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REACTION OF ISOPROPYLIDENE MALONATE WITH N-ARYLIDENE-1-NAPHTHYLAMINES

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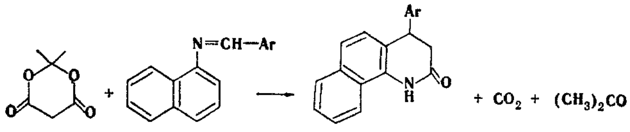
4-Aryl-2-oxo-1,2,3,4-tetrahydro-7,8-benzoquinolines were obtained by reaction of isopropylidene malonate with N-arylidene-1-naphthylamines. It is shown that the products are associated in the solid state by intermolecular hydrogen bonds. The IR and PMR spectral data are presented.

We have shown [1] that 4-aryl-2-oxo-1,2,3,4-tetrahydro-5,6-benzoquinolines are formed in the reaction of isopropylidene malonate (I) with N-arylidene-2-naphthylamines.

The reaction of I with N-arylidene-1-naphthylamines (II) proceeds similarly. 4-Aryl-2-oxo-1,2,3,4-tetrahydro-7,8-benzoquinolines (III) are formed in this case, and carbon dioxide evolution (which was proved by means of barium hydroxide solution) the production of acetone (which was isolated from the reaction mixture and identified in the form of the 2,4-dinitrophenylhydrazone) are also observed.



I II a-m III a-m

The formation of III is confirmed by the close chemical shifts of the protons in the PMR spectra for 4-phenyl-2-oxo-1,2,3,4-tetrahydroquinoline [2] and IIIa (Fig. 1).

Compounds III are strongly associated by intermolecular hydrogen bonds in the solid state. A shift of the absorption band of the stretching vibrations of the carbonyl group ($\nu_{C=O}$) to higher frequencies is observed in the spectrum of a carbon tetrachloride solution of IIIa (Table 1). The ratio of the molar extinction coefficients for the bands of the stretching vibrations of the associated N–H group (at 3230 cm^{-1}) (ε_{as}) and the nonassociated N–H group (at 3439 cm^{-1}) (ε_{free}) changes as a function of the concentration of IIIa in solution (Fig. 2).

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TABLE 1. IR Spectra of 4-Aryl-2-oxo-1,2,3,4-tetrahydro-7,8-benzoquinolines (IIIa-m)

Comp. III	Substituent Ar	IR spectra, cm^{-1}	
		1800—1500[a]	3600—2900
a	C_6H_5[b]	1676 (72), 1605 (sh), 1571 (35)	3350, 3225, 3198, 3124
b	$4\text{-}CH_3OC_6H_4$	1676 (55), 1642 (sh), 1612 (sh), 1596 (33)	3322, 3118, 3116, 3082
c	$2,4\text{-}(CH_3O)_2C_6H_3$	1667 (84), 1612 (53), 1582 (53)	3308, 3194, 3166, 3115
d	$3,4\text{-}(CH_3O)_2C_6H_3$	1671 (69), 1640 (sh), 1627 (sh), 1576 (52)	3323, 3291, 3120, 3086
e	$3,4\text{-}CH_2O_2C_6H_3$[c]	1675 (55), 1640 (sh), 1568 (30)	3332, 3232, 3187, 3119
f	$3,4,5\text{-}(CH_3O)_3C_6H_2$	1681 (77), 1645 (sh), 1591 (65)	3343, 3236, 3196, 3130
g	$4\text{-}(CH_3)_2NC_6H_4$	1667 (79), 1609 (52)	3307, 3204, 3169, 3103
h	$4\text{-}(C_2H_5)_2NC_6H_4$	1674 (75), 1608 (55)	3325, 3220, 3177, 3110
i	$4\text{-}ClC_6H_4$	1673 (67), 1632 (sh), 1566 (49)	3339, 3228, 3195, 3124
j	$2,4\text{-}Cl_2C_6H_3$	1681 (68), 1580 (47)	3335, 3229, 3197, 3126
k	$2\text{-}O_2NC_6H_4$	1674 (75), 1634 (sh), 1606 (49)	3322, 3230, 3186, 3117
l	$3\text{-}O_2NC_6H_4$	1676 (71), 1575 (31), 1606	3329, 3217, 3187, 3121
m	$4\text{-}O_2NC_6H_4$	1689 (91), 1646 (sh), 1597 (53)	3343, 3221, 3195, 3125

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[a] The absorption in percent is given in parentheses. [b] These bands are found at 1695 and 1600 cm^{-1} in the spectrum of a solution in dioxane. [c] These bands are found at 1695 and 1575 cm^{-1} in the spectrum of a solution in dioxane.

