- 4. I. I. Furlei, V. P. Yur'ev, V. I. Khvostenko, G. A. Tolstikov, and S. R. Rafikov, Dokl. Akad. Nauk SSSR, <u>222</u>, 1163 (1975).
- 5. V. I. Khvostenko, I. I. Furlei, and I. Kh. Aminev, Khim. Vys. Energ., 3, 502 (1969).
- 6. V. I. Khvostenko, I. I. Furlei, V. S. Fal'ko, L. A. Baltina, G. A. Tolstikov, and A. Sh. Sultanov, Khim. Vys. Energ., <u>11</u>, 15 (1977).
- 7. V. I. Khvostenko and I. I. Furlei, Teor. Eksp. Khim., 4, 816 (1968).
- 8. I. Kh. Aminev and V. I. Khvostenko, Filed in VINITI, No. 3643-71.
- 9. V. I. Khvostenko, I. I. Furlei, V. A. Mazunov, and R. G. Kostyanovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 680 (1973).
- 10. J. N. Bardsley and F. Mandl, Rept. Progr. Phys., 31, 471 (1968).
- 11. V. I. Khvostenko and G. A. Tolstikov, Usp. Khim., 45, 251 (1976).
- 12. M. Krauss and F. H. Mies, Phys. Rev., A1, 1592 (1970).
- 13. G. J. Schulz, Rev. Mod. Phys., 45, 423 (1973).

### GEOMETRICAL STRUCTURES OF CERTAIN

CYCLOPROPYL ETHERS

B. A. Arbuzov, A. M. Kamalyutdinova, UDC 541.63:547.512
S. G. Vul'fson, A. N. Vereshchagin,
S. M. Shostakovskii, T. K. Voropaeva,
and A. A. Retinskii

There have been relatively few studies of the conformations of molecules showing internal rotation around a bond joining a heteroatom with a three-membered ring C atom [1-3]. As a special case, it has been shown that cyclopropyl methyl ether exists in gauche conformation (Fig. 1g). Steric overloading excludes the possibility of realizing the trans (t) conformation in these molecules. Unsymmetrical ring substitution leads to establishment of an equilibrium between the g1 and g2 gauche forms (cf. Fig. 1). Study of the role played by radical R in fixing the conformal equilibrium point is of interest for estimating the relative significance of steric and polar effects in these systems. We have studied the dipole moments (DM) and Kerr constants (KC) of gem-dichloro-substituted cyclopropyl alkyl, cyclopropyl aryl, and cyclopropyl vinyl ethers, working with certain model compounds designated in what follows as (I)-(XIV).

 $\begin{array}{c} N_2 & \longrightarrow \\ OR \\ X=H, R=C_2H_3(I); X=H, R=i\cdot C_aH_7(II); N=H, R=t\cdot C_aH_9(III); X=H, R=C_6H_6(IV); \\ X=H, R=C_2H_3(V); X=CI, R=i\cdot C_aH_7(VI); N=CI, R=t\cdot C_4H_9(VII); X=CI, R=C_6H_6(VIII); \\ N=CI, R=p\cdot CH_3C_6H_4(IX); X=CI, R=2,6\cdot (CH_3)_2C_6H_3(X); X=CI, R=2,4,6\cdot (CH_3)_2C_6H_2(XI); X=CI, R$ 

Experimental data on these compounds are summarized in Table 1.

Study of the geometrical structures of the aryl ethers (IV), (VIII)-(XIII) is of interest in itself for the information it might give concerning rotation of the aromatic ring with respect to the C—O—C plane. Although the angle of rotation is only 20° in anisole [4], introduction of an electronegative substituent (carbonyl [5], or sulfo [6] groups) at the oxygen atom increases the molecular nonplanarity markedly. It is interesting to note that  $CH_3$  group substitution has essentially no effect on the conformation in this last case, even if the substitution is carried out at both of the ortho positions. Since the cyclopropane C atom does exist in tetrahedral hybridization, and the pseudounsaturated ring can conjugate with the unshared electron pair of the oxygen, it is reasonable to expect that the geometrical orientation of the aromatic system would differ in some respects from that met in anisole. There can be no doubt that the lack of symmetry in the cyclopropyl radical, especially with X = Cl, limits the possibility of determining the magnitude and direction of aryl rotation. The limitations imposed on certain types of compounds will be considered below.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 599-604, March, 1978. Original article submitted November 22, 1976.

