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SYNTHESIS, STRUCTURE, AND BIOLOGICAL ACTIVITY OF DERIVATIVES OF [2,2]-*para*-CYCLOPHANE. 2.* 4-HYDROXYMETHYL(ACYLOXYMETHYL, ALKENYL)-[2,3]-*para*-CYCLOPHANES

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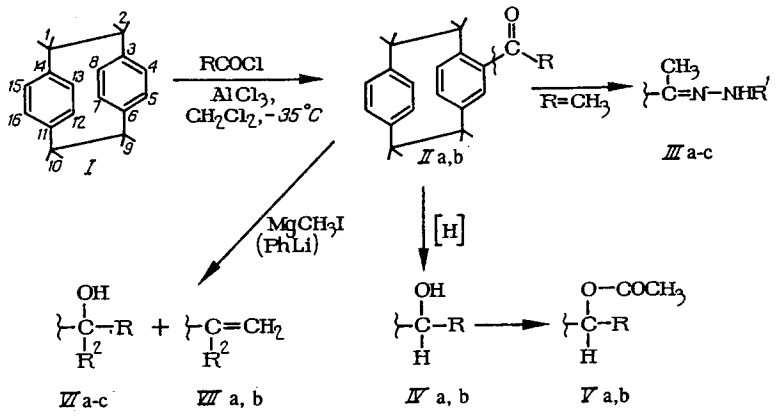
With the goal of studying the structure and biological activity of new compounds of the [2,2]-*para*-cyclophane (PCP) series (I), based on its 4-acyl derivatives (II) we synthesized 4-hydroxymethyl-, 4-acyloxymethyl-, and 4-alkenyl-substituted *para*-cyclophanes (III-VII). The starting 4-acetylPCP (IIa) was obtained as in [4]. We synthesized 4-benozoylPCP (IIb) in good yield (70%) by benzoylation of PCP I with benzoyl chloride in the presence of $AlCl_3$ at −35°C in dichloromethane. Earlier [5], compound IIb was obtained in four steps through 4-PCP carboxylic acid (≈50% yield). Based on ketone IIa, we obtained three new imines: the semicarbazone, the thiosemicarbazone, and the 2,4-dinitrophenylhydrazone (IIIa-c respectively; the characteristics and PMR spectra of the compounds are presented in Table 1 and 2).

By reduction of ketones II by sodium borohydride, we obtained methyl- (IVa) and phenyl- (IVb) {[2,2]-*para*-cyclophane-4-yl}carbinols having an asymmetric center and a plane of asymmetry for the monosubstituted *para*-cyclophane moiety. According to the PMR spectral data, mixtures of diastereomeric racemic alcohols IVa are obtained in an ≈1:2 ratio. The major diastereomer, which according to the Cremer rule [3] should have the S configuration relative to the alcohol C-atom, was isolated by crystallization from hexane (m.p. 99-101°C). Its ^1H and ^{13}C NMR spectra are presented in Table 2 and in the Experimental section.



R=Me(IIa, IVa—VIa, VIb), Ph(IIb, IVb—VIc); R^1= =$CONH_2$(IIIa), $CSNH_2$(IIIb), $C_6H_3(NO_2)_2$-o,p(IIIc); R^2= =CH_3(VIa, VIIa), Ph(VIb,c, VIIb).

*For Communication 1, see [2].

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TABLE 1. Characteristics of Compounds

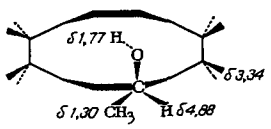
Compound	m.p, °C	IR spectrum, ν, cm^{-1}	Found/calculated, %		Empirical formula	Yield, %
			C	H		
IIIa*	200—203	3490, 3260, 1712	74,1/74,3	6,9/6,8	$C_{19}H_{21}N_3O$	90
IIIb**	176—177	3290, 1640, 1630	70,6/70,6	6,6/6,5	$C_{19}H_{21}N_3S$	69
IVa(S)	99—101	3580, 3390, 3280	85,6/85,7	7,8/7,9	$C_{18}H_{20}O$	30
IVb	***	3535, 3375, 3280	87,9/87,9	6,8/7,0	$C_{23}H_{22}O$	90
Va	114—116	1732	81,3/81,6	7,3/7,5	$C_{20}H_{22}O_2$	70
Vb	128—130	1742	84,6/84,3	6,5/6,7	$C_{25}H_{24}O_2$	70
VIa	***	3480 br.	85,9/85,7	8,2/8,3	$C_{19}H_{22}O$	20
VIc	***	3580 br.	89,2/89,2	6,5/6,7	$C_{29}H_{26}O$	50
VIIa	61—63	1666, 1640	92,1/91,9	7,9/8,1	$C_{19}H_{20}$	15—80

*N 14.0/13.7.

