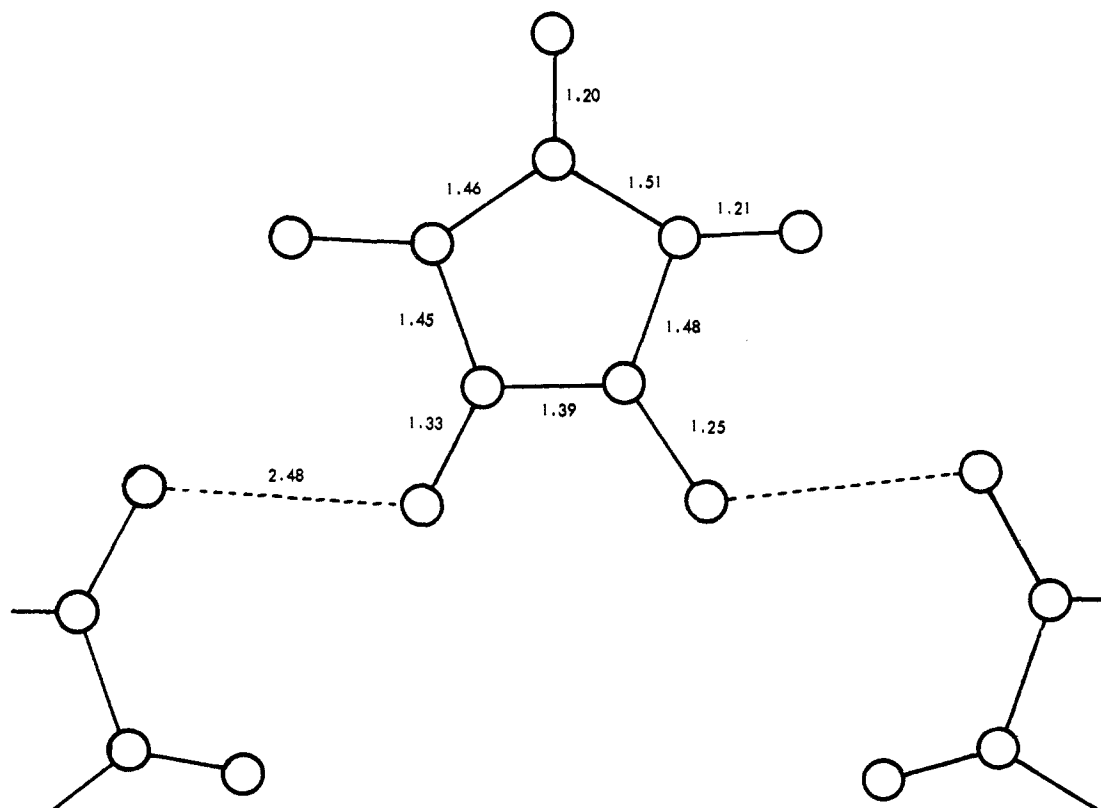


Fig. 2.—Dotted line indicates presumed hydrogen bond. Distances are given in Ångstroms; average standard deviations in bond distances are 0.017 for C-C distances, 0.015 for C-O distances.

combination of Patterson and electron density methods. Least-squares refinement, based on the rubidium salt, did not give satisfactory precision on the light atom positions. The least-squares refinement of the ammonium hydrogen croconate structure began with the atom positions found for the rubidium salt. The  $R$  value at the present stage of refinement is 16% (indi-

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