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4H-3,1-BENZOXAZOLES.

4.* EXAMINATION OF THE FORMATION OF 1,2-DIHYDRO-4H-3,1-BENZOXAZINES USING TAGGED ATOMS

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A mechanism is proposed for the formation of 4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazines, which has been proved by introducing a $^{17}O/^{18}O$ isotopic label into the starting 2-aminophenyldiphenylmethanols and carbonyl compounds. ^{17}O NMR and mass spectrometry show that the 3,1-benzoxazine ring contains the oxygen atom from the alcohol group in the starting 2-aminophenyldiphenylmethanol.

We have previously examined the reaction of 2-aminophenyldiphenylmethanol (APM) with carbonyl compounds in acidic media [1, 2], and shown that 4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazines are formed. It was of interest to examine the mechanism of this reaction. It has been reported [3] that the closure of the 3,1-oxazine ring on reaction of APM with aldehydes may follow two courses. In one of these, the carbonyl carbon attacks the amino-group in the starting APM, followed by elimination of a molecule of water and heterocyclization to 1,2-dihydro-4H-3,1-benzoxazine. In the other, the o-aminophenyldiphenylcarbenium cation initially formed in the acidic medium attacks the oxygen atom of the carbonyl group in the oxo-compound [3, 4].

In order to determine the mode of closure of the heterocycle in the acid-catalyzed synthesis of 1,2-dihydro-4H-3,1-benzoxazines, the products (II*) were obtained from compounds tagged with labeled oxygen isotopes $^{17}O/^{18}O$ (Scheme 1). The compounds were analyzed by ^{17}O NMR and mass spectrometry. The starting material used was benzaldehyde enriched in isotopes $^{17}O/^{18}O$ [5], the ^{17}O NMR spectrum of which showed it to contain 7.6% of ^{17}O. In the ^{17}O spectrum of the product of reaction of APM hydrochloride with enriched benzaldehyde, no signal for ^{17}O was seen, showing that the oxygen atom of the APM hydroxyl group had been retained in (II) (Scheme 1).

2,4,4-Triphenyl-1,2-dihydro-4H-3,1-benzoxazine (II*) was obtained by direct synthesis from $^{17}O/^{18}O$-enriched APM hydrochloride (I*). The presence of a signal for ^{17}O in the spectra of the products (II*) (δ 67 ppm) showed that the C—^{17}O bond in the APM had been retained. This provides further confirmation that the reaction of APM with carbonyl compounds occurs by the first of these mechanisms.

*For Communication 3, see [1].

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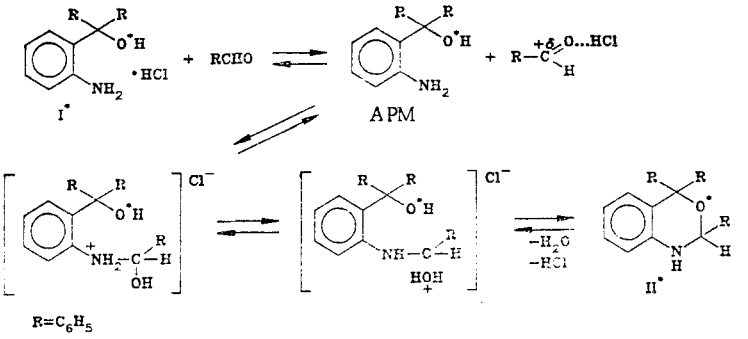
Scheme 1



The benzoxazines (II) were obtained by boiling the starting materials in dry benzene, with azeotropic distillation of the water formed. The acid catalyst used was HCl, which is present in dynamic equilibrium with the salt form of the APM. The free amino group attacks the carbon atom of the oxo-group, causing a shift in the equilibrium toward ring closure.

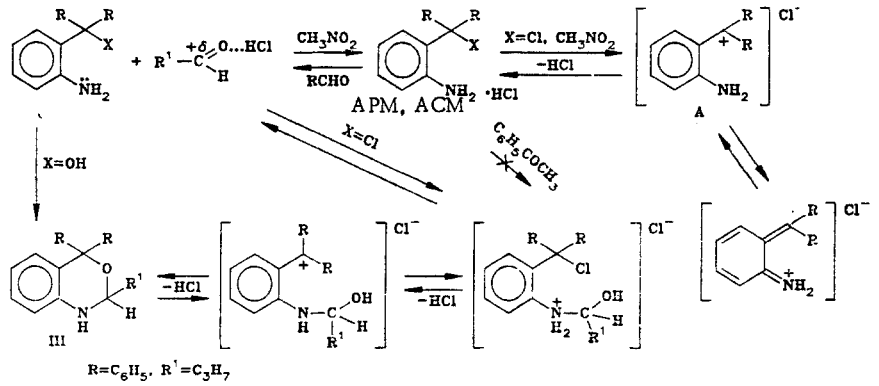
The mass spectra of the benzoxazine (II*) and its precursor APM hydrochloride (I*) show that all the tagged oxygen atoms are transferred from the starting material to the product, since in both compounds the ^{18}O content was the same.