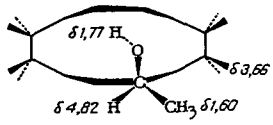
**N 12.6/13.0.

***Waxy substance.

Examination of Dreiding models and analysis of the NMR spectra of the diastereomeric alcohols IVa show that owing to steric hindrances (hindered rotation about the C_4-C_1' bond) and the electronic factor (orientation of the proton of the OH group toward the π-excess "nucleophilic gap" in the *para*-cyclophane moiety), the conformations illustrated below are the most stable:



IVa (*S*-configuration), m.p. 99—101 °C (δ, ppm)



IVa(R-configuration [characterized in a mixture with IVa(S)]

The methyl group in the isomer IVa(R) experiences the shielding effect of the ring current of the cyclophane ring, and its protons resonate 0.3 ppm further upfield than in the isomer IVa(S) (the corresponding difference in the chemical shifts of the signals from the carbon rings is 4.6 ppm). An analogous effect is observed for the methine proton of the carbonyl group in the IVa(R) isomer, i.e., it gives a signal which is 0.06 ppm further upfield. When taking the PMR spectra in DMSO-d_6 with heating, a signal from the OH group also becomes characteristic, appearing at 4.55 ppm in the alcohol IVa(S) and 4.27 ppm in the case of IVa(R), in the form of a doublet with spin—spin coupling constant 6 Hz (at 80°C).

Replacing the methyl group with a phenyl group when obtaining the diastereomeric alcohols (IVb) does not lead to an appreciable change in their ratio. In the PMR spectrum of the obtained mixture of diastereomers IVb (in $CDCl_3$), there are two signals from the phenyl radical with centers at 7.22 and 7.43 ppm and ratio $\approx$1:2. The proton of the —HCO group appears as overlapping broadened singlets. Taking the PMR spectra in DMSO-d_6 with heating allows us to obtain two individual narrow signals from the carbonyl methine proton ($\Delta\delta$ = 0.03 ppm at 150°C) with ratio of integrated intensities $\approx$1:2. The proton of the OH group in this case resonates in the form of two signals: a broadened singlet at 5.8 ppm and a broad signal at 5.38 ppm at 60°C. At 150°C, the first signal is shifted by $\approx$0.25 ppm downfield (probably as a result of intramolecular association of the hydroxyl with the "nucleophilic gap"), and the second is shifted upfield and appears at $\approx$3.4 ppm ($\Delta\delta$ = 2.15 ppm) owing to degradation of the intermolecular associates.

The diastereomeric alcohols IV are acetylated (as the starting mixtures) by acetic anhydride in pyridine to the corresponding esters (Va, Vb), which as shown by the PMR spectra are formed as diastereomeric racemates with unvarying ratio $\approx$1:2 (see Tables 1 and 2; the diastereomeric esters are characterized as mixtures).

By reaction of methylmagnesium iodide with the ketone IIa, we obtained the tertiary alcohol (VIa), which is not very stable and is easily dehydrated upon treatment of the reaction mixture with formation of the alkene (VIIa). The yield of the latter varies depending on the conditions for the Grignard reaction and separation of the alcohol VIa, which even in the crystalline state after several days of storage with access to the air is 80% converted to the alkene VIIa.

