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RESEARCHES ON THE CHEMISTRY OF CARBAZOLE DERIVATIVES

XXXI. Addition of Carbazole to Simple Vinyl Ethers

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A method of preparing a number of 9-(α-alkoxyethyl)-carbazoles by adding carbazole to the corresponding simple vinyl ethers in the presence of acid catalysts is described. Data relating to the effects of various factors on the reaction are given. The synthetic method developed for 9-(α-alkylhydroxyethyl) carbazoles differs from that previously used in that reaction conditions are milder, yields of vinyl ethers lower, and yields of products higher.

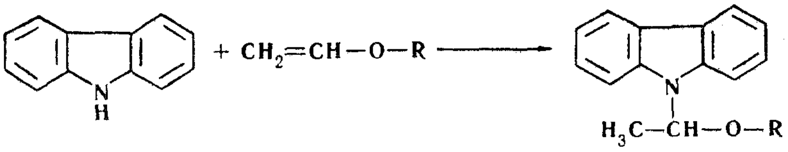
Furukawa and Goi [1] postulated that, in the presence of BF_3 etherate in benzene, vinylethyl ether adds to carbazole at position 3. Subsequently, one of these authors [2, 3] heated carbazole with a six-fold excess of vinylethyl ether in an autoclave at 180° C for 5 hr, and obtained a 54% yield of 9-(α-ethoxyethyl) carbazole. The identity of the products obtained by the two methods was shown by the close agreement between their physical properties. The ability of the addition product prepared in the presence of the catalyst, to undergo nitrosation [1] is not a convincing proof of structure, since, in the course of the present work, it was shown that treatment of 9-(α-ethoxyethyl) carbazole with sodium nitrite in acetic acid also gives 9-nitrosocarbazole.

Experimental Conditions for the Synthesis of 9-(α-Alkoxyethyl)-carbazoles

Starting vinyl ether	Temperature, ° C	Catalyst	Amount of catalyst as % of Carbozole weight	Reaction time min	Addition product yield, %
Vinylethyl	24—26	$NaHSO_4$	1	40	92,0
		HCl (d 1.19)	1	40	90,9
		$HgSO_4$	2	40	91,4
		$HgSO_4$	4	40	75,2
Vinylbutyl	20	H_2SO_4	1	30	50
	30		1	30	88
	35		1	30	98
	40		1	30	98
Vinylallyl	40	$CH_3C_6H_4SO_3H$	1	80	65,4
		$NaHSO_4$	1	80	63,0
		H_2SO_4	1	75	66,1

Information in the literature [4] indicates that addition to simple vinyl ethers takes place rather more rapidly and under milder conditions in the presence of acid catalysts. Hence the problem of investigating addition of carbazole to simple vinyl ethers in the presence of acid catalysts arose.

The very first experiments on reacting carbazole with vinylbutyl ether in acetone in the presence of sulfuric acid or freshly prepared mercuric sulfate (II) as catalysts showed reaction to be fast, and gave the desired product in high yields, though considerably less vinyl ether was employed. Subsequently, the reaction was run with other vinyl ethers, when the effects of some other factors on the reaction were also investigated. The following equation covers the examples included in the research:



$R=C_2H_5,\ C_4H_9,\ CH_2=CH-CH_2$

The data showed that in all cases addition occurs under mild temperature conditions (25°–40° C), each vinyl ether having an optimum run temperature, above or below which the yield of addition product is less. Cutting temperature naturally cuts the reaction rate, with increase in total reaction time, while raising the reaction temperature over the optimum results in the reaction products undergoing secondary changes, leading to tar formation, and making isolation and pufication of the reaction products difficult.

Catalysts which can be used for the reaction are mineral acids, p-toluenesulfonic acid, freshly-prepared mercuric sulfate (II), prepared directly in the reaction medium, starting from mercuric acetate (II) and sulfuric acid, sodium bisulfate and potassium bisulfate. Organic acids (acetic, benzoic, mono- and trichloroacetic) are inactive, and so are zinc and aluminum chloride. Reaction product yield is most affected by the amount of catalyst used. 1-2% on the weight of carbazole was enough for the reaction to proceed completely. With more catalyst, there was appreciable tar formation making isolation and purification of the addition product harder. This was particularly noticeable when using freshly-prepared mercuric sulfate (II). Increasing the reaction time has a similar effect. Tar formation in the reaction mixture, which is observed at increased temperature, with increase in the amount of catalyst, or of the reaction time, is due to further conversion of the 9-(α-alkoxyethyl) carbazoles under such conditions to low-molecular polymers of 9-vinylcarbazole. After reacting the vinyl ether with carbazole in the presence of 5% freshly-prepared mercuric sulfate (II), for 6 hr at 26° C, these oligomers were isolated from the reaction products by precipitation with methanol. A similar phenomenon was noticed before [1].

