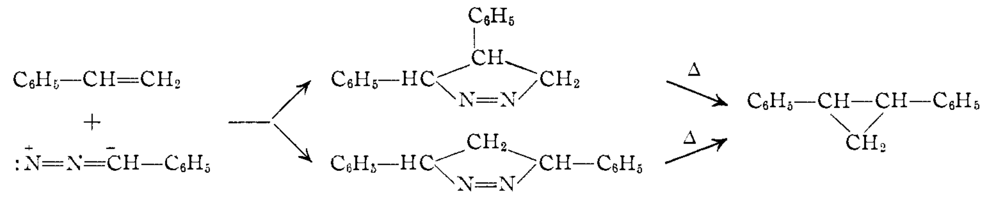
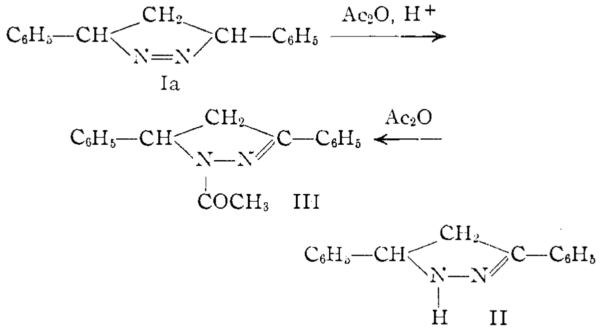


The reaction of Ia with acetic anhydride in the presence of a catalytic amount of *p*-toluenesulfonic acid gave 1-acetyl-3,5-diphenyl-2-pyrazoline (III), m.p. 125–125.5°, identical (infrared spectra and mixed melting point) with an authentic sample prepared by the reaction of acetic anhydride with II.[5a,b] Compound Ia is the first stable 1-pyrazoline[6] having an α-hydrogen capable of isomerizing to a conjugated system. This type of 1-pyrazoline usually rearranges spontaneously to a 2-pyrazoline under conditions of their synthesis. The isomerization of Ia to II in dilute ethanolic hydrochloric acid was followed spectrophotometrically by the appearance of the hydrazone peak at 291 mμ.



Thermal decomposition of Ia, presumably a mixture of the D,L-*trans*-isomers at 70°, resulted in only one product, *trans* 1,2-diphenylcyclopropane[7] (D,L pair), n^{25}_{D} 1.5951 (n^{20}_{D} 1.5995, prepared by base catalyzed decomposition of the corresponding 2-pyrazoline[8]) in contrast to the nonselectivity exhibited by the seven- and eight-membered ring compounds (I, n = 3, 4). Photochemical decomposition in hexane solution at 25° also gave this same selectivity. One explanation may be that there is much less time for the radicals to become relatively free in the formation of the cyclopropane than in the case of formation of the cyclopentane or the cyclohexane. This might be due to the closer proximity of the two radicals in the five-membered ring case. We can safely discount the possibility that the five-membered ring azo compound is the *cis* isomer and that the formation of the *trans* cyclopropane represents the formation of the most stable isomer since the base catalyzed decomposition of 3,5-diphenyl-2-pyrazoline (II) at 200° gave both *cis*- and *trans*-1,2-diphenylcyclopropanes (about 50:50 mixture) as was shown by Curtin, *et al.*,[8] and checked by us.

Acknowledgment.—We thank the Susan Greenwall Foundation of the National Starch Company and Grant NSF-G-17448 from the National Science Foundation for their generous support of this work.

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[5] (a) S. G. Beech, J. H. Turnbull and W. Wilson, *J. Chem. Soc.*, 4684 (1952). (b) M. Hamada, *Botyu Kagaku*, **21**, 22 (1956).

[6] Smith and co-workers, *J. Am. Chem. Soc.*, **65**, 159 (1943), claimed to have isolated some 1-pyrazolines but these claims have not been substantiated by any data.

[7] The n.m.r. spectrum clearly shows that the *trans* isomer is the only product formed and was identical with that reported in reference 8.

[8] D. Y. Curtin, H. Gruen, Y. G. Hendrickson and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961).

INHERENTLY DISSYMETRIC CHROMOPHORES. OPTICAL ROTATORY DISPERSION OF α,β-UNSATURATED KETONES AND CONFORMATIONAL ANALYSIS OF CYCLOHEXENONES[1,2]

Sir:

Derivation of the octant rule[3] for the 290 mμ n-π^* transition of saturated ketones rests, *inter alia*, on the local symmetry of the carbonyl chromophore which exhibits two orthogonal reflection planes. In α,β-unsaturated ketones, one or both of these planes is lost and hence the octant rule is in general no longer applicable.