The tertiary carbinol (VIb), which has one CH_3 group and two aryl radicals, is significantly more stable. Earlier [5], it was synthesized (by action of methyllithium on 4-benzoyl-*para*-cyclophane) in the form of an almost equimolar mixture of diastereomeric racemates, separated by crystallization into two diastereomers with m.p. 123 and 145°C. We obtained this

TABLE 2. PMR Spectra of Synthesized Compounds (in $CDCl_3$)*

Compound	Chemical shift, δ, ppm									
	protons of para-cyclophane moiety						protons of substituents			
	5	7	8	12, 13, 15, 16	2	1, 9, 10	CH_3	CH	OH	Ph
IIb	6,75	6,8	6,34	6,46—6,75	3,33	2,8—3,2	—	—	—	—
IIIa	6,7	6,40—6,63			2,8—2,6		2,18	—	—	—
IIIb	6,7	6,42—6,55			2,85—3,5		2,25	—	—	—
IVa (S)	6,6	6,43	6,37	See note			1,3	4,88 (6,4 and 3,7 Hz)	1,77 (3,7 Hz)[4]	—
IVa (R)	6,55	6,43	6,37	Same			1,6	4,82 (6,5 and 3,7 Hz)	1,77 (3,7 Hz)[4]	—
IVb (S)	6,8	6,45—6,55	6,12	6,45—6,55	3,8	2,8—3,25	—	5,77	2,1[5]	7,4
IVb (R)	6,75	6,45—6,55	6,32	6,45—6,55	3,8	2,8—3,25	—	5,80	2,1[5]	7,22
Va (S)	6,6	6,2—6,55			2,8—3,45		1,25 (6,4 Hz) 2,27	5,95 (6,4 Hz)	—	—
Va (R)	6,6	6,2—6,55			2,8—3,45		1,58 (6,4 Hz) and 2,05	6,12 (6,4 Hz)	—	—
Vb (S)	6,85	6,1—6,65			2,75—3,45		2,05	5,83	—	7,43
Vb (R)	6,75	6,3—6,6			2,75—3,45		2,28	7,03	—	7,18
VIa	6,6	6,25—6,55			3,7	2,8—3,2	1,5 and 1,6	—	1,7	—
VIb	6,7	6,2—6,6			2,65—3,3		1,77	—	2,3	7,18
VIc	5,9	6,25 and 6,85 (two doublets, 7,8 Hz) 6,32—6,65 (4H)			2,67—3,3		—	—	6,17	7,14—7,44
VIIa		6,58 m		6,34, m	3,3	2,85—3,1	2,06, m	—	—	—
VIIb	6,6	6,9	6,3—6,6		2,5 and 2,8 (each 2H); 2,94—3,18		—	—	—	7,25

[1]KCCB, $J_{7,8}$ = 7.8 Hz; J_5 = 1.5-1.7 Hz.

[2]In DMSO-d_6; δ NH 9.1 and 9.9 ppm.

[3]Signals and spin—spin coupling constants for the rest of the protons are assigned according to a two-dimensional DQF—COSY spectrum; δ IVa(S)/δ IVb(R); 3.02/3.04 (H-1); 3.12/3.12 (H-1), 3.29/3.62 (H-2), 2.79/2.87 (H-2'), 2.95-3.1 (H-9, 10), 6.42 (H-12), 5.59 (H-13), 6.45-6.51 (H-15, 16), $J_{1,1'}$ = 13.1; $J_{1,2}$ = 10.7, 10.0 (S and R), 6.2(S), 5.8(R), 2.2(S and R), $J_{2,2'}$ = 13.6(S) and 13.3(R).

[4]4.55 ppm (J = 6 Hz) for the S isomer and 4.27 ppm for the R isomer in DMSO-d_6 at 100°C.

[5]In DMSO-d_6, the OH proton resonates at 5.75 (20°C), 5.80 (60°C), and 6.0 ppm (150°C) for the S isomer and at 5.55 (20°C), 5.38 (60°C), and 3.4 ppm (150°C) for the R isomer.

[6]5.13 ppm (m, 2H, CH_2=C) for VIIa; 5.6 ppm (dd, 2H, J = 9.2 and 1.4 Hz, CH_2=C) for VIIb.

TABLE 3. Mass Spectra of Synthesized Compounds, m/z (intensity, %)

IIb: M^+312(7), [M—104]$^+$·208(100), [M—COPh]$^+$·207(40), 193(9), 191(11), 179(25), 178(25), 165(39), 105(48), [CH_2=C_6H_4=CH_2]$^+$·104(96), $C_7H_7^+$·91(10), 77(40).

IIIa: M^+307(1), [M—CONH]$^+$·(Fr_1) 264(33), 250(50), [Fr_1—104]$^+$·160(40), 146(48), 130(70), 129(55), 105(100), 194(25).

