SYNTHESIS OF (9-METHYL-3-CARBAZOLYL)-ARYLKETO EPOXIDES

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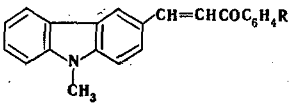
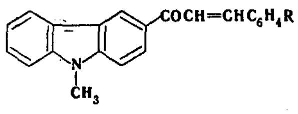
A number of new (9-methyl-3-carbazolyl)arylpropenones were synthesized. Oxidation of them with alkaline hydrogen peroxide gave (9-methyl-3-carbazolyl)arylketo epoxides.

Reaction of aryl β-chlorovinyl ketones and cinnamoyl chloride with 9-alkylcarbazoles in dry benzene in the presence of an equimolecular amount of anhydrous stannic chloride gives (9-alkyl-3-carbazolyl)-arylpropenones [1, 2]. In the present communication we describe the synthesis of (9-methyl-3-carbazolyl)-arylpropenones (I-VIII) obtained by ketovinylation (I-IV) and acylation (V-VIII) of 9-methylcarbazole. The structure of the compounds was proved by alternative synthesis by condensation of 9-methyl-3-formylcarbazole with substituted acetophenones.

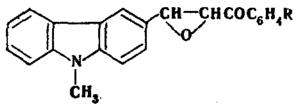


I-IV

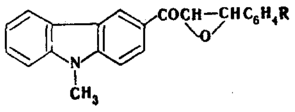


V-VIII

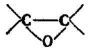
In order to obtain α-keto epoxides of the carbazole series, in the present research we studied the oxidation of (9-methyl-3-carbazolyl) arylpropenones with excess 28% hydrogen peroxide in the presence of an equimolar amount of sodium hydroxide. As a result of the oxidation, (9-methyl-3-carbazolyl)arylketo epoxides (IX-XVI, Table 2) with the following structures were obtained in good yields:



IX-XI



XII-XVI

The IR spectra of I-VIII contain characteristic absorption bands of the C = O group at 1650-1655 cm^{-1} and of an aromatic system of bonds at 1610 cm^{-1}, while the spectra of IX-XVI contain characteristic absorption bands of C = O groups at 1675-1680 cm^{-1} and of  groups at 1230 and 910 cm^{-1}.

EXPERIMENTAL

1-(9-Methyl-3-carbazolyl)-3-(4-tolyl)-3-propenone (I, Table 1). A. A 14.3 g (0.055 mole) sample of anhydrous stannic chloride was added dropwise with stirring and cooling to 10 g (0.055 mole) of p-tolyl β-chlorovinyl ketone and 9.95 g (0.055 mole) of 9-methylcarbazole in 100 ml of dry benzene, after which the mixture was stirred for 1 h, and 50 ml of water and 50 ml of ether were added. The organic layer was separated, washed successively with sodium carbonate solution and water, and dried over calcium chloride. The solvent was removed by distillation to give a yellow precipitate. The product was purified by recrystallization from acetone to give a material with mp 170°. Found,%: C 84.7; H 6.0; N 4.5. $C_{23}H_{19}NO$. Calculated,%: C 84.9; H 5.8; N 4.3.

V. I. Lenin Belorussian State University, Minsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1359-1361, October, 1973. Original article submitted October 12, 1972.

TABLE 1. (9-Methyl-3-carbazolyl)arylpropenones

Comp.	R	mp, °C (crystallization solvent)	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
I	4-CH_3	170 (dioxane)	$C_{23}H_{19}NO$	84,7 84,7	6,0 5,9	4,5 4,6	84,9	5,8	4,3	80
II	4-Cl	178 (dioxane)	$C_{22}H_{16}ClNO$[a]	76,2 76,2	4,8 4,9	4,4 4,2	76,4	4,6	4,1	76
III	3-Cl	130 (dioxane)	$C_{22}H_{16}ClNO$[b]	76,2 76,2	4,7 4,8	3,9 3,8	76,4	4,6	4,1	88
IV	3-Br	135 (dioxane)	$C_{22}H_{16}BrNO$[c]	67,9 67,9	4,3 4,4	3,9 3,8	67,7	4,1	3,6	85
V	2-OCH_3	140 (acetone)	$C_{23}H_{19}NO_2$	80,7 80,7	5,4 5,4	4,4 4,2	80,9	5,6	4,1	82
VI	4-OCH_3	150 (acetone)	$C_{23}H_{19}NO_2$	81,2 81,1	5,4 5,3	3,9 3,9	80,9	5,6	4,1	78
VII	4-NO_2	185 (dioxane)	$C_{22}H_{16}N_3O_3$	74,4 74,4	4,6 4,6	8,1 8,1	74,2	4,5	7,7	80
VIII	3-NO_2	180 (dioxane)	$C_{22}H_{16}N_2O_3$	74,4 74,5	4,8 4,6	8,0 8,0	74,2	4,5	7,7	72

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[a] Found,%: Cl 10.1. $C_{22}H_{16}ClNO$. Calculated,%: Cl 10.3. [b] Found,%: Cl 10.5. $C_{22}H_{16}ClNO$. Calculated,%: Cl 10.3. [c] Found,%: Br 20.8. $C_{22}H_{16}BrNO$. Calculated,%: Br 20.5.

