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REARRANGEMENT OF 1-CHLOROCAMPHENE IN THE PRESENCE OF BORON FLUORIDE AND THE MOLECULAR STRUCTURE OF CAMPHENE-4-MERCURIC CHLORIDE

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Rearrangements that accompany addition to the double bond of camphene, or dehydration, dehydrochlorination, and other reactions of camphane derivatives have been studied extensively and may be classified as nucleophilic rearrangements [1]. They take place in the presence of acids and different types of cations participate [2].

The racemization of optically active camphene, which takes place without any obvious reaction at the double bond, is catalyzed by medium-strength protonic acids and has been shown to consist of a collection of several rearrangements [3-5]. Predominant among these are the Nametkin rearrangement (migration of the exo-methyl group) and the Wagner–Meerwein rearrangement (6,2-hydride shift) in the intermediate carbocation [5-7]. The appearance of a positively charged particle in the presence of a protonic acid is explained logically by reverse protonation of the unsaturated unit in the camphene molecule.

In our synthesis of camphenyl derivatives of transition metals, we observed ready rearrangement of the original 1-chlorocamphene (I) in the presence of transition metal salts. The major product of this reaction is 4-chlorocamphene (II). Evidently, this process is closely similar in nature to the racemization of unsubstituted camphene. As in reactions with the protonic acids [3, 4, 6], we found a difference in the degree of the additives' catalytic activity and in the composition of the products formed. According to our information, the application of Lewis acids to the racemization of camphene has not been studied systematically, and we therefore considered it opportune to publish our accumulated data, since a transition metal that is free to form a π-complex and accelerate hydrogen transfer when it participates in the rearrangement can broaden existing concepts of the mechanism of these rearrangements.

The catalytic action of the salts $HgCl_2$, $FeCl_3$, and $SbCl_5$ on the rearrangement of camphene chlorohydrate in isobornyl chloride was described earlier in [8] and is associated with coordination of Cl^- and MCl_n. In our case, the chlorine is located at the head of the bridge and cannot ionize readily.

We studied the rearrangement of (I) in the presence of $Et_2O \cdot BF_3$, $CrCl_3$, $FeCl_3$, $TiCl_4$, $Fe(CO)_5$, $Fe(C_5H_7O_2)_3$, Ni(0), and UCl_4. This paper reports results with the first of these catalysts, a typical Lewis acid, which rules out the possible impurity of a protonic acid in the other instances.

(I) prepared by the procedure in [9] contains 7.8% of (II) and no other impurities [within the sensitivity limits of gas–liquid chromatography (GLC)]. It has not been possible to separate (I) and (II) by some preparative method. GLC data indicate that in the absence of catalytic additives, our specimens of (I) can be stored indefinitely without increasing the concentration of the (II) isomer. Rearrangement takes place at ∿20°C in an argon atmosphere in the presence of the catalyst. It was demonstrated by special tests that rearrangement does not occur under the conditions in which the products were separated and their composition determined.

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TABLE 1. Effect of the Amount of BF_3 and Reaction Time with (I) on the Yield of (II) (tests 1-25) and on the Reverse Rearrangement of (II) to (I) (tests 26 and 27)