IIIб: M^+323(50), [M—CH_3]$^+$·308(10), [M—H_2S]$^+$·289(8), [M—$CSNH_2$]$^+$·263(7), 106(90), 105(49), 104(100), 91(50).

IVa: M^+252(95), [M—2H]$^+$·250(70), [M—CH_3]$^+$·237(32), [M—OH]$^+$·234(9), [M—$HOCHCH_3$]$^+$·207[8], [M—104]$^+$·148(21), 130(90), 129(37), 118(53), 105(100), 104(78), 91(11)

IVb: M^+314(43), [M—2H]$^+$·312(7), [M—H_2O]$^+$·296(15), [M—105]$^+$·209(63), 193(4), 192(25), 191(35), 131(50), 105(100), 104(75), 91(18), 77(25).

Va: M^+294(22), [M—CH_3]$^+$·279(9), [M—CH_3CO]$^+$·=$Fr_1$251(4), 250(5), [Fr_1—OH]$^+$·=$Fr_2$234(13), 189(10), 175(10), 147(15), 131(50), [Fr_2—104]$^+$·130(100), [Fr_2—105]$^+$·129(90), 105(80), 104(80), 91(40), 78(70), 77(35).

Vb: M^+356(8), [M—$COCH_3$]$^+$·=$Fr_1$313(7), [Fr_1—OH]$^+$·=$Fr_2$296(50), [Fr_2—104]$^+$·192(52), [Fr_2—COPh]$^+$·191(75), 132(55), 106(49), 105(100), 104(63).

VIa: M^+266(2), [M—2H]$^+$·264(1), [M—OH]$^+$·249(10), [M—H_2O]$^+$·=$Fr_1$248(48), 168(90), [Fr_1—104]$^+$·144(19), 143(100), 105(39), 104(19).

VIb: M^+328(44), [M—CH_3]$^+$·313(41), [M—H_2O]$^+$·310(6), 250(22), [M—C_7H_7]$^+$·237(9), [M—105]$^+$·223(16), 205(50), 146(56), 105(100), 104(78).

IVc: M^+390(27), [M—H_2O]$^+$·372(100), [M—Ph]$^+$·313(15), [M—105]$^+$·=$Fr_1$285(12), 281(15), 269(42), 255(46), [Fr_1—CH_2OH]$^+$·254(77), 252(46), [Fr_1—C_4H_3]$^+$·234(62), 232(65), [M—$(Ph)_2COH$]$^+$·207(60).

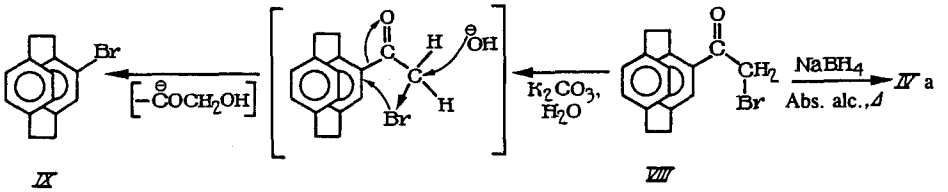
VIIa: M^+248(71), [M—CH_3]$^+$·233(2), [M—C_3H_4]$^+$·208(12), 156(5), [M—104]$^+$·144(53), 143(100), 129(21), 105(48), 104(43).

VIIb: M^+310(100), 250(21), 248(14), [M—C_5H_5]$^+$·245(6), 244(14), 208(93), [M—104]$^+$·206(12), 205(50), 105(14), 104(71).

alcohol by another route: by action of phenyllithium on 4-acetylPCP. In this case, we chromatographically isolated the low-melting diasteromer VIa, and also the product of dehydration of the alcohol: diarylethylidene (VIIb). Furthermore, by reaction of phenyllithium with 4-benzoylPCP we obtained the stable triaryl-substituted carbinol (VIc).