Compound	αε,	ß	۰¥	8	μ,D	m <sup>K · 101*</sup>
(i) (i1) (I1i) (IV) (V) (V1) (V1) (V11) (V11) (X) (X) (X11) (X11) (X11) (X11)	8,623 7,800 7,469 6,786 7,988 10,202 13,994 4,658 5,457 8,109 11,647 5,903 10,674 7,109	 	 0,046 0,075  0,013 0,073 0,065 0,065 0,065 0,065 0,062 0,793 	 42,262 16,837  52,170 28,740 11,540 37,446 75,071 76,530 	1,36 1,36 1,43 1,35 1,29 2,41 1,33 1,53 1,53 1,53 1,58 2,46 1,89 2,30 1,56	

 TABLE 1. Dipole Moments and Kerr Constants for the Various

 Compounds



Fig. 1. Conformations of cyclopropyl ethers at the C(cy) - O bond.

The unchlorinated ethers (I)-(V) were used as model compounds for testing the system additive of bond polarities. A system of bond moments, applicable to cyclopropane derivatives, has been described in [7]. The C(cy)-O bond moment was, however, determined only from data on the halo derivatives [2]. Furthermore, the dipole moments of (I)-(III) and cyclopropyl methyl ether (1.20 D [1]) were obtained from the C-O-C valence angle, the m(R-O) moment (mean value for the dialkyl ethers, 1.17 D [8]), and the independently determined  $m(C_3H_5-O)$ , the latter equal to the sum of the moments of the H-C(cy) and C(cy)-O bonds. The experimentally determined values for (I)-(III) are identical, and somewhat larger than the DM for the methyl analog. Vector subtraction based on the geometry of 1 [1] gave  $m(C_3H_5-O) = 1.40$  D. This value is close to the moment obtained for alkoxyl radicals, the direction of the molecular dipole being in near coincidence with the bisector of the C-O-C angle [1]. With the H-C(cy) bond moment set equal to 0.52 D, [7], one finds m<sup>(C(cy)</sup>-O) = 0.88 D. This value is quite different from the 0.2 D obtained through analysis of the DM of the dichlorinated ether [2]. The polarities of the (VI), (VII) and the analogous ethyl ether [2] were such as to confirm the reality of this last value for the halogenated derivatives, description being impossible in terms of a 0.88 D moment. Thus the introduction of two Cl atoms into the cyclopropyl radical markedly alters the polarity of the C-O vicinal bond. Electron shift from the oxygen atom to the ring gives rise to a 0.7 D interaction moment.

The Kerr constants of compounds such as (III) which contain an axially symmetrical alkyl radical are dependent on the angle of the tert-butoxy group rotation around the C(cy)-O bond. Calculation of these constants made use of the geometrical parameters of [1], and the polarizability tensor components listed in Table 2. The Kerr constant of (III) varied from  $-8.8 \cdot 10^{-12}$  in the trans conformation ( $\varphi$ , the angle of rotation around the C-O bond, equal to 0°) to  $27 \cdot 10^{-12}$  at  $\varphi = 180^\circ$ . The fact that mK(III) was essentially constant over the  $\varphi$  interval from 120 to 240° made it impossible to determine the rotation exactly. However, the data of [1] indicate clearly that preference between the t and g conformations is to be decided in favor of the latter.

The dipole moment of the phenoxy group is quite sensitive to changes in the substituent at the oxygen atom [5, 14]. Its value in the cyclopropyl ethers was therefore calculated from the moment of (IV), using the cyclopropoxy group polarity given above. The equation  $\mu(IV) = f[m(C_6H_5-O)]$  had two roots, one at 1.30 D and the other at 0.10 D. With account taken of the C—H bond polarity [6], the corresponding  $C_{SP2}$ —O bond moments would be +0.60 and -0.60 D. It will be shown below that the DM's of (X)-(XII) are such as to give preference to the first of these values. The DM of (V) was used in the same manner to obtain the dipole moment of the  $C_2H_3$ —O bond as 1.14 D, a value close to that for the phenyl ether. The parameters of the ellipsoid of molecular polarizability of (IV) depend on two angles of internal rotation, one around the C(cy)—O bond ( $\varphi$ ) and the other around the C(ar)—O bond ( $\psi$ ). In view of what was said above, discussion will be limited to the case of the gauche conformer with  $\varphi = 120$  or 240°. The KC of (IV) is affected by the

