The Conformations of Substituted Cyclopentanes. I. The Infrared Analysis and Structure of the α-Halocamphors, the α-Halo-2-indanones and the α-Halocyclopentanones

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For the α-halogen atoms in the halocamphors, which make an angle of 60° in projection with the carbonyl group, shifts of 14 cm.$^{-1}$ for α-bromine and 18–19 cm.$^{-1}$ for α-chlorine have been observed. The values for the α-halogens in α-bromo- and α-chlorocyclopentanone are measurably less than these which means that the latter halogens have quasi-axial character. Interpretation of new dipole moment data also leads to this conclusion. To account for this it is proposed that cyclopentanone and its halogen derivatives are predominantly in the cyclopentane half-chair form (IV, IX). A practical analysis of the forms which substituted cyclopentane rings can adopt is presented briefly.

It is a peculiar feature of the cyclopentane ring that although it is known to be non-planar, its classical reactions as late as 1954 have been rationalized by Brown, Brewster and Shechter[1a] on the basis of an "idealized planar structure."[2] The analysis has been based on the supposition that five- and six-membered rings are different in geometry and therefore should differ in reactivity. By considering reactions which reflect this difference, Brown, Brewster and Shechter have made some interesting and useful generalizations. Nevertheless, the fact remains that the ring is puckered[3] and this non-planarity might be detected through studies of reactions of the four-center type where at least two ring carbon atoms are involved. However, since most of the studies of four-center reactions[4] have been in the cyclohexane series, the literature is of little assistance in ths connection.

In view of our interest in cyclopentane[5] chemistry, we have studied the rates of several four-center type reactions such as epoxide opening and closing in both the cyclopentane and cyclohexane series for comparison purposes.[5a,e] Our results clearly show that the rates of these reactions are similar for both rings and therefore may reflect a somewhat similar geometry for the reaction sites on the rings. Similar conclusions from studies of other reactions have been reported independently by Weinstock, Lewis and Bordwell[6] and by Winstein and Marshall.[7] While the assembled data make it clear that the puckering of the cyclopentane

ring assists attainment of a coplanar transition state, no detailed structure of the ring has been proposed to explain how this is accomplished. It is the purpose of this paper to discuss the non-planar structures of several cyclopentane derivatives in order to form a basis for deciding later what form of the cyclopentane ring is involved in a particular reaction.

For our study we have employed the infrared method of Jones[8] and Corey[9] which distinguishes between axial and equatorial halogen atoms α to a carbonyl group in a cyclohexane ring by the small or large shift[10] of the carbonyl group's frequency.

It was necessary first, however, to establish the frequency shift for an intermediate, bisectional,[11] position between axial and equatorial such as might be found in a planar α-halocyclopentanone (I, R_1 = Br, Cl; R_2 = H). Here θ, the projected angle viewed along the C—C bond of —C—C=O is 60°.

X

Using this value as a standard, we could then tell by variations from it whether α-halogens in α-halocyclopentanones of interest to us had developed axial or equatorial character due to ring puckering.
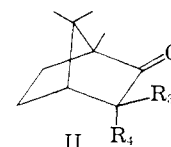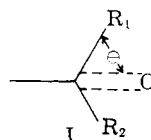
The α-halocamphors (II) were chosen as model compounds since the rigid R—C—C=O geometry, in projection, is virtually the same as in a planar cyclopentanone (I). Cookson[12] has suggested from ultraviolet studies that the pressure of the

(1) (a) H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954); (b) R. B. Turner and R. H. Garner, ibid., **79**, 253 (1957); R. B. Turner and W. R. Meador, ibid., **79**, 4133 (1957), and papers cited therein; (c) R. Fleck, J. Org. Chem., **22**, 439 (1957); (d) H. C. Brown, ibid., **22**, 439 (1957).

(2) The authors[1a] pointed out that in fact cyclopentanone was a somewhat less strained, non-planar structure, but did not develop this point, since it was not essential to the particular reactions they analyzed.

(3) J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2483 (1947).

(4) D. H. R. Barton and R. C. Cookson, Quart. Revs., **10**, 44 (1956); S. J. Cristol, N. L. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951); H. D. Orloff, Chem. Revs., **54**, 347 (1954).

(5) (a) F. V. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, THIS JOURNAL, **78**, 1507 (1956); (b) F. V. Brutcher, Jr., and N. Pearson, Chemistry and Industry, 1295 (1957); (c) F. V. Brutcher, Jr., and F. J. Vara, THIS JOURNAL, **78**, 5695 (1956); (d) F. V. Brutcher, Jr., and H. J. Cenci, J. Org. Chem., **21**, 1543 (1956); (e) F. V. Brutcher, Jr., and T. Roberts, Abstracts of Papers, 127th Meeting, American Chemical Society, Cincinnati, Ohio, April, 1955, p. 39-N.