Test number	Substrate: BF_3 molar ratio	Reaction time, h	Product comp., %			Test number	Substrate: BF_3 molar ratio	Reaction time, h	Product comp., %		
			(I)	(II)	(V)				(I)	(II)	(V)
		0	92,2	7,8	–	15	1 : 1	1	87,5	12,5	–
1	5 : 1	2	90,6	9,4	–	16	1 : 1	2,5	79,1	20,9	–
2	5 : 1	4	86,4	13,6	–	17	1 : 1	4,5	73,0	27,0	–
3	5 : 1	22	84,8	15,2	–	18	1 : 1	24	32,8	67,2	–
4	5 : 1	48	80,5	19,5	–	19	1 : 1	72	27,2	72,8	–
5	5 : 1	120	70,1	20,8	9,1	20	1 : 1	168	18,2	76,3	5,5
6	2 : 1	4	85,7	14,3	–	21 *	1 : 1	24	91	9	–
7	2 : 1	7	84,0	16,0	–	22	1 : 2	2	56,7	43,3	–
8	2 : 1	24	62,7	37,3	–	23	1 : 2	72	19,7	76,1	4,2
9	2 : 1	48	48,6	51,4	–	24	1 : 5	1	41,2	58,8	–
10	2 : 1	54	36,9	63,1	–	25	1 : 5	24	24,3	70,0	5,7
11	2 : 1	100	24,6	75,4	–			0	4,5	88,5	7
12	2 : 1	144	24,2	75,8	–	26	1 : 1	48	12,3	81,1	6,6
13	2 : 1	168	22,6	77,4	–	27	1 : 5	24	10,6	83,4	6
14	2 : 1	190	24,0	76,0	–						

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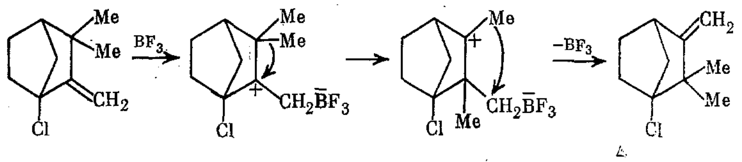
*In the presence of 10 moles of ether.

The presence of free protons is not very probable in the reaction media that we investigated. Indeed, reactant (I) cannot be a proton source; otherwise, it would not retain its isomeric composition on long storage. No reaction between water and BF_3 leading to formation of the strong acid $H^+(BF_3OH)^-$ is described for the etherate of BF_3 and, furthermore, we used dry reagents in an argon atmosphere. Therefore, the observed effect may be attributed to a reaction of BF_3 with the unsaturated unit of the camphene molecule according to the equation



(I) (Ia) (Ib) (II)

As Table 1 and Fig. 1 indicate, the rearrangement rate depends mainly on the substrate: catalyst ratio and on dilution by ether. BF_3 has an especially strong accelerating effect in the first stages of the reaction. Whereas the content of (II) in the mixture increases from 7.8 to ∿9% after 1 h at a 5:1 molar ratio of (I):BF_3, at equimolar proportions it increases to 12.5% within the same time frame, and at a 1:5 ratio it increases to 59%. Note that we did not obtain complete rearrangement in any of the cases studied and enrichment with 4-chlorocamphene generally reached ∿80%. The tests with a large BF_3 excess indicate that the process could not have been decelerated by catalyst deactivation on extended reaction. Apparently we must assume that the process is reversible. In fact, special tests (see Table 1, tests 26 and 27) demonstrate the presence of reverse rearrangement that takes place much more slowly. Test 21 shows that dilution with ether completely suppresses the rearrangement even at the most favorable ratio of (I) to BF_3.

We can see from Table 1 that very long contact (100 h) results in the formation of still another product (V), which we have not yet identified. This product was obtained with the greatest yield (9%) in the test that had the least favorable (I):BF_3 ratio for the major reaction. Apparently, this product cannot itself react actively with BF_3 (see Table 1, tests 26 and 27).

In order to confirm the structure of the major reaction product, (II) (the constants of the sample are close to those given in the literature, but the structure of (II) given in [9] was not proved), we prepared the lithium derivative from a mixture containing ∿90% of (II), then the mercury derivative camphene 4-mercuric chloride (III), for which we performed a structural x-ray diffraction analysis. The isomer camphene 1-mercuric chloride (IV) had been studied by us earlier [10] and we had been able to effect a reliable separation.