These ^{17}O NMR and mass spectral findings for the $^{17}/^{18}O$-enriched products provide unambiguous proof of the mechanism of formation of the 3,1-oxazine ring annelated with the benzene nucleus, involving initial attack of the nucleophilic center of the starting aminoalcohol (the NH_2 group) on the carbonyl carbon atom. The subsequent stages comprise cleavage of a molecule of water containing the oxygen atom of the carbonyl group, and heterocyclization to give the 1,2-dihydro-4H-3,1-benzoxazine (Scheme 1).

We have carried out the reaction of APM hydrochlorides and 2-aminophenyldiphenylchloromethane (ACM) with butyraldehyde and acetophenone. The syntheses were effected in nitromethane by mixing the reactants in equimolar amounts at ambient temperatures under nitrogen.

Addition of dry nitromethane to ACM hydrochloride results in the formation of a bluish-green mixture. The UV spectrum of the solution shows strong absorption in the visible region, with λ_{max} 390 nm. This fact, together with the color of the solution (the halochromism phenomenon) indicates the presence in this solution of a highly conjugated system, such as the cation A (Scheme 2).

Scheme 2



On adding butyraldehyde to the nitromethane solution of ACM hydrochloride and stirring the mixture for 30 min, the color disappeared, the mixture becoming colorless. The solid which separated was filtered off, purified by chromatography (yield 70%), and identified as 2-propyl-4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazine (III) [2].

Under these conditions, ACM hydrochloride failed to react with acetophenone (the bluish-green coloration did not disappear during the course of the experiment).

Similar behavior was seen in the reaction of APM hydrochloride with the same carbonyl compounds under the same conditions (Scheme 2). No halochromism was seen.

Qualitative assessment of the experimental data shows that the formation of the cation A in the reaction mixture and the nature of the substituent X in the starting material have no effect on the reaction times and product yields. It is clear that this reaction, both in nitromethane and in benzene, involves initial attack of the amino-group in the ACM or APM in the basic form on the carbonyl carbon atom. Acetophenone fails to react under similar conditions as a result of increased steric hindrance and a reduction in the electrophilicity of the ketonic carbon atom.

EXPERIMENTAL

IR spectra were obtained in Specord-71 and UR-20 instruments, in Vaseline oil. Electronic spectra were obtained on a Specord UV-VIS spectrophotometer, in nitromethane. ^{17}O NMR spectra were obtained on a Bruker WP-200 SY spectrometer in $CDCl_3$ in impulse mode followed by Fourier transformation. The recording conditions for the spectra were: operating frequency for ^{17}O nuclei, 27.13 MHz; scan width 50 KHz; impulse duration 50 μsec. The ^{17}O chemical shifts were measured in parts per million relative to $H_2{}^{17}O$ as external standard. Positive values of δ indicate descreening of the oxygen nucleus. Mass spectra were recorded on an MX-1320 mass spectrometer, with direct introduction of the sample into the ion source and an ionizing energy of 70 eV. Column chromatography was carried out on silica gel grade L 40/100 (h = 32 cm, d = 3 cm), and thin layer chromatography on Silufol UV-254 plates (eluent benzene, developed with iodine vapor).

2-Aminophenyldiphenylmethanol (APM) was obtained from methyl anthranilate as described in [6].

2-Aminophenyldiphenylchloromethane (ACM) Hydrochloride. To a mixture of 0.69 g (2.50 mmoles) of APM and 5 ml of dry chloroform was added portionwise with external ice-cooling over 15 min 1.04 g (5.00 mole) of finely-divided phosphorus pentachloride, a colorless precipitate of AFM hydrochloride (I) separating. Stirring was continued at ambient temperature under nitrogen until the colorless solid had disappeared, and been replaced by a greenish-gray solid. This was filtered off, washed with dry ether, and transferred immediately into a weighing bottle. ACM hydrochloride should be stored in a sealed ampul, since on contact with atmospheric moisture it is spontaneously converted into APM hydrochloride (I). Yield 0.5 g (61%), mp 131-133°C. IR spectrum: 3030, 1910, 1590, 1500, 1320, 1210, 1190, 1150, 1130, 1090, 1010, 910, 780, 750 cm^{-1}. Found, %: C 69.6; H 5.6; N 4.4; Cl 22.0. $C_{19}H_{17}Cl_2N$. Calculated, %: C 69.2; H 5.2; N 4.4; Cl 21.5.

