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CATALYTIC SYNTHESIS OF 2-ALKYLBENZOXAZOLES

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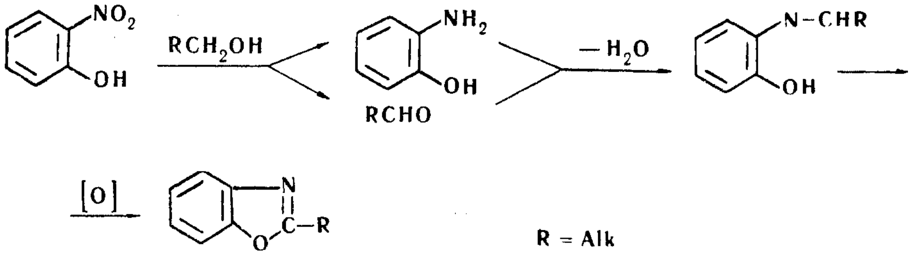
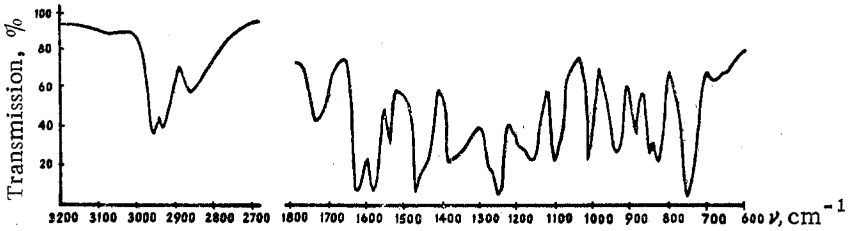
A method of synthesizing 2-alkylbenzoxazoles, by reacting o-nitrophenol with aliphatic alcohols over a copper-alumina catalyst, has been devised. The IR spectra of the compounds prepared have been measured, and the results are interpreted.

2-Alkylbenzoxazoles are mainly prepared from o-aminophenol, and acids [1], amides [2], nitriles [3], acid anhydrides [4], and amidines [5] are condensed with the latter. A method described by us [6] makes it possible to synthesize such compounds in one stage directly from nitro compounds. The present paper gives the results of a study of the catalytic reaction of o-nitrophenol with various aliphatic alcohols (methyl to decyl inclusive) over a copper-alumina catalyst. The probable course of the reaction is:



Oxidation-reduction on the catalyst leads to conversion of the o-nitrophenol to o-aminophenol, while the alcohol forms the aldehyde. These products then condense together to give an azomethine, oxidized by excess o-nitrophenol to the 2-alkylbenzosazole (table).



IR spectrum of 2-n-butylbenzosazole.

The IR spectra of all the compounds were determined. A strong band at 746 cm^{-1} corresponds to benzosazole, which can be regarded as an o-disubstituted benzene. The absence of absorption frequencies in the range 4000-3100 cm^{-1}, which a free hydroxyl or primary amine group would have occasioned, indicates that the o-disubstituted compound has cyclized. The 1246 cm^{-1} absorption band indicates the presence of ether-type oxygen. The 2960-2800 cm^{-1} region absorption band is considerably increased in intensity by increasing the number of methylene groups, confirming the structure of the compounds. An absorption band frequency 1375 cm^{-1} corresponding to deformation vibrations of a symmetric Me group in unbranched compounds, is doubled with compounds having an iso structure (i−C_3H_7m i−C_4H_9), forming a doublet consisting of two bands of approximately equal intensity. It is difficult to come to any conclusion regarding the presence of a frequency corresponding to the −C=N− group, since −C=N− is conjugated with −C=C−, and the frequencies of the two groups are very close together. Consequently, one can speak only of the frequencies of the benzoxazole group as a whole. A 1477-1440 cm^{-1} band is characteristic of all the benzoxazole derivatives. Further, in the case of benzoxazole itself, a 1600 cm^{-1} band is found. Replacement of a hydrogen at position 2 by an alkyl group leads to splitting of the band into two: 1616 and 1575 cm^{-1}. The figure gives one of the spectra.

The spectra were observed with an IKS-14 spectrophotometer using NaCl and LiF prisms, layer thickness 0.04 mm. We wish to thank M. S. Gaisinovich for determining the IR spectra.

2-Alkylbenzoxazoles

Alkyl	Bp, ° C (pressure mm)	d_4^{20}	n_D^{20}	MR_D		Formula	N, %		Yield, %
				Found	Calculated		Found	Calculated	
H	180—182 (760)[8]* mp 31°	—	—	—	—	C_7H_5NO	11.79, 11.82	11.76	20
CH_3	201 (760)[4]	1.12	1.5531	37.984	37.662	C_8H_7NO	10.49, 10.51	10.52	31
C_2H_5	98—99 (10)[1]	1.0879	1.5420	41.881	42.280	C_9H_9NO	9.60 9.58	9.52	34
n-C_3H_7	116—118 (10)	1.066	1.5338	46.819	46.898	$C_{10}H_{11}NO$	8.52, 8.59	8.69	69
i-C_3H_7	109—111 (10)	1.0799	1.5391	46.682	46.898	$C_{10}H_{11}NO$	8.60, 8.62	8.69	32
n-C_4H_9	133—135 (10)	1.042	1.5271	51.514	51.516	$C_{11}H_{13}NO$	8.10, 8.15	8.00	21
i-C_4H_9	120—122 (10)[2]	1.028	1.5090	51.060	51.516	$C_{11}H_{13}NO$	8.00, 8.08	8.00	15
C_5H_{11}	145—147 (10)[1]	1.0072	1.5173	56.310	56.134	$C_{12}H_{15}NO$	7.36, 7.34	7.40	30
C_6H_{13}	164—165 (10)[1]	0.983	1.5000	60.298	60.752	$C_{13}H_{17}NO$	6.72, 6.75	6.89	25
C_7H_{15}	176—178 (10)[1]	0.943	1.4818	65.310	65.370	$C_{14}H_{19}NO$	6.50, 6.52	6.45	30
C_8H_{17}	mp 26°	—	—	—	—	$C_{15}H_{21}NO$	6.10, 6.12	6.06	27
C_9H_{19}	mp 22—23°	—	—	—	—	$C_{16}H_{23}NO$	5.80, 5.78	5.71	20

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*The superscript numbers refer to the references at the end of the article.

Experimental

The catalyst was prepared by coprecipitation of the hydroxides, using 10% alkali, from a solution containing Cu and Al nitrates, the alkali being added until the solution was slightly alkaline to phenophthalein. The catalyst was worked up as previously described [7]. As ready for use it contained 30% Cu and 70% Al_2O_3.

2-Alkylbenzoxazoles (table). The reactor tube contained 30 g catalyst, and 0.1 mole o-nitrophenol and 0.3 mole of the appropriate alcohol was passed over it after first being preheated, feed rate 20 g/hr, reaction temperature 300°–310° C. The catalyzate was first distilled to obtain unreacted alcohol and the ether. The residue was treated with alkali to remove phenols, washed with water, then dried over $MgSO_4$. Next, it was distilled under reduced pressure. The yield of product obtained by distillation was calculated on a basis of the o-nitrophenol taken.

For determining the IR spectra, the compounds were further purified by boiling them in ethanol solution with alumina. Solids were repeatedly recrystallized from petrol ether. From the 2-alkylbenzoxazoles were prepared either picrates (in the cases of 2-methyl- and 2-ethylbenzoxazole), or the quaternary ethiodides, (in the cases of the other compounds), which gave undepressed mixed melting points with the same derivatives prepared as described in [1].

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