The crystals of $C_{10}H_{15}HgCl$ (III) are monoclinic and at −120°C a = 6.943(2), b = 11.915 × (4), c = 6.831(2) Å, ν = 106.89(2)°, Z = 2, d_{calc} = 2.28 g/cm^3, space group $P2_1$. The unit

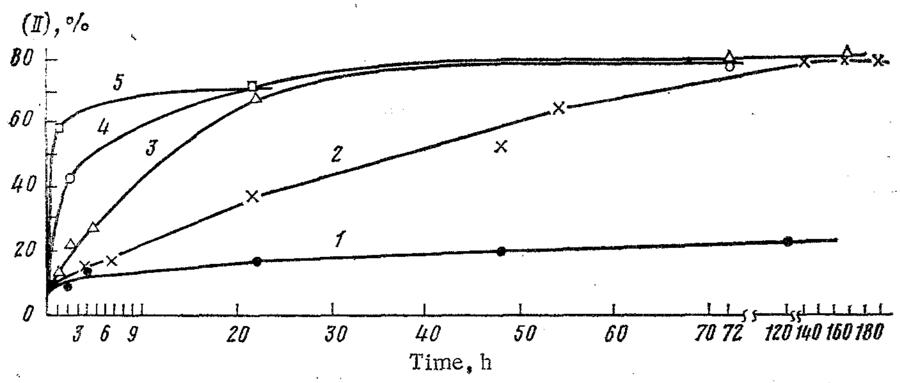


Fig. 1. 4-Chlorocamphene (II) content in the mixture with 1-chlorocamphene (I) vs amount of BF_3 added (in moles) and reaction time. (I):BF_3 molar ratio: 1) 5:1; 2) 2:1; 3) 1:1; 4) 1:2; 5) 1:5.

cell parameters and the intensities of the 820 reflections were measured with $I > 2\sigma$ on a Syntex $P2_1$ 4-disk automatic diffractometer (—120°C, Mo K_α-radiation, graphite monochromator, $\theta/2\theta$-scanning, $2\theta_{max}$ 48°). The absorption was calculated for the real shape of the crystal by a procedure in [11].

The structure was deciphered by the heavy-atom method. The coordinates of the Hg and Cl atoms were determined from a Patterson synthesis. All the C atoms were identified by a series of successive electron density syntheses. However, refinement of the structure by a block-diagonal approximation led to very large shifts in the positions of the light atoms with practically constant R-factors and to unreasonable spacings between the light atoms. Therefore, they were further refined by calculating successive electron density syntheses: before each new synthesis, the heavy atoms were refined by the method of least squares by a block-diagonal isotropic (Cl) approximation anisotropically with respect to Hg. At one of the subsequent steps of the refinement, a correction was introduced for anomalous scatter of the x-ray beams by the Hg atom (with a tabular value of $\Delta f'' = 9.223$) and both the direct and inverted models of the structure were refined. R = 13.73% (R_w = 11.24%) for the one and R = 13.96% (R_w = 11.74%) for the other. The model with the lower R-factor had the same absolute camphene framework configuration as (IV) [10], conforming to true chiral symmetry with camphene. The final value of R = 13.46% (R_w = 10.79%) for the 673 reflections with $F^2 > 2.5\sigma$ was obtained from the final refinement of the model with the lower R-factor. The coordinates of the atoms are shown in Table 2.

The low precision of the structure is apparently due to the low quality of the crystals, incomplete correction for the absorption because of imperfect crystal faces, and the somewhat exceptional arrangement of the molecules in the crystal (the Cl, Hg, C^1, C^2, C^3, C^4, and C^8 atoms lie on a pseudosymmetry plane with the z-coordinate close to zero and the C^9 and C^{10} atoms are connected to this pseudoplane).

The structure of the molecule is shown in Fig. 2 and the bond lengths and valence angles are shown in Tables 3 and 4. The structural x-ray study determined that the Hg atom is bound to the C^4 atom of the camphene ring. The length of the Hg—Cl bond is 2.35(2) Å as customary and agrees with that found in (IV). The norbornane system of camphene is considered tricyclic: a $C^1C^2C^3C^4C^5C^6$ cyclohexane ring and two $C^1C^2C^3C^4C^7$ and $C^1C^6C^5C^4C^7$ five-membered rings. The torsion angles of these rings (Fig. 3) agree with those found in (IV) and in the other norbornanes discussed in [10] within the limits of accuracy in this study. The distribution of the torsion angles complies with the trough and envelope conformations of six-membered