This reduction in local symmetry can be turned to advantage if one shifts attention from the n-π^* to the shorter wave length π-π^* transition of the C=C—C=O grouping, which, if nonplanar, may be regarded as an inherently dissymmetric chromophore.[4,5] Because of the similarity in the π-systems of C=C—C=O and C=C—C=C, the helicity rule for cisoid dienes[6] is expected to apply also to α,β-unsaturated ketones. Calculations utilizing simple Hückel type wave functions bear out this point: cisoid conformation A and transoid conformation B are to be associated with a positive Cotton effect centered at the wave length corresponding to the K-band, *i.e.*, the lowest π-π^* transition near 240–260 mμ, while a negative Cotton effect would be exhibited by their mirror-image representations. For sufficiently large angles of skew, the rotational strengths of the π-π^* transitions of the above discussed inherently dissymmetric chromophore will be an order of magni-

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[1] "Optical Rotatory Dispersion Studies." LXXII. For paper LXXI, see C. S. Barnes and C. Djerassi, *J. Am. Chem. Soc.*, **84**, in press (1962).

[2] Financial support by the Alfred P. Sloan Foundation (K. M.) and by the National Science Foundation (grants No. G15746 and G-19905) is gratefully acknowledged.

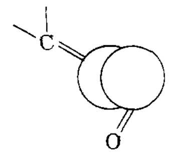
[3] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

[4] A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

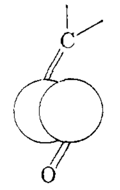
[5] A. Moscowitz, K. Mislow, M. A. W. Glass and C. Djerassi, *J. Am. Chem. Soc.*, in press; K. Mislow and J. G. Berger, *ibid.*, in press; K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss and C. Djerassi, *ibid.*, in press.

[6] A. Moscowitz, E. Charney, U. Weiss and H. Ziffer, *J. Am. Chem. Soc.*, **83**, 4661 (1961).

tude greater[4,5,6] than the rotational strengths of the n-π^* transitions, which, in previous considerations involving saturated ketones,[3] were most conveniently associated with asymmetrically perturbed symmetric chromophores.



A



B

Utilizing a spectropolarimeter built by E. B. which employs a Faraday effect-type analyzer, we now have been able to measure (cell path lengths 1–10 mm., concentrations, c, 0.03–0.002 in methanol) the Cotton effects in the region of the K-band (240–260 mμ, ϵ 8000–20,000) of a number of α,β-unsaturated ketones, the long-wave length n-π^* Cotton effects of which have been recorded previously.[7] The cisoid α,β-unsaturated ketones jervine (I) and 4α-methyl-$\Delta^{8(14)}$-cholesten-3β-ol-7-one acetate (II) show strong negative Cotton effects (Fig. 1) centered near 250 mμ, while that of Δ^4-cholesten-4-one (III) occurred at slightly lower wave length. Similarly, the transoid ketones 4-methyl-Δ^4-cholesten-3-one (IV), 4-bromotestosterone (V) and B-nor-Δ^4-cholesten-3-one (VI) exhibit high amplitude Cotton effects (Fig. 1) in the 240–260 mμ region.

In the above examples, the sign of the Cotton effect reflects the *absolute conformation* of the C=C—C=O grouping which makes the dominant contribution to the observed optical activity; a positive sign indicates conformation A (cisoid) or B (transoid), and a negative sign the appropriate enantiomers. Since Dreiding models[8] of many α,β-unsaturated steroids or terpenoids permit construction of two (or more) conformations differing in the chirality of the C=C—C=O grouping, *optical rotatory dispersion—through the sign of the Cotton effect of the K-band—may now often permit for the first time a choice between such conformational representations.* When Dreiding models[8] point definitely to a given chirality—*viz.*, the negative helicity of II—the sign of the relevant Cotton effect (Fig. 1) proves to be in agreement with prediction.

The C-1 isomeric 1-methyl-19-norprogesterones (VII, VIII) are particularly interesting since their C=C—C=O groupings have opposite chiralities, as demonstrated by the positive (VIII) and negative (VII) K-band Cotton effects, respectively. This reversal is the result[7,9] of the interaction between the equatorial 1β-methyl group (VII) and the 11α-hydrogen atom, which forces ring A into an alternate conformation, thus reversing the sense of twist of the C=C—C=O functionality.