TABLE 2. (9-Methyl-3-carbazolyl)arylketo Epoxides

Comp.	R	mp, °C (crystalliz. solvent)	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
IX	4-CH_3	125 (acetone)	$C_{23}H_{19}NO_2$	80,7 80,7	5,9 6,0	4,4 4,4	80,9	5,6	4,1	80
X	4-Br	140 (dioxane)	$C_{22}H_{16}BrNO_2$[a]	65,3 65,2	4,1 4,2	3,8 3,7	65,0	3,9	3,4	70
XI	3-Br	115 (dioxane)	$C_{22}H_{16}BrNO_2$[b]	65,3 64,9	3,8 3,8	3,6 3,2	65,0	3,9	3,4	80
XII	H	165 (acetone)	$C_{22}H_{17}NO_2$	80,7 80,5	5,3 5,4	4,4 4,5	80,7	5,1	4,3	80
XIII	2-OCH_3	130 (dioxane)	$C_{23}H_{19}NO_3$	77,2 77,5	5,5 5,6	4,1 4,2	77,3	5,3	3,9	65
XIV	4-OCH_3	138 (dioxane)	$C_{23}H_{19}NO_3$	77,5 77,4	5,5 5,6	4,1 4,1	77,3	5,3	3,9	74
XV	4-NO_2	210 (dioxane)	$C_{22}H_{16}N_2O_4$	70,8 70,7	4,5 4,6	7,8 7,8	70,9	4,3	7,5	60
XVI	3-NO_2	150 (dioxane)	$C_{22}H_{16}N_2O_4$	71,1 71,0	4,0 4,0	7,8 7,8	70,9	4,3	7,5	68

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[a] Found,%: Br 20.0. $C_{22}H_{16}BrNO_2$. Calculated,%: Br 19.7. [b] Found,%: Br 19.9. $C_{22}H_{16}BrNO_2$. Calculated,%: Br 19.7.

A similar method was used to obtain (9-methyl-3-carbazolyl)arylpropenones I-IV (Table 1).

B. A 3 g (0.014 mole) sample of 9-methyl-3-formylcarbazole and 2.7 g (0.02 mole) of p-methylacetophenone were dissolved in 70 ml of methanol, and an alcohol solution of an equimolecular amount of potassium hydroxide was added at 70°. The mixture was heated for 30 min, cooled, and neutralized with acetic acid. Water was added, and the precipitate was removed by filtration, washed with water, and recrystallized from acetone to give a product with mp 170°. Found,%: C 84.7; H 5.9; N 4.5. $C_{23}H_{19}NO$. Calculated,%: C 84.9; H 5.8; N 4.3.

No melting-point depression was observed for a mixture of samples of I obtained by methods A and B.

1-(9-Methyl-3-carbazolyl)-3-(4-methoxyphenyl)-1-propenone (VI). This compound was obtained from 10 g (0.051 mole) of p-methoxycinnamoyl chloride, 9.2 g (0.051 mole) of 9-methylcarbazole, and an equimolecular amount of anhydrous stannic chloride in 100 ml of cold dry benzene. The reaction product was isolated via method A above. Compounds V-VIII (Table 1) were similarly obtained.

1-(9-Methyl-3-carbazolyl)-3-(p-tolyl)-3-propenone Epoxide (IX, Table 2). A 10 g (0.03 mole) sample of 1-(9-methyl-3-carbazolyl)-3-(p-tolyl)-3-propenone was dissolved in 100 ml of dioxane and 20 ml of methanol, and an equimolecular amount of 2 N sodium hydroxide and 30 ml (0.25 mole) of 28% hydrogen peroxide were added gradually with stirring and heating to 50°. The mixture was held at 50° until the yellow color disappeared, after which it was cooled to give a precipitate, which was purified by crystallization from acetone. The analytical data for the synthesized oxides are presented in Table 2.

LITERATURE CITED

1. V. F. Belyaev and A. I. Abrazhevich, Author's Certificate No. 239,342 (1969); Byul. Izobr., No. 11 (1969).
2. V. F. Belyaev, V. I. Grushevich, and A. I. Abrazhevich, Zh. Organ. Khim., 8, 610 (1971).