The results of the experiments on preparing the addition products between carbazole and vinyl ether are given in the table. The reaction was run in acetone, using a carbazole, simple vinyl ether molar ratio of 1:1.2.

The reaction can be run not only in acetone and methylethyl ketone, but also in aromatic solvents, e.g., benzene, toluene, xylene. Reaction does not proceed in alcohols, aliphatic hydrocarbons, or diethyl ether.

The structure of the carbazole-vinyl ether addition product which corresponds to 9-(α-allyloxyethyl) carbazole, is confirmed by determining unsaturation by a method involving addition of mercuric acetate in methanol [5], and by investigating the hydrolysis products, as well as by the fact that allyl alcohol does not react with carbazole under the conditions used.

The 9-(α-alkoxyethyl) carbazoles are stable to heat and alkalies. They readily decompose in the presence of acids to give acetaldehyde, carbazole, and the corresponding alcohol. Decomposition by heating with 0.1 N hydrochloric acid was used for identification. When heated with sodium bisulfate, they split off the alcohols and give 9-vinylcarbazole oligomers.

Experimental

Vinylethyl (I) and vinylbutyl (II) ethers were distilled before the runs, and their physical constants agreed with those given in the literature [4].

Vinylallyl ether (III) was prepared from allyl alcohol and II in the presence of $Hg(OAc)_2$ [6], and had bp 66°-68° C, n_D^4 1.4106. The literature [6] gives bp 67.5° C; n_D^{20} 1.4109.

9-(α-Ethoxyethyl) carbazole. A three-necked flask was fitted with stirrer, dropping funnel, and thermometer, and in it were put, one after the other, 8 ml acetone (IV), 0.05 g $NaHSO_4$, and 5 g carbazole (V). The flask was put in a thermostat at 24°-26° C, and 3.5 ml I dropped in with constant stirring; the carbazole gradually dissolved, and when all I had been added, the mixture was kept in the thermostat for a further 15 min, then poured into water. The solid was filtered off and dried. Yield 6.6 g (92%), mp 69°-71° C. After purifying by recrystallizing from MeOH or by distilling, it had mp 75°-76° C, bp 318°-320° C (760 mm), 165°-168° C (6 mm). Found: C 79.90; H 7.28; N 5.82%. Calculated for $C_{16}H_{17}NO$: C 80.30; H 7.16; N 5.85%. The literature gives [2] mp 74°-74.5° C.

9-(α-Butoxyethyl) carbazole. This was prepared similarly, from 10 g V, 11.6 g II, and 30 ml IV, at 40° C, in the presence of 0.1 g $HgSO_4$. After precipitating in water, the products were extracted with ether, the ether layer separated off, dried over anhydrous Na_2SO_4, the ether distilled off, and the residue vacuum-distilled to 15 g (98% theory) passing over at 190°-192° C (6 mm), mp 49°-52° C. After recrystallizing from MeOH, it had mp 52°-52.5° C. Found: C 80.63; H 7.94; N 5.28%. Calculated for $C_{18}H_{22}NO$: C 80.83; H 7.85; N 5.23%.

9-(α-Allyloxyethyl) carbazole. This was prepared similarly, from 10 g V and 8 ml III in 20 ml IV, in the presence of 0.1 g p-toluene-sulfonic acid, using petrol ether for extraction. Yield 9.82 g (65.4%). Colorless oily liquid, bp 172°-174° C (5 mm); n_D^{22} 1.6260. Found: C 81.00; H 6.55; N 5.52%. Calculated for: $C_{17}H_{17}NO$: C 81.23; H 6.77; N 5.58%.

REFERENCES

1. J. Furukawa and M. Goi, Bull. Inst. Chem. Res., Kyoto Univ., 22, 84, 1950; C. A., 48, 6427, 1954.

2. J. Furukawa, A. Onishi, T. Tsuruta, and S. Oshimo, Bull. Chem. Soc. Jap., 27, 184, 1954.
3. J. Furukawa, A. Onishi, and T. Tsuruta, J. Org. Chem., 23, 673, 1958.
4. M. F. Shostakovskii, Simple Vinyl Ethers [in Russian], Izo-vo AN SSSR, Moscow, 190, 1952.
5. R. W. Martin, Anal. Chem., 21, 921, 1949.
6. W. H. Watanabe and L. E. Conlon, J. Am. Chem. Soc., 79, 2828, 1957.

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