When the K-band Cotton effect is not experimentally realized in its entirety, it may still be possible to assign a chirality to the chromophore and hence a conformation to the cyclohexenone ring by taking into account the sign of the strong background dispersion which is in virtually all cases superimposed on the 330 mμ Cotton effect measured earlier.[7] In such instances, the sign and magnitude of the background dispersion may be correlated with geometries A, B or the respective mirror images. The conformational conclusions which may be reached by this approach are somewhat complicated by the fact that at times the less populous conformer may conceivably possess a much greater amplitude and thus control the sign of the observed Cotton effect. Nevertheless, the present rotatory dispersion results can be taken to indicate a significant population of boat-like form for ring A in Δ^5-cholesten-4-one (III), and for ring B in Δ^4-cholesten-6-one. The present method also indicates which conformation is primarily responsible for the rotatory dispersion curves of B-nor-Δ^4-cholesten-3-one (VI) (Fig. 1) and 8,19-epoxy-3-oxo-Δ^4-etienic acid,[10] which already exhibit antipodal curves[7,10] in the 300–400 mμ region as compared to those[7] of the usual Δ^4-3-ketones, this inversion in sign again being due to the oppositive signs of the K-band Cotton effect which makes itself felt in the background rotation

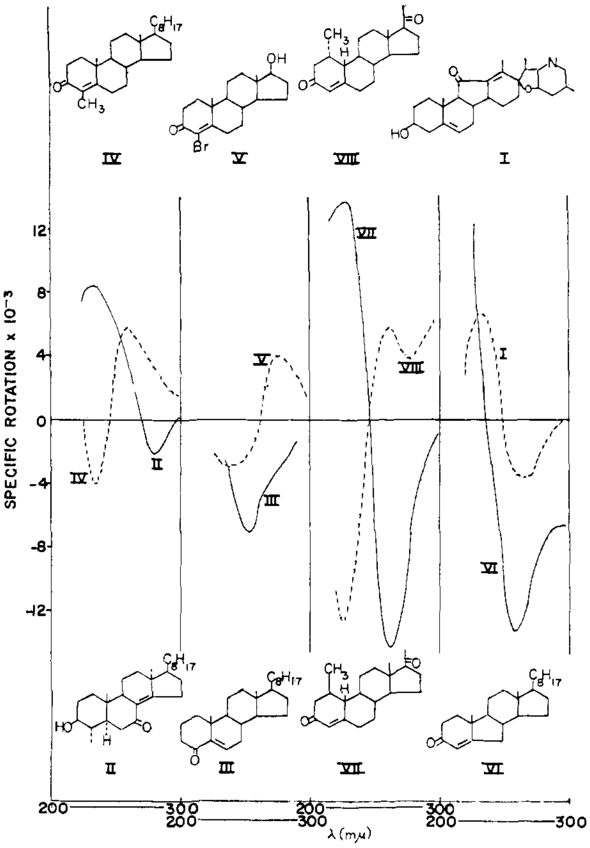


Fig. 1.—Optical rotatory dispersion curves (methanol) of steroidal α,β-unsaturated ketones I–VIII in the region 200–300 mμ.

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[7] C. Djerassi, R. Riniker and B. Riniker, *J. Am. Chem. Soc.*, **78**, 6362, 6377 (1956).

[8] A. Dreiding, *Helv. Chim. Acta*, **42**, 1339 (1959).

[9] C. Djerassi, E. Lund and A. A. Akhrem, *J. Am. Chem. Soc.*, **84**, April (1962).

[10] K. Otto and M. Ehrenstein, *J. Org. Chem.*, **26**, 2871 (1961).

above 300 mμ superimposed on the n-π^* Cotton effect.

[11] On leave from the Department of Chemistry, University of Minnesota, Minneapolis 14, Minnesota.

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RECEIVED JANUARY 9, 1962

OXIDATION OF CHROMIUM(II) BY IRON(III) IN THE PRESENCE OF CHLORIDE ION

Sir:

The oxidation of Cr^{2+} by Fe^{3+} in aqueous perchloric acid produces Fe^{2+} and $Cr(H_2O)_6^{3+}$, but in the presence of chloride ion the complex $Cr(H_2O)_5Cl^{2+}$ is produced along with $Cr(H_2O)_6^{3+}$ in proportions depending on the concentrations of Cl^- and H^+.[1] This reaction may proceed *via* the chloro complex of Fe(III) $FeCl^{2+} + Cr^{2+} \rightarrow Fe^{2+} + CrCl^{2+}$ in an inner sphere activated complex mechanism, similar to that observed in the oxidation of Cr^{2+} by $Co^{3+}(NH_3)_5X$.[1,2] Alternatively, Fe^{3+} may enter the activated complex without prior substitution by Cl^-, in a mechanism similar to that taking place in the oxidation of Cr^{2+} by $Co(NH_3)_6^{3+}$ in the presence of Cl^-.[3] It is difficult to distinguish between the two mechanisms at room temperature because the equilibrium $Fe^{3+} + Cl^- \rightleftarrows FeCl^{2+}$ is attained too rapidly. At −50° the formation of the $FeCl^{2+}$ complex proceeds quite slowly, therefore this temperature was chosen to distinguish between the two alternative paths.