(6) J. Weinstock, S. N. Lewis and F. G. Bordwell, THIS JOURNAL, **78**, 6072 (1956), and papers cited therein.

(7) S. Winstein and H. Marshall, private communication; R. Heck, Ph.D. thesis, U.C.L.A.

(8) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2828 (1952).

(9) (a) E. J. Corey and H. J. Burke, ibid., **77**, 5418 (1955); (b) E. J. Corey, T. H. Topie and W. A. Wozniak, ibid., **77**, 5415 (1955); (c) E. J. Corey, ibid., **75**, 2301, 3297 (1953).

(10) Introduction[8,9] of an equatorial bromine causes a shift of +16 to +22 cm.$^{-1}$ while an axial bromine causes a shift of −2 to +8 cm.$^{-1}$. Equatorial chlorine[9a] leads to a shift of +26 to +31 cm.$^{-1}$ and axial chlorine leads to a shift of at least +10 cm.$^{-1}$.

(11) We define a bisectional bond (b) as one which makes an angle of precisely 54° 44' (one-half the tetrahedral angle) with the plane of reference. In projection, as in I, the apparent angle (θ) may be 60°. This bond is unique and distinct from axial (a), equatorial (e), quasi-axial (a') and quasi-equatorial (e'). Definition is required since each of the two limiting cyclopentane forms (III and IV) has two or more.

(12) R. C. Cookson, J. Chem. Soc., 282 (1954).

nearer methyl of the *gem*-dimethyl group on R_3 in II forces it to make, in projection, an angle of about 55° with the carbonyl group, while R_4 makes an angle of 65°. We have investigated this point further by nuclear magnetic resonance, dipole moment and infrared techniques. Nuclear magnetic resonance studies[13] show that the α'-bromine (R_3 of II) of α,α'-dibromocamphor (II, R_3, R_4 = Br) does indeed interact with the nearer methyl of the *gem*-dimethyl group giving rise to a new proton absorption at 208 c.p.s. However, this seems to be true only for bromine, since the less bulky chlorine atom in α'-chlorocamphor (II, R_3 = Cl, R_4 = H) does not interact with the methyl sufficiently to be detected. If the α'-halogen is depressed to a 55° angle or less it might be possible to detect a larger dipole moment for it compared with its α-epimer. Measurements of the two chloro epimers[14] as shown in Table I indi-

TABLE I[14,15]

	Heptane	μ D. Benzene	Dioxane
α-Chlorocamphor (II, R_3 = H, R_4 = Cl)[14]	4.12	4.12	4.11
α'-Chlorocamphor (II, R_4 = H, R_3 = Cl)[14]	3.98	4.14	4.26
1-Chloro-2-indanone[14]	3.92	3.73	4.09
2-Chlorocyclopentanone[15]	3.63	3.62	3.69

cate that the two dipole moments are nearly identical. In fact in heptane the dipole moment of α'-chlorocamphor is less than α-chlorocamphor. Therefore, the dipole moment data lend support to an arrangement as in I and do not support the arrangement suggested by Cookson. It is interesting to note that α'-chlorocamphor shows a variation of the moment in different solvents. While this may be due to an inherent instability of the compound, it also may be due to a flexibility of the α'-chlorine. This would mean that the methyl group is not sterically compressing the chlorine atom. Finally, as shown in Table II, within the limits of

TABLE II[a]

Ketone	$\nu_{C=O}^{max}$, cm.$^{-1}$	$\Delta\nu$, cm.$^{-1}$
Camphor	1744	..
α-Bromo-	1758	14
α,α'-Dibromo-	1766	22
α-Chloro-	1763	19
α'-Chloro-	1762	18
α,α'-Dichloro-	1774	30
2-Indanone[b]	1753	..
1-Bromo-	1766	13
1-Chloro-	1772	19
Cyclopentanone	1742	..
2-Bromo-	1750	8
2-Chloro-	1755[9c]	13

[a] Measured in carbon tetrachloride solution on a Perkin-Elmer model 21· double beam infrared spectrophotometer. [b] Kindly prepared by Mr. Elmer Maurer, Eastern Regional Research Laboratories, Phila. 18, Pa.

experimental error (± 2 cm.$^{-1}$) the infrared shifts of the two chlorocamphors are identical. This

(13) W. D. Kumler, J. N. Shoolery and F. V. Brutcher, Jr., THIS JOURNAL, 80, 2533 (1958).

(14) W. D. Kumler, N. Pearson and F. V. Brutcher, Jr., in preparation.