Fragment	b <sub>L</sub> (!1)	$le_T(le_2)$	$b_V(b_3)$	Literature reference
С-Н	0,65	0,65	0,65	[9]
C-C	0,98	0,27	0,27	[9]
C-0	0,89	0,46	0,46	[9]
$C_3H_6$	2.46	1,35	1,35	[9]
C(cy)Cl <sub>2</sub>	6.35	5,24	3,54	[9]
Catis	10,55	10,55	6,79	[10]
$C(ar) - CH_3$	3,26	2,02	2,34	[11]
1,3,5-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	11.64	16,51	16,51	[12]
1,3,5-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	9.85	17.15	17,15	[13]

TABLE 2. Bond and Group Polarizability Parameters, A<sup>3</sup>



Fig. 2 Fig. 3 Fig. 2. Angular dependence of the Kerr constant for compound (IV).

Fig. 3. Angular aryl radical orientations in the cyclopropyl aryl ethers.

orientation of the molecular DM, the latter, in turn, being determined by the phenoxy group polarity, mK(IV) was accordingly developed as a function of the angle  $\psi$  (Fig. 2), working through the equations m[C(ar)-O] = +0.60 D (A) and -0.60 D (B). It can be seen that the KC was quite insensitive to change in both  $\varphi$  and  $\psi$ . The absolute value of the angle of phenyl group rotation relative to the C–O–C plane could be accurately determined independently of the moment, but the direction of the C(ar) - O dipole could not be fixed on the basis of the KC alone. Assuming, for reasons which will be outlined below that this vector is positively directed, the true conformation would be that corresponding to  $\psi = 35^\circ$ , the angle marked out by the experimentally determined  ${}_{m}K$  point on the A curve. The fact that the angle is greater here than in anisole [4] probably reflects the reduction in conjugation of the unshared electron pair of the oxygen atom with the aromatic system resulting from competitive interaction with the cyclopropyl substituent. Both the bond polarity and the molecular conformation suggest that the three-membered cycle is a more active electron acceptor than the oxygen atom. The positive direction of phenyl radical rotation  $(0 < \psi < 90^{\circ})$  in the gauche conformation was chosen to be that leading to an increase in the distance of separation between the nearest ortho positions in the aromatic ring and the methylene (dichloromethylene) group of the cyclopropane ring (Fig. 3). Steric considerations definitely indicate this to be the more probable of the two directions of rotation.

The molecules of the dichloroderivatives (VI)-(XIV) each have two dipoles, mutually oriented in dependence on the angle  $\varphi$ . With the exception of compound (XIII), each R-O group dipole is directed toward the oxygen atom. It can be seen from Fig. 1 that this dipole is nearly perpendicular to the CCl<sub>2</sub> dipole in the gl conformation, and parallel to the CCl<sub>2</sub> dipole in the g2 conformation. In other words, the g2 is the more polar of the two forms. The value of the R-O moment therefore fixes the difference of the DM's, and the possibility of using this difference for determining the g1 = g2 equilibrium point. The interval of change of polarity in the alkyl ethers is rather wide; with the above values for the bond moments:  $\mu$  (g1) = 1.22,  $\mu$  (g2) = 2.47 D [2]. Study of the DM's of the dichlorocyclopropyl alkyl ethers showed that both the polarity and the g2 conformer content increase in going from ethyl ether (1.86 D, 0.4 [2]) to isopropyl ether (1.99 D, 0.55) to tert-butyl ether (2.41 D, 1.0). The presence of even one C-H bond in the  $\alpha$  position permits a considerable proportion of the molecules to pass into the g1 conformation with a cis-vicinal chlorine atom and alkyl radical approach. It was stabilized by attraction of the R-O and CCl<sub>2</sub> dipoles. The butyl