Upon reduction of 4-bromoacetylPCP VIII [2] with sodium borohydride in absolute alcohol at 70°C, instead of the expected bromomethyl-substituted carbinol we isolated in 59% yield IVa with ratio of the diastereomeric racemates equal to

≈1:1.5. Above we showed that this alcohol is easily formed upon action of $NaBH_4$ on 4-acetylPCP IIa. Consequently, introduction of the bulky (I) substituent into the acetyl group on the one hand leads to strong shielding of the carbonyl carbon from attack by the hydride ion, and on the other hand promotes the process of enolization, which in turn should activate reductive cleavage of the bromo anion. Using aqueous ethanol in the analogous reductive process (alkaline pH values) and also heating the bromomethyl ketone VIII in an aqueous K_2CO_3 solution led to base cleavage of the acetyl group (possibly in the form of the oxalate) and transbromination of the PCP action. As a result, we obtained the 4-bromo-[2,2]-*para*-cyclophane IX in 62 and 60% yields respectively; the melting point, PMR, and mass spectrum of this compound matched the values presented in [6].



IX VIII

The structure of all the compounds obtained was also confirmed by mass spectral data (Table 3). In the mass spectra of most of the compounds, we see M^+ molecular ion peaks of high and medium intensity (except for compounds IIb, IIIa, Vb, VIa). In the mass spectra of practically all the compounds, we also see characteristic peaks for the ions $[M-104]^{+\cdot}$ and $[104]^{+\cdot}$, which are due to cleavage of a *para*-xylene moiety from the molecular ion. The mass spectra of the secondary and tertiary alcohols IV and VI are characterized by the presence of peaks for the ions $[M-2H]^{+\cdot}$, $[M-OH]^{+\cdot}$ and/or $[M-H_2O]^{+\cdot}$. Dissociative ionization of the acetates Va, b involves the appearance in their mass spectra of peaks for the ions $[M-COCH_3]^{+\cdot}$ (Fr_1), $[Fr_1-OH]^{+\cdot}$ (Fr_2), $[Fr_2-104]^{+\cdot}$ and $[Fr_2-105]^{+}$. In the case of the alkenes VII, loss of the species $[C_3H_4]^+$ and $[C_5H_5]^+$ by their molecular ions M^+ is characteristic.

We studied the pesticidal activity of six compounds *in vitro*. None of the compounds exhibit bactericidal action on the bacteria *Xanthomonas malvacearum* except for diarylethylidene VIIb (30% suppression). The fungicidal activity is low for all the tested imines, alcohols, and alkenes on all five test specimens. Only thiosemicarbazone IIIb stands out somewhat: this compound displayed fungicidal action on three specimens close to the median value (40-50%), see Table 4.

The fungicidal activity was determined by the technique in [1] by V. I. Abelentsev and T. V. Solov'eva, coworkers at the Scientific Research Institute of Chemical Plant Protection (Moscow).*

EXPERIMENTAL

The IR spectra were taken on the UR-20 in KBr disks. The mass spectra were obtained on the MKh-1303 and on the Kratos MS-25PF spectrometer. The PMR spectra were recorded on the Bruker W-80 with operating frequency 80 MHz; $CDCl_3$ was used as the solvent, TMS was used as the internal standard. The PMR spectra of compounds IV were recorded on the Bruker WM-400 with operating frequency 400 MHz. The course of the reaction and the purity of the compounds were monitored by TLC on Silufol UV-254 plates using the solvent mixture hexane–chloroform, 1:3. The compounds were separated by column chromatography on L-60(40/100) silica gel. The elemental analysis results correspond to the calculated values.

4-Benzoyl-[2,2]-*para*-cyclophane (IIb). One portion of 0.5 g (2.4 mmoles) *para*-cyclophane I was added to a mixture of 0.64 aluminum chloride and 0.67 g (4.8 mmoles) benzoyl chloride in 20 ml sym. tetrachloroethane. The temperature of the mixture was reduced to −15°C to −20°C and stirred for 40 min. Then the mixture was cooled down to −40°C and 30 ml 1 N HCl solution was added. The aqueous phase was separated and extracted with chloroform. The organic phases were combined, washed with water and then with a solution of sodium bicarbonate and then again with water, and then dried. The residue after removal of the solvent was crystallized from hexane. Compound IIb was obtained in 70% yield, beige crystals, m.p. 153-155°C [4], R_f = 0.7. IR spectrum, ν, cm^{-1}: 1658, 1600.

4-Acetyl-[2,2]-*para*-cyclophane (IIa) was obtained as in [5].