TABLE 2. Coordinates of the Atoms

Atom	X	Y	Z	Atom	X	Y	Z
Hg	0,1352(4)	0,4264(4)	0*	C^5	0,554	0,261	−0,204
Cl	−0,025(2)	0,575(2)	0,016(9)	C^6	0,402	0,331	−0,201
C^1	0,291	0,301	0,007	C^7	0,455	0,310	0,172
C^2	0,159	0,189	0,032	C^8	0,272	−0,002	−0,008
C^3	0,310	0,117	0,010	C^9	−0,004	0,155	−0,135
C^4	0,526	0,204	0,015	C^{10}	0,063	0,178	0,252

*Taken in order to fix the origin on the Z-axis.

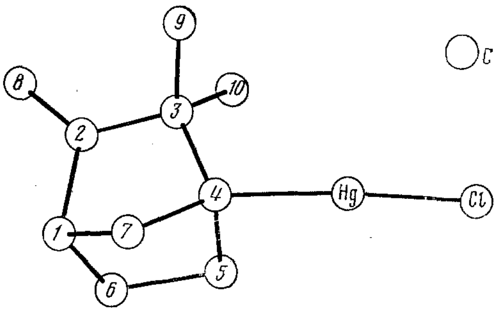


Fig. 2. Molecular structure of camphene-4-mercuric chloride (III).

TABLE 3. Bond Lengths

Bond	d, Å	Bond	d, Å
C^1–C^2	1,55	C^1–C^7	1,80
C^2–C^3	1,54	C^4–C^7	1,58
C^3–C^4	1,40	C^2–C^8	1,38
C^4–C^5	1,61	C^3–C^9	1,57
C^5–C^6	1,52	C^3–C^{10}	1,63
C^1–C^6	1,63	C^4–Hg	2,08
		Hg–Cl	2,35(2)

rings, respectively. Such a ring conformation is dictated by cis-joined five-membered rings in the norbornane system.

Thus, we have shown that the basic trend of the rearrangement under the given conditions is to a 4-substituted camphene and its mechanism fits Nametkin's rearrangement scheme [1]. Note that there is no competing Wagner–Meerwein rearrangement at the early stages of the reaction. The compound with an unknown structure that appears on extended contact may be a product of a second such rearrangement. However, as already stated, it starts to form much later after the major reaction has attained equilibrium and it is therefore easy to keep this impurity out of the major product.

The initial stage of the suggested rearrangement scheme (Ia) is analogous to polymerization and cis,trans-isomerization of alkenes catalyzed by BF_3 [12]. In our case, the reaction of BF_3 with the unsaturated unit may be stimulated by the high reactivity of camphene's double bond. Indeed, the energy of the π-molecular orbital of camphene is 1.65 eV higher than that of ethylene [13]. The C–B bond in the intermediate that is formed is evidently strongly polar (kinetic instability) and assures that the BF_3 will be replaced easily by a proton at stage (Ib), i.e., the process is reversible.

EXPERIMENTAL

All the reagents, solvents, and argon were carefully dried before use.

The GLC analysis was performed on a Varian Aerograph 1860-4 chromatograph with a 90 × 0.25-mm steel capillary column filled with neopentylglycol adipate (NPGA) and a flame-ionization detector. The analysis was performed isothermally at 70°C. The gas-carrier was helium, inlet pressure 1.6 atm. The electrometer sensitivity was $4 \cdot 10^{-12}$ A at full recorder scale. The sample volume was 0.1 to 0.2 µl. Peak area normalization was employed to calculate the composition, with a reproducibility of <2% in the concentration range of the measurements.

1-Chlorocamphene (I) was prepared as in [9]; bp 197-200°C; by GLC contained 7.8% of isomer (II). PMR spectrum (CCl_4): 4.71, 5.08, 4.58, 4.74 ppm [$=CH_2$ (I) and (II), respectively].