	$\mu_{\rm p}, m (\rm C - 0) = 0,60 \rm D$		$\mu_{\rm p}, m (\rm C - \rm O) = -0,60  \rm D$			
Compound	gi	g2	£1	<u>g</u> 2	μexp	n(g2)
(VIII) (IX) (X) (XI) (XII)	1,22 1,42 1,12 1,22 1,22	2,49 2,84 2,15 2,49 2,49	1,31 1,16 1,18 1,31 1,31	1,44 1,74 1,54 1,44 1,44	1,33 1,53 1,98 2,46 1,89	0,06 0,1 0,8 1,0 0,4
- 1 30 130	$\begin{array}{c c} \mu^2(\mathbf{XI}) \\ & \mathbf{g} \\$	a	90 - 60 120 - exp	150 0 90 90 12	0 60 150	$   \begin{array}{c} \mu^{2} (\Psi) \\                                    $

TABLE 3. Dipole Moments for Dichlorocyclopropyl Aryl Ethers, D

Fig. 4. Comparison of Kerr constants and second-power dipole moments for (VIII) (a) and (XII) (b).

180

240

300

360

420 "K·10<sup>12</sup>

radical must occupy the sterically unhindered g2 position. The measured KC for compound (VII),  $68 \cdot 10^{-12}$ , was identical with the value calculated for this conformation.

-60

0

60

120

Study of the aromatic derivatives (VIII)-(XII) required not only a knowledge of the  $g_1 = g_2$  equilibrium point but also a determination of the direction of the C(ar)-O dipole. Here use was made of the measured CH<sub>3</sub>--C<sub>Sp2</sub> group moment for toluene [8]. Since the dipoles of the three meta-oriented substituents mutually cancel out, the calculated DM's of (XI) and (XII) were the same as for (VIII). With the Ph-O group moment equal to 0.10 D, the molecular moment is practically unaffected by internal rotation, the maximum difference being  $\pm m$  (RO) sin COC =  $\pm 0.09$  D. The fact that the polarity increases by more than 1 D in passing from (VIII) to (XII) speaks in favor of the higher moment. The results obtained in these calculations are presented in Table 3.

The data for (X)-(XII) show that  $m(C_{sp}^{2}-O) = -0.60$  D cannot be considered as having physical reality. The tendency to pass into the g1 position is even greater in the sterically unhindered (lacking ortho substituents) aryl' radicals of (VIII) and (IX) than in the ethyl radical [2]. It may be that stabilization of this conformation is due, in part, to interaction between the polar CCl<sub>2</sub> group and the dipole which this group induces in the easily polarizable aromatic system. Comparison of the experimentally determined DM for (XIII) with the values calculated for the g1 (2.57 D) and g2 (1.04 D) shows clearly that the g1 conformation must predominate in the conformational equilibrium. The two ortho substituents tend to destabilize this form; the same is also true, to a lesser degree, of the Cl atoms, and, to a still greater degree, of the CH<sub>3</sub> groups. Thus electrostatic and steric effects compete to fix the gauche-conformer equilibrium point in the alkyl and aryl ethers. Since the presence of the vinyl radical does not give rise to appreciable steric interactions, it can be anticipated that the less polar g1 conformation ( $\mu = 1.39$  D) would predominate over the more polar g2 conformation ( $\mu = 2.46$  D) in (XIV). The fact is, however, that the measured moment leads to n (g2) = 0.1, just as in the case of sterically unhindered aryl ethers.

In treating the aromatic radical rotation in the dichloro derivatives (VIII)-(XII), account must be taken of differences of rotation in the g1 and g2 conformations, of differences in the unsubstituted and the diortho-substituted derivatives, and of differences in positive and negative values of the angle  $\psi$ . All told, determination of the aryl group orientation is considerably difficult. The information obtained through a study of the Kerr constants proves to be more useful in confirming the position of the conformational equilibrium point marked out by the DM method. Since aryl group rotation around the C(ar)-O bond does not lead to alteration of the DM, the g1 and g2 conformations in the KC vs second-power DM plot fall on a  $\mu =$ const line joining KC's calculated for  $\psi = 0$  (180°) and  $\psi = 90^\circ$ , just as in [2]. The plot for compound (IX)



Fig. 5. Angular variation of the Kerr constant for (X).

was similar to that for (VIII) shown in Fig. 4a. The KC values would also be consistent with the phenyl group rotation of  $\pm 35^{\circ}$  found for (IV). The electrooptical properties of (XII) confirmed the value of the g1: g2 ratio found by the DM method at each value of the angle  $\psi$  (cf. Fig. 4b). There is no doubt that steric overloading such as is met in the g1 form of the diortho-substituted derivatives can lead to a marked alteration in the aryl group rotation. The fact is that the values of the g1:g2 ratio found for (X) and (XI) (Fig. 5) by the DM method impose limitations on the values of  $\psi$  in the two conformations, which entails, in turn, acceptance of the minimal values  $_{\rm m}$ K (g1) 0 (180°) and  $_{\rm m}$ K (g2) (90°).