*We thank them for providing the test results.

TABLE 4. Fungicidal Activity of Compounds

Test specimen	Fungicidal activity*					
	IIIa	IIIb	IIIc	IVa	VIIa	VIIb
Sclerotinia sc.	13	33	0	15	33	20
Fusarium gr.	27	46	0	16	11	0
Venturia in.	17	40	17	27	33	10
Helminthosporum sativum	33	50	27	17	33	0
Rhizoctonia sol.	38	28	13	13	8	0

*The percentage suppression of the growth of the mycelium of fungi or mold is indicated compared with the reference TMTD (100%).

Semicarbazone of 4-acetyl-[2,2]-*para*-cyclophane (IIIa). Water (8 ml) and 10 mmoles semicarbazide hydrochloride were added to 15 ml ethanol, and then 1.6 g sodium acetate was added. The mixture was heated for 15 min on a water bath. The precipitate was separated, washed with water, and dried. Obtained: 1.1 g semicarbazone IIIa, colorless crystals.

Thiosemicarbazone of 4-acetyl-[2,2]-*para*-cyclophane (IIIb). A hot solution of 1 g (4 mmoles) compound IIa in 30 ml ethanol was added to a solution of 1.1 g (12 mmoles) thiosemicarbazide in a mixture of 6 ml water and 4 ml ethanol. A few drops of an alcohol solution of HCl was added (to a pH of 4.0-5.0). This was stirred for 1 h at 55°C; the precipitate was separated, washed with water, ethanol, ether, and dried. Obtained: 0.9 g thiosemicarbazone IIIb, colorless crystals.

2,4-Dinitrophenylhydrazone of 4-acetyl-[2,2]-*para*-cyclophane (IIIc), orange crystals, m.p. 196°C [5]. IR spectrum, ν, cm^{-1}: 3550 broad, 1630, 1540, 1340.

Methyl(IVa)- and phenyl-{[2,2]-*para*-cyclophan-4-yl}carbinols (IVb). NBH_4 (0.3 g) was added in portions with stirring over the course of 0.5 h to a solution of 1 g (4 moles) acetyl-*para*-cyclophane IIa in 10 ml ethanol. The mixture was heated for 2 h, the solvent was partially evaporated, 20 ml water was added, and it was extracted with ether. Obtained in 90% yield: a mixture of diastereomeric racemates of the carbinol IV(R,S) with ratio $\approx$ 1:2 according to PMR data, colorless crystals, m.p. 75-80°C. The diastereomer IVa(S) was obtained in 30% yield by crystallization from ethanol, m.p. 99-101°C. The carbinol IVb was obtained analogously from 4-benzoylPCP IIb. ^{13}C NMR spectrum of the alcohol IVa(S/R) δ, ppm: 25.7/21.1 (CH_3); 33.1/33.2, 34.3/34.7, (C-2.9); 35.2/35.1, 35.2/35.2 (C-1.10); 67.8/67.5 (CO); 134.8/138.4, 140.2/140.1 (C-3.6); 139.5/139.4, 139.2/139.4 (C-11, 14); 129.9/127.7, 131.5/131.9 (C-7.8); 133.5/133.2, 135.0/135.5, 132.9/133.0. 132.1/132.5 (C-12, 13, 15, 16).

Acetate of methyl(Va)- and phenyl-{[2,2]-*para*-cyclophan-4-yl}carbinols (Vb). A mixture of 0.15 g (0.6 mmoles) diastereomeric carbinols IVa, 1.5 ml (14 mmoles) acetic anhydride, and 1 ml pyridine was heated for 2 h at 80°C and then cooled. 10 ml water was added and it was extracted with ether. The extract was washed with water, dried, evaporated down to 5 ml, and cooled. Obtained: 0.12 g light-yellow crystals of the ester Va. The acetate Vb was obtained analogously in the form of colorless crystals.