(15) W. D. Kumler and A. C. Huitric, THIS JOURNAL, 78, 3369 (1956).

means that by infrared technique and within the limits of the method the orientations of the two epimeric chlorines are shown to be identical.[16] We therefore conclude that while bulkier bromine may interact with the *gem*-dimethyl group, chlorine for all practical purposes does not and therefore it is not necessary to adopt Cookson's suggestion but rather to use I as a satisfactory average representation of II's geometry.

Table II lists our shifts. We have obtained for α-bromine a shift of 14 cm.$^{-1}$ and for α-chlorine a shift of 18–19 cm.$^{-1}$. These are intermediate or borderline values between those reported for axial and equatorial halogens in six-membered rings. If the halogen atoms have an arrangement as in I, further substitution should result in a sizable additional shift. Table II shows this to be the case; the second bromine in α,α'-dibromocamphor gives rise to an additional shift of 8 cm.$^{-1}$ and the second chlorine in α,α'-dichlorocamphor to 11 cm.$^{-1}$.

With our standard established, we wished to check our values against α-halocyclopentanones which, on conformational grounds alone, might be expected to be planar. The 1-halo-2-indanones (i)[17] should

(i)   (ii)
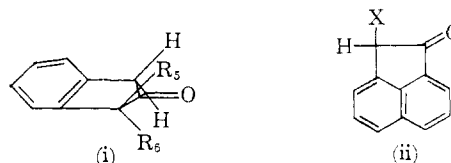
have the same halo-carbonyl geometry as I, since the five-membered ring has four carbon atoms which must be in one plane and a fifth, the carbonyl group, which can maintain favorable bisections with the α-substituents by remaining in the plane.[17]

Indeed, as shown in Table II, values of 13 cm.$^{-1}$ for 1-bromo-2-indanone (i,[17] R_5 = Br, R_6 = H) and 19 cm.$^{-1}$ for 1-chloro-2-indanone (i,[17] R_5 = Cl, R_6 = H) check closely with our standard values from the halocamphors in keeping with the planarity of i.[17,18]

In sharp contrast, however, with these results are those relevant to the parent α-halocyclopentanones. If they are planar, the shift for α-bromine should be about 14 cm.$^{-1}$ and α-chlorine about 18–19 cm.$^{-1}$ In actual fact, the shift for α-bromocyclopentanone, as measured by Corey and confirmed by us, is

(16) The correspondence between infrared shifts and dipole moments demonstrates that the infrared method does indeed give a valid measure of the orientation of α-halogen atoms. The previously reported discrepancies between dipole moments and infrared shifts for simple α-halocyclohexanones[15] have been resolved by Allinger and Allinger (*Tetrahedron*, 2, 64 (1958)) by assuming a mobile equilibrium between axial and equatorial conformations. It might be pointed out that not only have the nuclear magnetic resonance spectra of the halocamphors in Table II been reported, but also their dipole moments have been studied[14] and their optical rotatory powers have been measured (C. Djerassi, J. Osiecki, R. Riniker and B. Riniker, THIS JOURNAL, 80, 1216 (1958)).

(17) In i, R_5 = Cl, Br, R_6 = H, the repulsion between halogen and oxygen would favor puckering. Apparently the rigidity of the ring inhibits this effect. For α-bromocyclohexanone the CO and CBr dipoles' repulsion has been estimated by Allinger and Allinger[16] to be 1.53 kcal./mole and by Corey[9c] to be 2.7 kcal./mole.

(18) The camphor and 2-indanone systems represent saturated ketones. Interestingly enough we get about the same shifts for α-chlorine (18 cm.$^{-1}$) and α-bromine (14 cm.$^{-1}$) in the acenaphthenone series[5b] (ii) where the ketone group is conjugated with the aromatic ring and the halogens have bisectional positions.

only 8 cm.$^{-1}$ and for α-chlorocyclopentanone the shift is only 13 cm.$^{-1}$. These values are well outside the limit of error for bisectional values and within the axial range. However, since they are larger than the lowest axial values obtained in fused rings, they suggest quasi-axial character.

Our next problem was to decide on a structure for cyclopentanone which would have quasi-axial α-positions. Literature work revealed, however, that very little attention had been paid to the detailed structure of cyclopentanone and to the detailed structures of other substituted cyclopentane compounds. Further, it developed that there was even question as to the structure of the parent of the series cyclopentane itself. In spite of this, however, we have been able to develop a fairly consistent picture from the small amount of useful data available.

Since LeFevre and LeFevre[19] have excellently summarized in detail the early structural work on cyclopentane, and Dauben and Pitzer[20] have reviewed the general conformational principles, neither topic will be detailed here. Instead, this paper will discuss only the relevant information needed for our purposes which has become available very recently.

