SYNTHESIS OF ADAMANTYLBISPHENOLS

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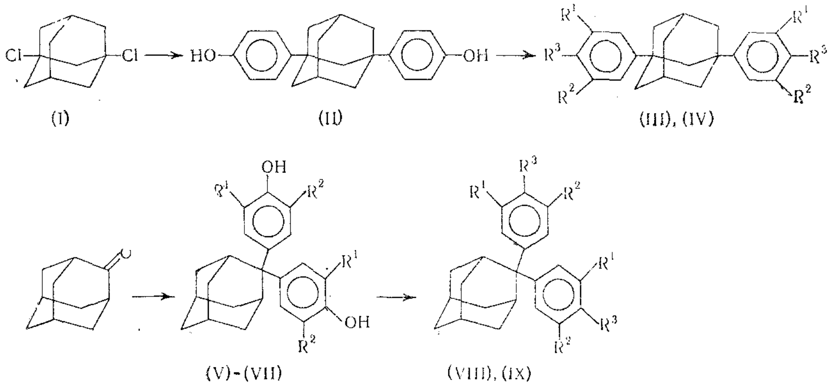
The dimethyladamantylbisphenols attract attention as starting compounds for the preparation of polymeric materials with a high heat resistance [1-3]. In this connection the bisphenols of adamantane itself are of interest.

We had previously reported [4] the preparation of 1,3-bis-(4-hydroxyphenyl)adamantane (II) by the condensation of phenol with 1,3-dichloroadamantane, which was obtained by a new method [5]. The method for the preparation of 2,2-bisphenols by the condensation of ketones with phenols in the presence of strong mineral acids was used to synthesize the isomeric 2,2-bis-(4-hydroxyphenyl)adamantane (V). A study of the reaction of adamantanone with phenol disclosed that in the presence of H_2SO_4, even under the optimum conditions, the condensation product is formed in 12% and is strongly contaminated with polymers; the use of HCl makes it possible to obtain the pure 2,2-bisphenol (V) in ~2% yield. Since it is known that certain thiocarboxylic acids promote the reaction of acetone with phenol [6], we investigated the possibility of increasing the yield of the bisphenol by adding either thioacetic or thioglycolic acid. The performed experiments disclosed that only the use of CH_3COSH with HCl makes it possible to obtain the pure 2,2-bisphenol (V) in 80% yield. Under the same conditions the reaction of adamantanone with o-cresol leads to 2,2-bisphenol (VI), while reaction with 2,6-dimethylphenol leads to 2,2-bisphenol (VII). Attempts to obtain the 1,3-(4-hydroxymethylphenyl)adamantanes by the condensation of dichloride (I) with methylphenols proved unsuccessful.



(III), (VIII) R^1, R^2 = Br; R^3 = OH; (V) R^1, R^2 = H;
(IV), (IX) R^1, R^2 = H; R^3 = $OCOCH_3$; (VI) R^1 = CH_3; R^2 = H; (VII) R^1, R^2 = CH_3

The structure of the obtained bisphenols is confirmed by a number of transformations. Thus, the bromination of 1,3-bisphenol (II) gave tetrabromide (III), while acetylation gave diacetate (IV). Tetrabromide (VIII) and diacetate (IX) were obtained in a similar manner from 2,2-bisphenol (V). The constants and yields of the obtained compounds are given in Table 1.

The IR spectra of the adamantylbisphenols contained bands in the 1500-1520 and 1600-1620 regions which are characteristic for the benzene ring, while the spectra of compounds (II) and (V) also contained

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TABLE 1. Adamantylbisphenols and Their Derivatives

Compound	Yield, %	T. mp °C	Found, %			Empirical formula	Calculated, %		
			C	H	Br		C	H	Br
(II)	92	203—204	82,66	7,79	—	$C_{22}H_{24}O_2$	82,46	7,65	—
(III)	71	247—248	41,4	3,24	50,25	$C_{22}H_{20}Br_4O_2$	41,50	3,20	50,32
(IV)	88	157—159	77,20	7,12	—	$C_{26}H_{28}O_4$	77,20	6,97	—
(V)	79	323—324	82,43	7,48	—	$C_{22}H_{24}O_2$	82,46	7,55	—
(VI)	67	292—293	81,80	8,35	—	$C_{24}H_{28}O_2$	82,76	8,04	—
(VII)	12	293—294	82,90	8,48	—	$C_{26}H_{32}O_2$	82,97	8,51	—
(VIII)	81	326	41,49	3,12	50,31	$C_{22}H_{20}Br_4O_2$	41,51	3,14	50,31
(IX)	94	207—208	76,87	6,93	—	$C_{26}H_{28}O_4$	77,22	6,93	—

bands at 820-835 cm^{-1} (p-substituted benzene ring). A broad band in the 3000-3500 cm^{-1} region corresponded to the stretching vibrations of the OH group in bisphenols (II) and (V), and a narrow band in the 3490-3500 cm^{-1} region in the case of bisphenols (VI)-(VII).