TABLE 2. Characteristics of 4-Aryl-2-oxo-1,2,3,4-tetrahydro-7,8-benzoquinolines (IIIa-m)

Comp. III	Substituent Ar	Reac. time, h	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
a	C_6H_5	1,5	201	84,0	5,5	5,2	$C_{19}H_{15}NO$	83,5	5,5	5,1	74
b	$4\text{-}CH_3OC_6H_4$	5	195—196	79,1	5,7	4,6	$C_{20}H_{17}NO_2$	79,3	5,7	4,6	50
c	$2,4\text{-}(CH_3O)_2C_6H_3$	4	185—186	75,2	5,8	4,1	$C_{21}H_{19}NO_3$	75,7	5,7	4,2	45
d	$3,4\text{-}(CH_3O)_2C_6H_3$	4	169—170	75,4	5,6	4,3	$C_{21}H_{19}NO_3$	75,7	5,7	4,2	30
e	$3,4\text{-}CH_2O_2C_6H_3$	8	189—190	—	—	4,5	$C_{20}H_{15}NO_3$	75,7	4,8	4,4	47
f	$3,4,5\text{-}(CH_3O)_3C_6H_2$	4	187—188	72,3	5,7	4,0	$C_{22}H_{15}NO_4$	72,7	5,8	3,9	55
g	$4\text{-}(CH_3)_2NC_6H_4$	10	215—216	—	—	9,0	$C_{21}H_{20}N_2O$	79,7	6,4	8,9	50
h	$4\text{-}(C_2H_5)_2NC_6H_4$	10	221—222	—	—	8,1	$C_{23}H_{24}N_2O$	80,3	7,0	8,1	44
i	$4\text{-}ClC_6H_4$[a]	0,5	209—210	—	—	4,7	$C_{19}H_{14}ClNO$	—	—	4,6	67
j	$2,4\text{-}Cl_2C_6H_3$[b]	1	251—252	66,8	3,8	4,0	$C_{19}H_{13}Cl_2NO$	66.7	3,8	4,1	82
k	$2\text{-}O_2NC_6H_4$	1	253—254	71,8	4,3	8,7	$C_{19}H_{14}N_2O_3$	71,8	4,4	8,8	66
l	$3\text{-}O_2NC_6H_4$	2	194—195	—	—	8,8	$C_{19}H_{14}N_2O_3$	71,8	4,4	8,8	66
m	$4\text{-}O_2NC_6H_4$	3	220—221	—	—	8,7	$C_{19}H_{14}N_2O_3$	71,8	4,4	8,8	64

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[a] Found: Cl 11.5%. Calculated: Cl 11.5%. [b] Found: Cl 20.7%. Calculated: Cl 20.8%.

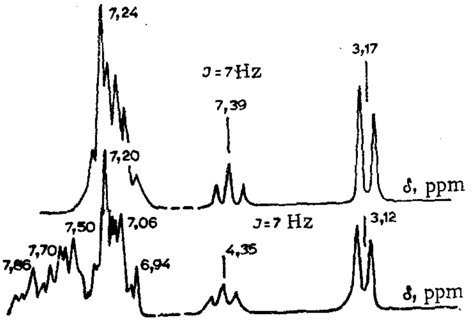

Fig. 1

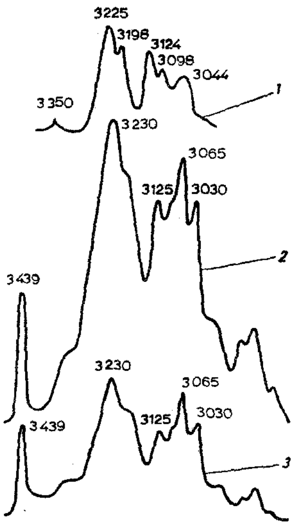

Fig. 2

Fig. 1. PMR spectra: a) 4-phenyl-2-oxo-1,2,3,4-tetrahydroquinoline; b) 4-phenyl-2-oxo-1,2,3,4-tetrahydro-7,8-benzoquinoline (IIIa).

Fig. 2. IR spectra of 4-phenyl-2-oxo-1,2,3,4-tetrahydro-7,8-benzoquinoline (IIIa): 1) suspension in hexachlorobutadiene; 2) solution (0.01 M) in carbon tetrachloride ($\varepsilon_{as}:\varepsilon_{free} = 2.23$); 3) solution (0.004 M) in carbon tetrachloride ($\varepsilon_{as}:\varepsilon_{free} = 1.35$).

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CF_3COOH were recorded with a Perkin–Elmer R-12A spectrometer (60 MHz) on the δ scale relative to the cyclohexane internal standard. The IR spectra of mineral oil suspensions of the compounds at 1500-1800 cm^{-1} were recorded with an IK-14A spectrometer with an NaCl prism; the IR spectra of hexachlorobutadiene suspensions at 2900-3600 cm^{-1} were recorded with an IK-14A spectrometer with an LiF prism.

4-Aryl-2-oxo-1,2,3,4-tetrahydro-7,8-benzoquinolines (IIIa-i) (see Table 2). The N-arylidene-1-naphthylamines (II) were not isolated in the free form but rather were obtained during the reaction from 1-naphthylamine and the appropriate aldehyde. A mixture of 0.01 mole of 1-naphthylamine and 0.01 mole of the appropriate aldehyde in 5 ml of benzene was refluxed for 10-15 min, after which 0.01 mole of I was added to the hot solution of naphthylamine II, and refluxing was continued (see Table 2). The tetrahydrobenzoquinolines (III) that precipitated during the reaction or when the mixture was cooled were removed by filtration, washed with ethanol, and crystallized: IIa from benzene: IIIb, k-m from CH_3COOH and water, IIIc, e-g, i,j from dioxane and water, IIId from ethanol, and III h from dioxane. The products were white or light-yellow substances that were quite soluble in dioxane, DMF, and acetic acid and moderately or slightly soluble in chloroform, carbon tetrachloride, benzene, and ethanol.

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