#### EXPERIMENTAL

The syntheses and properties of the various compounds have already been described: (I)-(III) and (V) in [15]; (IV) in [16]; (VII) in [17]; (VI), (VIID, and (IX) in [18]; (XIV) in [19].

gem-Dichlorocyclopropyl Ether of 2,6-Xylenol (X). This compound was prepared by adding dichlorocarbene (DCC) (obtained from CHCl<sub>3</sub>, 50% NaOH, and 2% triethylbenzylammonium chloride) to the vinyl ether of 2,6-xylenol at 0°C. Yield, 48%; bp 115°C (4 mm);  $n_D^{20}$  1.5345;  $d_4^{20}$  1.2114. Found: C 56.97; H 5.23; Cl 30.61%. C<sub>11</sub>H<sub>12</sub>OCl<sub>2</sub>. Calculated: C 57.00; H 5.15; Cl 30.73%.

<u>gem-Dichlorocyclopropyl Ether of Mesitol (XI)</u>. This compound was synthesized through the reaction of DCC with the vinyl ether of mesitol, the procedure being similar to that described for the preparation of (X). Yield, 46%; bp, 110°C (1 mm);  $n_D^{20}$  1.5340;  $d_4^{20}$ , 1.1823. Found: C 58.80; H 5.74; Cl 28.28%.  $C_{12}H_{14}OCl_2$ . Calculated: C 58.77; H 5.71; Cl 28.28%.

<u>gem-Dichlorocyclopropyl Ether of 2,4,6-Trichlorophenol (XII)</u>. This compound was synthesized through the reaction of DCC with the vinyl ether of 2,4,6-trichlorophenol, the procedure being similar to that described for the preparation of (X). Yield, 61%; bp, 132°C (1 mm);  $n_D^{20}$ , 1.5765;  $d_4^{20}$  1.5595. Found: C 35.80; H 2.01; Cl 57.80%. C<sub>9</sub>H<sub>5</sub>OCl<sub>5</sub>. Calculated: C 35.53; H 1.63; Cl 57.83%.

gem-Dichlorocyclopropyl Ether of p-Chlorophenol (XIII). This compound was synthesized by reacting DCC with the vinyl ether of p-chlorophenol, the procedure being similar to that followed in preparing (X). bp,  $106^{\circ}$ C (1-2 mm);  $n_D^{20}$  1.5525;  $d_4^{20}$  1.3706. Found: C 45.70; H 2.84; Cl 44.95%.  $C_9H_7OCl_3$ . Calculated: C 45.52; H 2.98; Cl 44.84%.

The procedures following in measuring the dipole moments and Kerr constants have been described in [2]; the results obtained from the measurement of dielectric constants ( $\epsilon$ ), densities (d), indices of refraction (n), and electrical double refractions (B) in CCl<sub>4</sub> solution at 20°C are summarized in Table 1.

### CONCLUSIONS

1. The relation of polar and steric effects determines the position of the two-gauche-conformer equilibrium point in the gem-dichlorocyclopropyl alkyl and gem-dichlorocyclopropyl aryl ethers with radical orientation toward the  $CCl_2$  and  $CH_2$  groups.

2. The C(cy)-O bond polarity varies, depending on whether the molecule does or does not contain vicinal C-Cl bonds.

3. The phenyl radical of cyclopropyl phenyl ether is rotated by  $35^{\circ}$  with respect to the C-O-C plane.

## LITERATURE CITED

- 1. R. E. Penn and J. E. Boggs, J. Chem. Phys., 59, 4208 (1973).
- 2. B. A. Arbuzov, S. G. Vul'fson, L. A. Monetina, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 331 (1975).