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-20 instrument. The GLC was run on a Tswett-3-66 chromatograph equipped with a flame-ionization detector at 150°; 3 mm × 3 m column; Carbowax M (10%) deposited on Chromosorb W; carrier gas = nitrogen.

Admantanone was obtained in ~60% yield by the oxidation of adamantane as described in [7].

1,3-Dichloroadamantane (I). To 20 ml of $ClSO_3H$ was slowly added 10 g of admantane in small portions, and the mixture was kept for 4 days at ~20°. The obtained solid mass was treated with 50 ml of water, and the precipitate was filtered, dried, and chromatographed on Al_2O_3 (hexane). We obtained 13.7 g (91%) of (I) with a purity of 97.7%, mp 131-132°; cf. [8].

1,3-Bis-(4-hydroxyphenyl)adamantane (II). A stirred mixture of 22 g of 1,3-dichloroadamantane and 220 g of freshly distilled phenol was heated at 174-178° for 10 h in a nitrogen atmosphere, after which the mixture was cooled to 80-90° and diluted with hot water. The obtained precipitate was filtered, washed with hot water until neutral, and recrystallized twice from MeOH.

2,2-Bis-(4-hydroxyphenyl)adamantane (V). To a stirred mixture of 90 g of molten freshly distilled phenol and 2.5 g of glacial CH_3COOH were added 8.3 g of finely ground adamantanone and 3.1 g of CH_3COSH. The obtained mixture was saturated with HCl for 3 h, allowed to stand overnight, and diluted with 10 ml of glacial CH_3COOH. The precipitate was filtered, washed with glacial CH_3COOH, dried in the air, and recrystallized from MeOH.

2,2-Bis-(4-hydroxy-3-methylphenyl)adamantane (VI). Similar to (V), (VI) was obtained from 1 g of adamantanone, 10.8 g of o-cresol and 0.76 g of CH_3COSH. The compound was purified by recrystallization from aqueous MeOH.

2,2-Bis-(4-hydroxy-3,5-dimethylphenyl)adamantane (VII). Similar to (V), (VII) was obtained from 1 g of adamantanone, 12.2 g of 2,6-dimethylphenol, 1 ml of CH_3COOH and 0.21 g of CH_3COSH. The compound was purified by recrystallization from MeOH.

3,3,5,5-Tetrabromo Derivatives (III) and (VIII). As described in [9], the bromination of the bisphenols with bromine in methanol, containing CH_3COOH, gave (III) and (VIII). The compounds were purified by recrystallization from 9:1 benzene–methanol.

Acetyl Derivatives (IV) and (IX). A mixture of the bisphenol, pyridine and acetic anhydride, taken in equal molar amounts, was refluxed for 1.5 h, after which the mixture was cooled, diluted with water, and the precipitate was filtered, washed with water, dried, and purified by recrystallization from MeOH.

The yields and properties of the obtained bisphenols are given in Table 1.

CONCLUSIONS

A method was developed for the synthesis of the 2,2-bisphenols of adamantane by the reaction of adamantanone with either phenol or methylphenols in the presence of hydrogen chloride and thioacetic acid.

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For the N,N-dimethyl protons of aminoacetal (Ia), which at 34° give a singlet absorption line in the NMR spectrum, only a partial separation of the signals (~0.08 ppm) is observed when the temperature is lowered to −100°. This indicates the quite low (<8.7 kcal/mole) barrier of rotation around the $(CH_3)_2N-\overset{|}{C}=$ bond (cf. [19]), possibly due to the presence of the OCH_3 group.

EXPERIMENTAL METHOD

The ^{19}F NMR spectra at 34° were taken on a Hitachi instrument (56.46 MHz). The ^{1}H and ^{19}F NMR spectra of bis(trifluoromethyl)ketene O,N,N-trimethylaminoacetal (Ia) (as a 39% solution in CH_2Cl_2) at reduced temperatures were taken on a RN-2305 instrument (60 and 56.46 MHz, respectively).

CONCLUSIONS

1. The $(CF_3)_2C=C<$ fragment is characterized by a chemical shift in the ^{19}F NMR spectrum that ranges from −15 to −25 ppm (relative to CF_3COOH), which can be used to establish the structure of organofluoro compounds.

2. The C=C double bond in bis(trifluoromethyl)ketene aminoacetals $(CF_3)_2C=C(OR'')NR'_2$ exhibits stereochemical lability; rotation around this bond at room temperature leads to an equivalence of the trifluoromethyl groups.

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