Typical Rearrangement Test. 0.7 g (4 mmoles) of (I) and a corresponding quantity of freshly distilled $Et_2O \cdot BF_3$ (see Table 1) were placed in an Ar-filled hermetically seated flask equipped with a magnetic stirrer and stirred at 20°C. The mixture was diluted with hexane and passed through a 6 × 1.5-cm column containing Al_2O_3 (activity II); the pH of the aqueous extracts was 9-10 and the catalyst was thus separated. After all the products had

TABLE 4. Valence Angles ω, deg

Angle	ω	Angle	ω	Angle	ω	Angle	ω
$ClHgC^4$	175	$C^5C^4C^7$	109	$C^9C^3C^{10}$	104	$C^6C^1C^7$	106
HgC^4C^3	111	$C^2C^3C^4$	99	$C^1C^2C^3$	108	$C^1C^6C^5$	102
HgC^4C^5	98	$C^2C^3C^9$	110	$C^1C^2C^8$	123	$C^6C^5C^4$	105
HgC^4C^7	118	$C^2C^3C^{10}$	112	$C^3C^2C^8$	129	$C^1C^7C^4$	83
$C^3C^4C^5$	117	$C^4C^3C^9$	112	$C^2C^1C^6$	103		
$C^3C^4C^7$	104	$C^4C^3C^{10}$	109	$C^2C^1C^7$	94		

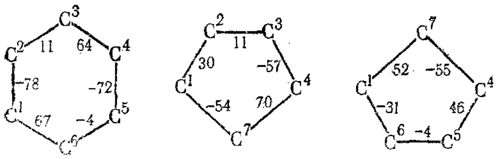


Fig. 3. Torsion angles in 6-membered and 5-membered rings of the camphene-4-mercuric chloride (III) molecule, deg.

been removed (monitored by chromatography on Silufol with I_2 treatment), the eluate was analyzed by GLC under the above conditions.

A sample of (I) kept 170 h over Al_2O_3 contained 7% of (II), one kept 24 h over NPGA contained 8.9% of (II), i.e., the composition was constant within the limits of experimental accuracy.

4-Chlorocamphene (II) obtained by rearrangement of (I) was crystallized three times from methanol; bp 120-124°C[9]. Percentage composition found: C 70.39, H 8.83, Cl 20.80. Percentage calculated for $C_{10}H_{15}Cl$: C 70.36, H 8.86, Cl 20.77. IR spectrum: 1660 cm^{-1} (ν C=C).

Camphene 4-Mercuric Chloride (III). To a suspension of 6.2 g (23 mmoles) of $HgCl_2$ in 80 ml absolute ether, was added dropwise a solution of 23 mmoles 4-lithium camphene [obtained from (II)] in heptane, stirred 3 h in an argon atmosphere at 20°C and allowed to stand overnight. The precipitate was separated, washed with hot petroleum ether. The solutions were combined and the solvent evaporated in vacuum and the residue was subjected to thin-layer chromatography on SiO_2. With a 1:1 mixture of benzene and petroleum ether, the fraction with $R_f \simeq 0.6$ was separated which contains a small quantity of (IV) in addition to (III). PMR spectrum ($CHCl_3$, δ, ppm): 4.67, 5.42, 4.72, 5.02 [$=CH_2$ of (IV) and (III), respectively]. Total yield of the mercury derivatives was 1.5 g (17.5%). To separate pure (III), part of the mixture was subjected to chromatography on 15 × 15-cm plates with a stabilized bed of SiO_2 on Silufol UV-254, with heptane as the eluent. After about 30 passes of heptane through the same plate, the (III) and (IV) zones were separated by 1 cm (UV control) with the (III) zone close to the start. mp (III) 125-128°C (needles from benzene).

CONCLUSIONS

We have studied the rearrangement of 1-chlorocamphene to 4-chlorocamphene in the presence of boron trifluoride etherate. The optimum conditions for the rearrangement were determined.

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