Cyclopentane.—There are three reports of immediate interest to the cyclopentane problem. The first, in 1947 by Kilpatrick, Pitzer and Spitzer,[3] pointed out on the basis of thermodynamic and spectral data that the cyclopentane ring was nonplanar, but more importantly that neither one nor two carbon atoms were exclusively out of the plane of the others. Rather, puckering rotated around the ring (pseudorotation) in such a way that no single non-planar structure could be drawn to represent cyclopentane. During the course of their analysis they pointed out briefly that there were at least two non-planar forms which retained some symmetry, the C_s and the C_2. We have developed in some detail these forms as shown below. The C_s(III), the *cyclopentane envelope*,[21] has a single carbon atom out of the plane of the other four while the C_2 (IV), the *cyclopentane half-chair*,[21] has three adjacent carbons in one plane and the other two adjacent carbons twisted so that one is as much above the plane as the other is below. According to Kilpatrick, Pitzer and Spitzer[3] neither of these forms as well as a multitude of intermediate types differ much in energy; hence any given cyclopentane molecule might be expected to pass through most of the possible forms during pseudorotation. These authors concluded therefore that it was not possible to describe cyclopentane itself by a single structure.

In direct contrast to these results, LeFevre and LeFevre[19] have shown recently by polarizability

(19) C. G. LeFevre and R. J. LeFevre, *J. Chem. Soc.*, 3549 (1956).

(20) See M. S. Newman, "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1956, Ch. 1.

(21) We term this form the envelope in view of the obvious structural analogy. The half-chair is analogous to the cyclohexene half-chair (IVa, C_1 = C=C). For cyclopentane itself, the cyclopentane envelope and cyclopentane half-chair do not represent potential minima and therefore are termed forms and not conformations. On the other hand, in cases where substitution of groups for hydrogen stabilizes one form over the other the lower energy arrangement at least would represent a potential minimum and therefore could be termed a conformation. For a definition of the term conformation, see ref. 20.

measurements that while a C_s cyclopentane structure does not fit their data, a C_2 form gives a good fit. They conclude that a C_2 structure best approaches an ideal equally staggered form of cyclopentane which cannot be readily represented. In spite of these results it is difficult to envisage any special factor stabilizing the C_2 form over the C_s for cyclopentane since the amount of eclipsing is about the same in each. In general this view is borne out by very recent work on the experimental vapor heat capacity of cyclopentane by McCullough[22] which demonstrates that only if cyclopentane is assumed to undergo pseudorotation can experimental and calculated entropy and vapor heat capacity data be reconciled. Since the same type of treatment is required for thiacyclopentane (a restricted pseudorotator) and pyrrolidine (a free or only slightly restricted pseudorotator), the consistent treatment is conclusive evidence that such molecules do undergo pseudorotation as originally proposed by Kilpatrick, Pitzer and Spitzer. This means that no single, simple structure will suffice for cyclopentane itself. The picture would be bleak, indeed, if substituted cyclopentanes behaved similarly.

III, C_s, envelope   IV, C_2, half-chair

IVa   V
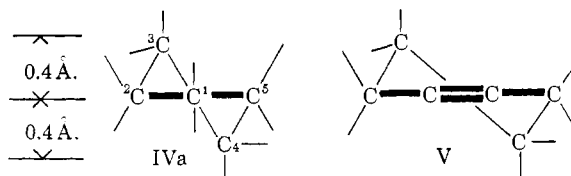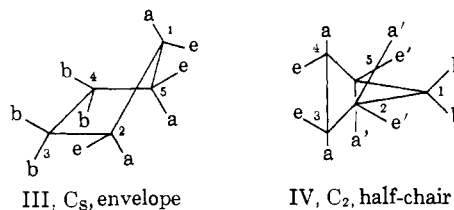
Substituted Cyclopentanes.—While the situation is more complicated in the cyclopentane series, a consistent picture can be drawn. The determining factor here is that substitution of hydrogen by a bulkier group will stabilize one of the two probable cyclopentane forms. It is necessary now to discuss these forms in greater detail. If one imagines a planar cyclopentane there is considerable strain in the molecule arising from eclipsing of the five methylene groups.[23] However, the 108° bond angles of the pentagon are not strained much. If one of the carbon atoms (C_1, III) twists up out of the plane of the other four, the methylene groups on either side (C_2, C_5) will develop less eclipsed staggered interactions with a reduction in the potential energy of the molecule. However, the puckering of C_1 will be opposed by the strain of deforming the bond angles.[23] Hence for any given molecule substituted at C_1 which might tend to adopt the cyclopentane envelope form the amount of puckering will depend on such factors as the bulk and

(22) J. P. McCullough, *J. Chem. Phys.*, **29**, 966 (1958).