The solvent used in this investigation was a eutectic aqueous solution of perchloric acid (5.27 *M*) having a melting point of −59.7°.[4] A Pyrex reaction vessel consisting of three compartments was used: two side compartments were connected through a common T-shaped mixing chamber to the main compartment. An inert atmosphere was maintained by a slow stream of CO_2 and the whole vessel was immersed in an ethanol bath, maintained at −50°. A chromous solution was placed in the main compartment, a ferric perchlorate solution in one of the side compartments and a hydrochloric acid solution in the other. By applying a pressure of CO_2 the ferric and the chloride solutions were driven through the common mixing chamber into the chromous solution, which they reached within 0.1 sec. after mixing. The concentrations of the reactants after mixing were: $[Fe^{3+}]$ 0.075 *M*, $[Cl^-]$ 0.075 *M*, $[Cr^{2+}]$ 0.031 *M*.

The oxidation reaction was "instantaneous" and produced a green solution. After warming to room temperature, this solution was separated chromatographically by absorption on a Dowex 50 (8%) cation exchange column and elution with 1 *M* perchloric acid. It consisted mainly of $CrCl^{2+}$ and a smaller amount of $Cr(H_2O)_6^{3+}$. The same reaction was carried out in the absence of chloride ion (which was replaced by the pure solvent) and was found to proceed quite slowly at −50°, thus demonstrating the marked catalytic activity of Cl^-. The only chromic species produced in this experiment was the hexaaquochromic ion, as expected.

The assumption that $FeCl^{2+}$ is not formed prior to the oxidation reaction was confirmed by another blank experiment in which Cr^{2+} was replaced by the pure solvent into which the ferric and chloride solutions were injected at −50° as above. After 60 seconds the yellow color of $FeCl^{2+}$ was not yet observed. A very faint color was first noted after three minutes, and even after one hour equilibrium concentration was not attained. These results are in accord with the kinetic data given by Connick and Coppel[5] for this reaction at room temperature. Using their values of the rate constants and activation enthalpies, we found that at the initial ferric and chloride concentrations used by us (0.075 molar) less than 0.4% of the total Fe^{3+} was converted to $FeCl^{2+}$ at −50° after 60 seconds.

The results of these experiments show that the chloride-catalyzed oxidation of Cr^{2+} by Fe^{3+} does not proceed *via* the $FeCl^{2+}$ complex at −50°, but they do not rule out this path at room temperature.

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[1] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[2] H. Taube, *ibid.*, **77**, 4481 (1955).

[3] H. Taube, *Chem. Soc. Spec. Publ.*, **13**, 57 (1959).

[4] L. H. Brickwedde, *J. Research Natl. Bur. Standards*, **42**, 309 (1949).

[5] R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959).

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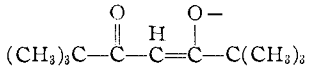
RECEIVED DECEMBER 8, 1961

ABSORPTION INTENSITIES AND ELECTRONIC STRUCTURES OF TETRAHEDRAL COBALT(II) COMPLEXES

Sir:

We wish to report some observations which seem to us to be both novel and important in respect to the problem of the intensities of electronic absorption bands in transition metal complexes.

Using the ligand I, the enolate anion of dipivaloylmethane, hereafter abbreviated DPM, we have prepared the complexes $Co(DPM)_2$



$$(CH_3)_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{H}{C}=\overset{\overset{\displaystyle O^-}{|}}{C}-C(CH_3)_3 \quad \text{I}$$

and $Zn(DPM)_2$. It has been shown previously that in $Ni(DPM)_2$ the size of the *t*-butyl groups prevents the trimerization which occurs in Ni(II) complexes with less hindered β-diketone enolates so that $Ni(DPM)_2$ is a planar, diamagnetic monomer.[1] $Co(DPM)_2$ has three unpaired electrons

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[1] F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961); J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **83**, 3775 (1961).