- 3. J. P. Galy, Thesesdoct, Sci. Phys. Univ. Provece, 1972.
- 4. M. J. Aroney, R. J. W. Le Fevre, R. K. Pierens, and M. G. N. The, J. Chem. Soc., B, 666 (1969).
- 5. B. A. Arbuzov, A. P. Timosheva, S. G. Vul'fson, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 1336 (1977).
- 6. B. A. Arbuzov, S. G. Vul'fson, G. G. Butenko, O. A. Samarina, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 94 (1976).
- 7. A. N. Vereshchagin and S. G. Vul'fson, Izv. Akad. Nauk SSSR, Ser. Khim., 1974 (1968).
- 8. A. L. McClellan, Tables of Experimental Dipole Moments, Vol. 1, San Francisco-London (1963), Vol. 2, El Cerrito (1974).
- 9. A. N. Vereshchagin and S. G. Vul'fson, Teor. Eksp. Khim., 4, 548 (1968).
- 10. B. J. W. Le Fevre, Adv. Phys. Org. Chem., 3, 1 (1965).
- 11. C. G. Le Fevre and R. J. W. Le Fevre, Rev. Pure Appl. Chem., 5, 261 (1955).
- 12. S. G. Vul'fson and A. N. Vereshchagin, Dokl. Akad. Nauk SSSR, 225, 593 (1975).
- 13. C. L. Cheng, D. S. N. Murthy, and G. L. D. Ritchie, Austr. J. Chem., 25, 1301 (1972).
- 14. L. K. Yuldasheva, A. P. Timosheva, A. B. Remizov, G. N. Sergeeva, A. I. Fishman, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 318 (1974).
- 15. G. A. Kalabin, D. F. Kushnarev, S. M. Shostakovskii, and T. K. Voropaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 2459 (1975).
- 16. S. M. Shostakovskii, A. I. L'vov, and Ya. M. Kimel'fel'd, Izv. Akad. Nauk SSSR, Ser. Khim., 1754 (1966).
- 17. A. Ledwith and H. J. Woods, J. Chem. Soc., B, 973 (1967).
- 18. M. F. Shostakovskii, A. A. Nikiforov, and V. V. Keiko, Izv. Akad. Nauk SSSR, Ser. Khim., 147 (1967).
- 19. S. M. Shostakovskii, A. A. Retinskii, and A. V. Bobrov, Izv. Akad. Nauk SSSR, Ser. Khim., 1818 (1974).

# SYNTHESIS AND GEOMETRICAL STRUCTURE OF 4-METHYL-

**3-CARENE AND CERTAIN OF ITS DERIVATIVES** 

L. K. Novikova, O. B. Skripnik,

UDC 541.63:542.91:547.597

- G. Sh. Bikbulatova, S. G. Vul'fson,
- Z. G. Isaeva, and A. N. Vereshchagin

The stereochemistry of the reactions of bicyclo [4.1.0] heptane systems have been thoroughly investigated for the special case of 3-carene and its derivatives [1]. Here the relations in question were relatively simple because of symmetrical substitution in the 3,4 positions. We have extended this earlier work by synthesizing 4-methyl-3-carene (IV), its epoxide (V), and dichlorocarbene adduct (VI), and studying the stereochemistry of electrophilic addition at the tetra-substituted double bond in the bicycloheptene system. Study of 4-methyl-3-carene and its cycloaddition products is of interest for the information which it might furnish concerning the conformations of six-membered rings with planar groups in the 1,4 positions. The data reported on these conformations is largely contradictory. Thus 1,4-cyclohexadiene has been variously reported as a planar structure and as a boat conformation with a dihedral angle of  $160^{\circ}$  between the C-C=C-C planes [2, 3]. PMR data has been interpreted as indicating planar structure for the six-membered ring of syn-boat 3-carene [6]. Consistent results have, indeed, been obtained from structural studies on the 3-carene oxide [2, 7]. But while diffraction measurements and theoretical calculations indicate that the central ring of the carene oxide addition products should have planar structure, measurement of the Kerr constants (KC) and study of the PMR spectra suggest that this ring is in boat conformation [2, 8-10]. Contradictory results have also been obtained from studies on the structures of the dihalocarbene bis-adducts with 1,4-cyclohexadiene [11]. Determination of the conformations of (IV)-(VI) should lead to a final decision as to whether the bicycloheptene and tricyclooctane six-membered rings have planar or twisted structure

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 605-609, March, 1978. Original article submitted November 2, 1976.