(23) Estimates of the energies involved have been made (*cf.* ref. 3 and also K. S. Pitzer, *Science*, **101**, 672 (1945)). It would seem that a moderate deformation of the bond angles of cyclopentane is not expensive energywise.[3]

electronic nature of the group. Since no extensive structural work has been reported on monosubstituted cyclopentanes to guide us, we have calculated the limiting C_1 displacement for III. The twisting of C_1 out of the plane cannot proceed past staggered ethane interactions on either side. Therefore the approximate limiting value for C_1 puckering out of the C_2-C_3-C_4-C_5 plane is about 0.75 Å. If a carbon displaces this much, the C_1,C_2 and C_1,C_5 axial bonds will be trans and coplanar [24] It is to be noted that C_3,C_4 are eclipsed in III with four bisectional bonds.

While we had previously noted from our extensive literature searches that certain molecules adopted this form, it has only been very recently that theoretical justification for this has been found. Pitzer[25,26] has reported that various types of substitution would be expected to stabilize either the C_2 or C_s forms. Thus any substitution which would raise the torsional potential about two adjacent bonds in the ring symmetrically would favor the C_s form.[25,26] A large group substituted on C_1 of III (most likely equatorially) could maintain minimum non-bonded interactions with the staggered flanking methylene groups of C_2 and C_5. If the group were substituted on C_3 (or C_4) of IV only one side would have a full staggered ethane interaction, the other would have a more nearly eclipsed a',e or e',a orientation.

We had previously found in the literature X-ray analyses of complicated cases in which to achieve minimization of unfavorable eclipsing the molecule preferred the envelope form in the crystal state. Thus, D-ribose in cytidine[27] (VI, R_7 = cytosine) has C_3 0.5 Å. out of the plane with two groups equatorial and one bisectional. The remaining alcohol group is axial. A more striking example is found in
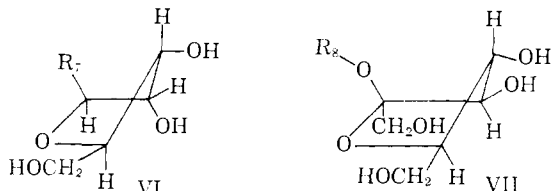

sucrose (VII).[23] Here as one might expect from simple alkyl substituted cyclohexanes, three groups can be equatorial and indeed they are. In both these cases where the substituent groups would presumably raise the potential barrier, a clearcut preference for the envelope conformation is demonstrated. We have been unable to find any case where the half-chair form has been preferred by similar molecules.

The other limiting form, the half-chair, is shown in IV. It is analogous to the half-chair of cyclo-

hexene (V). It can be imagined to be formed from a planar cyclopentane by holding C_1 -C_2 - C_5 in one plane and then allowing C_4 to twist as far above this plane as C_3 twists below. The maximum puckering occurs when C_3-C_4 are in a staggered ethane arrangement. We calculate that this occurs when C_4 is about 0.4 Å. above the C_1-C_2-C_5 plane and C_3 about 0.4 Å. below the plane. The bisectional, axial, equatorial quasi-axial and quasi-equatorial bonds are as shown in IV. In our experience it is this conformation which has been virtually neglected in early preliminary considerations of the non-planar substituted cyclopentane rings by organic chemists.

According to Pitzer[25,26] the C_2 form will be preferred by those molecules where substitution lowers the torsional potential about two bonds symmetrically. This is indeed borne out by the X-ray analysis of crystalline ethylene carbonate (VIII). Here the carbonyl group lowers the
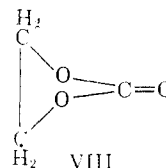
torsional potential symmetrically relative to the flanking oxygens.[29] In this molecule, however, the twist of the ethane group is not sufficient to pucker each carbon atom out of the $-O-\overset{O}{\overset{\|}{C}}-O-$ plane more than 0.3 Å. It is clear, however, that the structural analogy between cyclopentanone and ethylene carbonate, neglecting the fact that one is being scrutinized in solution and the other in the crystalline state, is so close as to suggest that cyclopentanone prefers the half-chair form. As can be seen in IV (C_1 = C=O) the positions flanking the carbonyl group are quasi-axial and equatorial. The shifts of 8 cm.$^{-1}$ for α-bromine and 13 cm.$^{-1}$ for α-chlorine are quasi-axial values since they are less than our bisectional values from the halocamphors. Our infrared data therefore clearly support the half-chair form (IX, R_9 = Cl, Br, R_{10} = H) for cyclopentanone. LeFevre and Le Fevre's polarizability studies[19] led them to suggest this form for cyclopentanone also.
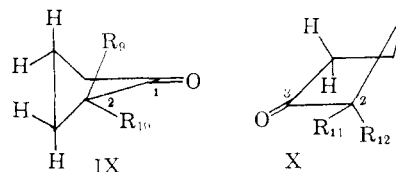
(24) In this case (III) θ_{12} = θ_{51} = 60°. It is important to recognize that cyclopentane itself is quite puckered as reported by Pitzer and Donath[25,26] and that in the envelope form the maximum puckering is 0.5 Å. In this form the C_1, C_2, C_5 trans-hydrogens are not quite coplanar (θ_{12} = θ_{51} = 46.10°).