Dimethyl-{2,2]-*para*-cyclophan-4-yl}carbinol (VIa) and 1-methyl-1{[2,2]-*para*-cyclophan-4-yl}ethylene (VIIa). A solution of 4 mmoles 4-acetylPCP IIa in 10 ml ether was added with stirring to a solution of Grignard reagent (prepared from 10 mmoles methyl iodide and 10 mg-atoms magnesium). The mixture was heated for 2 h on a water bath, then 10 g ice and 10 ml saturated aqueous ammonium chloride solution were added. The ether layer was separated, and the aqueous layer was extracted twice with ether. The extracts were combined, washed with a solution of sodium bicarbonate, then with water, and then dried. The residue obtained after driving off the ether consisted of a mixture of three compounds which were separated by chromatography on a column with silica gel (eluent, hexane; then a mixture of hexane with ether). First the alkene VIIa was separated (R_f = 0.74, 15% yield), colorless crystals; then a product with R_f = 0.59 was eluted, white crystals with m.p. 61-63°C (10% yield), which according to the PMR- and mass spectral data is the ethyl ester of dimethyl{[2,2]-*para*-cyclophan-4-yl}carbinol. Its PMR spectrum, δ, ppm: 1.15 (t, 3H, J = 7.4 Hz), 1.43 and 1.70 (both singlets 3 H each), 2.8-3.1 (m, 7H, $-CH_2-CH_2-$), 3.15 (q, 2H, J = 7.4 Hz), 3.8 (m, 1H, $-CH_2-CH_2-$), 6.3 (m, 4H, arom, H). Mass spectrum, m/z (in %): M^+ 294 (50), $[M-CH_3]^+$ 279 (3), $[M-C_2H_5]^+$ = Fr_1 265 (7), $[Fr_1-CH_3]^+$ 250 (25), $[M-OC_2H_5]^+$ 249 (16), $(M-HOC_2H_5]^+$ = F_2 248(36), $[F_2-$ 105$]^+$ 143 (100), 129 (55),118(16), 105(63), 104(38). Upon subsequent elution (1:1 hexane–ether mixture), the target carbinol VIa was separated (R_f = 0.32) in the form of a light-yellow oil, unstable under ordinary storage conditions, which after two weeks was 80% converted when accessible to air to the alkene VIIa.

The yield of the alkene VIIa increased to 50% when all the acetylPCP IIa was added at once, and up to 80% if the reaction mixture was treated with HCl with brief heating.

Analogously, by action of phenyllithium on 4-acetylPCP IIa we obtained the known [5] methyl-{[2,2]-*para*-cyclophan-4-yl}carbinol (IVb), by crystallization of which we isolated in 10% yield the low-melting diastereomer (m.p. 122-124°C [6], R_f = 0.65). 1-{[2,2]-*para*-cyclophan-4-yl}-1-phenylethylene (VIIb) was separated chromatographically from the reaction mixture in 40% yield, m.p. 129-131°C [5], R_f = 0.74.

Diphenyl-{[2,2]-*para*-cyclophan-4-yl}carbinol (VIc). Obtained analogously from 0.36 g (0.96 mmoles) 4-benzoylPCP IIb and phenyllithium [obtained from 0.16 g (1 mmoles) PhBr and 0.021 g (3 g-atoms) lithium] in the form of a waxy mass.

Reduction and Base Hydrolysis of 4-bromoacetyl-*para*-cyclophane (VIII). $NaBH_4$ (0.34 g, 9 mmoles) was added to a solution of 1 g (3 mmoles) 4-bromoacetylPCP VII [2] in 20 ml dry ethanol over the course of 0.5 h at 70°C and the mixture was stirred for 10 h. The alcohol was partially evaporated (down to 10 ml), the residue was treated with water and extracted with chloroform. Obtained after driving off the solvent: 0.9 g residue, which was separated on a column with alumina gel. Alcohol IVa (0.77 g, 59%) was isolated. In an analogous experiment, we used aqueous ethanol at 40°C and obtained 0.53 g (62%) 4-bromo-*para*-cyclophane IX, white crystals, m.p. 130-132°C (according to the literature data [6], m.p. 134-136°C). PMR spectrum, δ, ppm: 7.18 (dd, 1H, J = 7.9 and 1.6 Hz, the signal from the pseudogeminal proton H-13 characteristic for monohalo-substituted PCP [7]).

Hydrolysis was carried out by boiling a suspension of 1 g (3 mmoles) 4-bromoacetylPCP VIII in 50 ml saturated solution of potassium carbonate. After cooling, the mixture was extracted with chloroform. Obtained: 0.52 g (60%) 4-bromoPCP IX.

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