2-Aminophenylidiphenylmethanol Hydrochloride Enriched in $^{17}O/^{18}O$ Isotopes (I*). In a flat-bottomed 50 ml flask fitted with a magnetic stirrer and a Dean and Stark apparatus with a reflux condenser and a calcium chloride tube were placed 1 g (3.03 mmoles) of 2-aminophenyldiphenylchloromethane hydrochloride (III), 8-10 ml of dry benzene, and 1.5 ml of water tagged with $^{17}O/^{18}O$. The mixture was stirred in the cold for 30 min, then heated to the boiling point of benzene, and the excess of tagged water collected by azeotropic distillation in the Dean and Stark apparatus. After removal of the solvent, the residue was crystallized from light petroleum. Yield 0.87 g (2%), mp 153-154°C. IR spectrum: 3350, 3030, 2575, 1920, 1610, 1320, 1300, 1160, 1130, 1050, 1020, 900, 770 cm^{-1}. Found, %: C 73.7; H 6.0; N 4.4; Cl 11.5. $C_{19}H_{18}ClNO$. Calculated, %: C 73.2; H 5.8; N 4.5; Cl 11.4.

2,4,4-Triphenyl-1,2-dihydro-4H-3,1-benzoxazine Enriched in $^{17}O/^{18}O$ Isotopes (II*). In a flat-bottomed 50 ml flask fitted with a magnetic stirrer and a Dean and Stark apparatus with a reflux condenser and a calcium chloride guard tube were placed 0.95 g (3.03 mmoles) of $^{17}O/^{18}O$-enriched APM hydrochloride (I*), 8-10 ml of dry benzene, and 0.32 g (3.03 mmoles) of benzaldehyde. The mixture was stirred and heated to the boil. Heating was continued until no more water collected in the Dean and Stark apparatus. The solvent was removed, and the residue crystallized from light petroleum, to give 0.94 g(86%) of product, R_f 0.73, mp 158°C. IR spectrum: 3400, 3030, 1615, 1590, 1170, 1110, 1030 cm^{-1}. Found, %: C 86.1; H 5.6; N 3.6. $C_{26}H_{21}NO$. Calculated, %: C 86.0; H 5.8; N 3.9.

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N-HETARYLETHYLENES.

1.* SYNTHESIS AND ISOMERIZATION OF 10-ALLYL- AND 10-PROPENYLPHENOXAZINES

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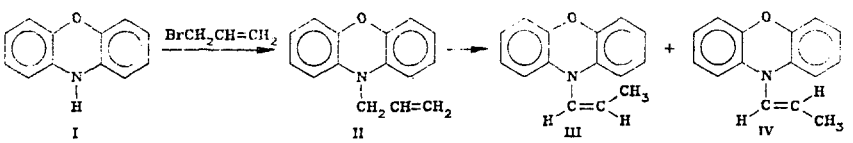
Alkylation of phenoxazine with allyl bromide has given 10-allylphenoxazine. The prototropic isomerization of 10-allylphenoxazine in DMSO on treatment with t-BuOK, KOH, and NaOH has been examined. At elevated temperatures, mixtures of cis- and trans-10-propenylphenoxazines are formed, but at room temperature in the presence of t-BuOK isomerization proceeds stereoselectively to give cis-10-propenylphenoxazine. The influence of temperature and reaction times on the isomeric composition of the 10-propenylphenoxazines has been studied. The cis-propenylphenoxazine obtained in the kinetically controlled reaction isomerizes under the reaction conditions to the equilibrium mixture of cis- and trans-isomers of 10-propenylphenoxazine.

Phenoxazines find extensive application, primarily as dyes [2]. Polymers derived from phenoxazine are used in electrophotography and related areas [3, 4]. There have, however, been no literature reports of the preparation of N-unsaturated phenoxazines, which might find applications for example in the preparation of polymers.

Enamines are commonly obtained preparatively by the base-catalyzed isomerization of N-allylamines (see [5] and citations therein), but the use of the reaction to obtain phenoxazines has not been reported.

We have examined the alkylation of phenoxazine (I) with allyl bromide, and studied the prototropic isomerization of the resulting 10-allylphenoxazine (II) in DMSO on treatment with t-BuOK, KOH, and NaOH.

Alkylation of (I) with allyl bromide was carried out with phase-transfer catalysis [6] in the system toluene–33% aqueous KOH–tetrabutylammonium bromide (10% of the weight of phenoxazine).



*For preceding communication, see [1]. The series "N-Hetarylethylenes" comprises 9-alkenylcarbazoles, 10-alkenylphenothiazines, and 10-alkenylphenoxazines.

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