(25) K. S. Pitzer, private communication; K. S. Pitzer, Abstracts of Papers, 133rd Meeting, American Chemical Society, San Francisco, Calif., April, 1958, p. 22N.

(26) K. S. Pitzer and W. E. Donath, This Journal, 81, 3213 (1959).

(27) S. Furberg, Acta Cryst., 3, 325 (1950).

(28) C. A. Beevers and W. Cochran, Proc. Roy. Soc. (London), A190, 257 (1947).

(29) C. J. Brown, Acta Cryst., 7, 92 (1954). As pointed out earlier[14] the two lone pairs of each oxygen atom in ethylene carbonate would produce a conformational effect similar to an α-methylene group of cyclopentane. The potential barrier in dimethyl ether (2.7 kcal./ mole) is not significantly different from propane (3.4 kcal./mole). For cyclopentanone, replacement of the methylene group in cyclopentane with a carbonyl group should reduce the potential barrier since such a substitution in propane (potential barrier, 3.3 kcal./mole) to give acetone (potential barrier, 1.4 kcal./mole) leads to a decrease of 1.9 kcal./mole.[1a] It might be pointed out that while no exact estimates have yet been made as to the energy of stabilization of the cyclopentanone half-chair over the envelope, it is not unreasonable, ac-

Our data support IX rather than X since one α-position in X has two bisectional bonds which would lead to larger shifts than observed. The other α-position (X, R_{11} = H, R_{12} = Br, Cl) has an axial position which would lead to smaller shifts than observed. There is also an equatorial position (X, R_{11}) which would lead to much larger shifts than observed. It is probable that some quasi-equatorial halogen (IX, R_{10} = Cl,Br, R_9 = H) is in equilibrium with the quasi-axial arrangement. For the α-halocyclohexanones, Corey[3] has reported shoulders on the main carbonyl absorption bands which were ascribed to the presence of equatorial conformations. Allinger and Allinger[16] estimate that in carbon tetrachloride as much as 25% of α-bromocyclohexanone may be in the equatorial conformation. However, we have not observed any shoulders on the main bands of either halocyclopentanones and neither has Corey reported any. It is probable that resolution of these bands, if present, is difficult since the difference in shifts between quasi-axial and quasi-equatorial halogens would be smaller than between extreme axial and equatorial orientations. We can tell, however, that the shift measured by our main band (Br = 8 cm.$^{-1}$, Cl = 13 cm.$^{-1}$) is due to quasi-axial halogen since the shift for quasi-equatorial bromine would have to be greater than our bisectional value of 12 cm.$^{-1}$ and for quasi-equatorial chlorine greater than 18–19 cm.$^{-1}$.

While we were confident of the significance of our infrared shifts it was deemed propitious to check our results against data we could glean from our dipole moments. The close correspondence between the moments of α- and α'-chlorocamphor demonstrates that in this system θ is 60°. We chose the moment of α'-chlorocamphor in heptane (3.98 D.) as representative since it was close to that of other quite different system, 1-chloro-2-indanone, where θ is also 60°. The chloroketone system was set up[30] along the three-dimensional coördinates in the usual way with a C—C=O angle of 120°, a C–C angle of 109°28', a value of 60° for θ and a /Cl value of μ = 3.98 D. By adjusting the apparent carbon–chlorine bond moment to 2.1 D. there was obtained a value of 2.91 D. for the apparent carbonyl moment. These values are quite reasonable. Thus as reported by Bender, Flowers and Goering[31] the apparent μ_{C-Cl} in 1,1-dichlorocyclohexane is 2.17 D., the apparent μ_{C-Cl} in cis-1,2-dichlorocyclohexane is 1.91 D. while the moment of cyclohexyl chloride itself is 2.24 D. The moment of camphor is reported to be 3.05 D.[32] and that of cyclopentanone is reported to be 3.00 D.[15] Our value of the apparent carbon–chlorine bond moment (2.1 D.) is slightly higher than that of cis-1,2-

dichlorocyclohexane (1.91 D.); however, the dipoles of the latter mutually reduce each other more since each carbon has tetrahedral angles.

It was now possible to solve for θ_{12} in 2-chlorocyclopentanone using the apparent moments of μ_{C-Cl} = 2.1 and $\mu_{C=O}$ = 2.91 D. In this way a value of 77° for the projected angle between C—Cl and C=O (IX, R_9 = Cl, R_{10} = H) was obtained. As can be seen from Table III,[33] this supports the

TABLE III

PROJECTED ANGLE (θ) BETWEEN HALOGEN AND CARBONYL GROUP

Half-chair (IV) C_4 displacement, Å.	θ_{12} (a')	Envelope (III) C_1 displacement, Å.	θ_{23} (a)	
0.4	78°	0.75	94°	This study
~ .3	75°	0.5	87°	Pitzer and Donath[25]
~ .4	~80°	..	..	Shoppee, et al.[34]

half-chair conformation for α-chlorocyclopentanone since our calculated value is 78°. We have converted Pitzer and Donath's slightly less puckered cyclopentane values to those for an hypothetical cyclopentanone arriving at a value of θ_{12} = 75°. Further, Shoppee's estimate[34] of Le Fevre's data calls for an angle of about 80°.

Our analysis does not support the envelope form since both our calculated value and estimates derived from Pitzer and Donath's data (Table III) place θ_{23} for the axial bond (X, R_{12}) near a value of 94°. Using this value of 94° we have calculated the hypothetical dipole moment of α-chlorocyclopentanone required to yield this angle. The value obtained, 3.40 D., is well outside the limit of error of these measurements (ca. ±0.03 D.[15]). The assumption of a 120° angle in camphor is probably reasonable but not precisely correct. Bridging of a cyclohexane boat with a gem-dimethyl group would require squeezing of the interior angle at the carbonyl group to less than 120°. Hence, the exterior angle would increase. As a result the C–Cl and C=O groups would tend even more to cancel each other. In order then to account for the observed moment of α'-chlorocamphor (θ = 60°) this way the apparent $\mu_{C=O}$ and μ_{C-Cl} would need to be even larger than our values. It is felt that our values of $\mu_{C=O}$ = 2.91 D. and μ_{C-Cl} = 2.1 D. are already moderately large; hence our assumed angle of 120° is presumably justifiable for this simple treatment.

Since our dipole moment and infrared data and Pitzer and Donath's calculations are in accord, the half-chair conformation of cyclopentanone is the most reasonable structure for systems of this sort.[35]

(33) Our analysis of the bromo series does not lead to such clearcut results. Since we[14] do not have the moment of α'-bromocamphor to use as a check on our value for α-bromocamphor (4.00 D., heptane) we cannot distinguish for α-bromocyclopentanone between θ = 83° (from α-bromocamphor) and θ = 74° (from 1-bromo-2-indanone, 3.76 D., heptane). However, these two values bracket the value for half-chair conformation and may be considered as supporting this conformation.

(34) C. W. Shoppee, R. H. Jenkins and G. H. R. Summers, J. Chem. Soc., 3048 (1958).

(35) That the trans diaxial β-hydrogens of α-chlorocyclopentanone are about coplanar can be inferred from some of our preliminary results in the α-halo-2-hexahydroindanones. Here the trans-hydrogens must be nearly coplanar due to the trans ring fusion.

cording to Pitzer, that the former be stabilized by about 1 kcal./mole. This would mean at least that about 86% of the half-chair would predominate at equilibrium and that by most structural techniques available cyclopentanone would have this arrangement.

(30) Thanks are due Dr. J. G. Miller and Dr. W. D. Kumler for helpful suggestions in this procedure.

(31) P. Bender, D. L. Flowers and H. L. Goering, THIS JOURNAL, 77, 3463 (1955).

(32) L. G. Wesson, "Table of Electric Dipole Moments," The Technology Press, Cambridge, Mass., 1948.

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Experimental[36]

d-α-Bromocamphor was prepared from d-camphor (Eastman Kodak Co.) as recorded elsewhere,[37] m.p. 75–76°, lit. m.p. 76–77°.

We get shifts in iii of 9 cm.$^{-1}$ for α-bromine and 14 cm.$^{-1}$ for α-chlorine. These are almost identical with the simple α-halocyclopentanones. This further suggests that 16-ketosteroids would prefer the half-chair conformation.
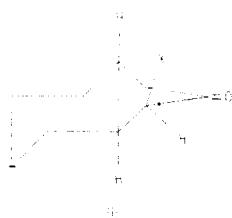
(36) All melting points are uncorrected.
(37) J. E. Marsh, *J. Chem. Soc.*, 828 (1890).

d-α,α'-Dibromocamphor was prepared from d-α-bromocamphor as in the literature,[38] m.p. 61°, lit. m.p. 60°.

d-α-Chlorocamphor.—Preparation was effected from d-camphor essentially as described by Kipping and Pope,[39] m.p. 94.5–95°, lit. m.p. 93.5°.

d-α'-Chlorocamphor was prepared from d-α-chlorocamphor as described by Lowry and Steele,[40] m.p. 117°, lit. m.p. 117°.

d-α,α'-Dichlorocamphor, prepared from d-camphor by direct halogenation,[41] had m.p. 95.5–96°, lit. m.p. 96°.

2-Indanone, prepared as mentioned in footnote b, Table I, had m.p. 56.4–57°, lit.[42] m.p. 56–57°.

1-Bromo-2-indanone.—Preparation was effected from 2-indanone as described by Creeth and Thorpe,[43] m.p. 91°, lit. m.p. 91°.

1-Chloro-2-Indanone.—One gram (0.0076 mole) of 2-indanone was dissolved in 5 ml. of chloroform. Chlorine was passed into the solution for five minutes. The solvent was evaporated and the residue was recrystallized from benzene to remove unreacted 2-indanone. The material was then recrystallized twice from ligroin (65–110°). The colorless prisms melted at 71–71.5°. *Anal.* Calcd. for C_9H_7OCl: C, 64.89; H, 4.24; Cl, 21.28. Found: C, 64.61; H, 4.23; Cl, 21.33, 21.39.

2-Bromocyclopentanone was prepared as described elsewhere,[9c] b.p. 67° (5 mm.), $n^{20}D$ 1.5085, lit.[9c] b.p. 82–83° (12 mm.), $n^{18.5}D$ 1.4778.

(38) T. M. Lowry, *ibid.*, 569 (1898).
(39) K. Kipping and W. Pope, *ibid.*, 548 (1893).
(40) J. Lowry and R. Steele, *ibid.*, 1382 (1915).
(41) P. Cazeneuve, *Compt. rend.*, **94**, 731 (1882).
(42) N. Levin, B. E. Graham and H. G. Kolloff, *J. Org. Chem.*, **9**, 380 (1944).
(43) N. Creeth and J. Thorpe, *J. Chem. Soc.*, 1507 (1908).

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Cyclopentene-3,5-dione. I. Synthesis and Properties[1]

By C. H. DePuy and E. F. Zaweski[2]

Cyclopentene-3,5-dione (I) has been prepared by oxidation of the corresponding diol. Attempts to prepare it by base-promoted elimination reactions led instead, or concurrently, to cyclopentadienone, isolated as its dimer. The dione is very acidic, although less so than the saturated dione. No evidence has been found for the existence of the enol form. The dione polymerizes readily in basic solution, possibly by Michael addition, but is stable toward acid. Some chemical and spectral properties of the compound are discussed, as well as the question of the stability of cyclopentadienone.

Introduction

Over the past ten years a tremendous amount of work has been carried out on the synthesis and reactions of highly unsaturated seven-membered ring compounds. This work has led to a completely new type of chemistry, and to new aromatic and pseudoaromatic ring systems. Although similarly interesting and unusual unsaturated *five-membered* ring compounds might be imagined, little synthetic work has so far appeared. In this paper we describe the synthesis and some of the properties of cyclopentene-3,5-dione (I), a molecule with a great deal of interest in its own right, and one which we anticipate will be a suitable starting material for the preparation of other molecules of theoretical and practical importance.

We considered cyclopentene-3,5-dione to be a potentially useful molecule for a number of reasons. First the only stable, completely unsaturated cyclopentane compounds known are those which are substituted with electron-donating groups (*i.e.*, di-

(1) A preliminary announcement of some of this work appeared as a "Communication to the Editor" in This Journal, **79**, 3923 (1957).
(2) Procter and Gamble Fellow, Summer, 1958.

azocyclopentadiene[3] (II) and triphenylphosphonium cyclopentadienylide[4] (III)). These compounds so far have not proved amenable to further elaboration.
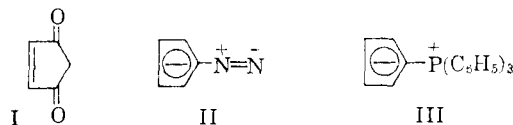
Secondly monosubstituted cyclopentadienes are susceptible to dimerization, and the mobility of the protons in a cyclopentadiene ring makes the isolation of a pure isomer difficult.[5] These considerations led us to the synthesis of the dione, which

(3) W. von E. Doering and C. H. DePuy, This Journal, **75**, 5955 (1953).
(4) F. Ramirez and S. Levy, *ibid.*, **79**, 67 (1957).
(5) For examples of this equilibrium see M. Rosenblum, *ibid.*, **79**, 3179 (1957), and R. J. Day, *Dissertation Abst.*, **19**, 39 (1950). We have observed a similar mixture of products from the pyrolysis of 3,5-diacetoxycyclopentene (C. H. DePuy, unpublished results). It seems probable that compounds of the type IVa would be relatively stable if they could be formed at moderate temperatures in the absence of bases.