8. A. N. Saverchenko, V. A. Kaminskii, and M. N. Tilichenko, Khim. Geterotsikl. Soedin., No. 3, 384 (1973).

REACTION OF ISOPROPYLIDENE MALONATE WITH N-ARYLIDENE-2-NAPHTHYLAMINES

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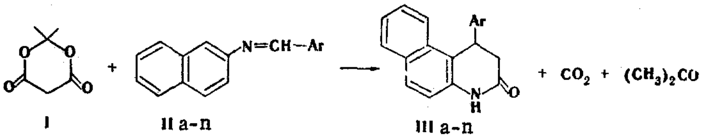
It is shown that 4-aryl-2-oxo-1,2,3,4-tetrahydro-5,6-benzoquinolines are formed in the reaction of N-arylidene-2-naphthylamines with isopropylidene malonate. The reaction takes place with cleavage of the isopropylidene malonate ring and the production of carbon dioxide and acetone. The structure of the benzotetrahydroquinolines obtained were confirmed by identification of the compound obtained by sulfur dehydrogenation of the product of the reaction of isopropylidene malonate with arylidenenaphthylamine (aryl=phenyl) with an authentic sample of 1,2-dihydro-2-oxo-4-phenyl-5,6-benzoquinoline and of the reaction product (in which the aryl group was absent) with an authentic sample of 2-oxo-1,2,3,4-tetrahydro-5,6-benzoquinoline. The IR and PMR spectra data are presented.

It is known that cyclohexane-1,3-diones, indane-1,3-diones, and 4-hydroxycoumarin react with N-arylidene-2-naphthylamines to give the corresponding benzoquinoline derivatives [1, 2]. We selected isopropylidene malonate (I) as the 1,3-dicarbonyl component to continue the study of the reaction of cyclic 1,3-dicarbonyl compounds with Schiff bases.

Isopropylidene malonate reacts readily with N-arylidene-2-naphthylamines (II), but we were unable to isolate the expected benzoquinoline derivatives (IV). It was observed that carbon dioxide is evolved during the reaction (which was proved by means of barium hydroxide solution); this constituted evidence for cleavage of the isopropylidene malonate ring. Another product of cleavage of the isopropylidene malonate ring – acetone – was also isolated from the reaction mixture and was identified in the form of the 2,4-dinitrophenylhydrazone. We assumed that the isopropylidene malonate ring in IV is cleaved during the reaction and that 2-aryl-4-oxo-1,2,3,4-tetrahydro-5,6-benzoquinolines (V) or 2-aryl-4-oxo-1,4-dihydro-5,6-benzoquinolines (VI) can be formed in this way. However, if it is assumed that cleavage of the isopropylidene malonate ring occurs prior to the formation of the cyclic condensation products, the formation of 4-aryl-2-oxo-1,2,3,4-tetrahydro-5,6-benzoquinolines (III), 4-aryl-2-oxo-1,2-dihydro-5,6-benzoquinolines (VII), and 2-naphthylamides of cinnamic (VIII) or hydrocinnamic (IX) acid is possible. It should be noted that the results of elementary analysis do not contradict any of structures III-IX, whereas absorption bands characteristic for secondary amides are observed in the IR spectra (Table 1).

Signals of aromatic protons in the form of a multiplet and of aliphatic protons in the form of a doublet (two protons) and a triplet (one proton) are observed in the PMR spectrum of a CF_3COOH solution of the



I II a-n III a-n

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TABLE 1. IR Spectra of 4-Aryl-2-oxo-1,2,3,4-tetrahydro-5,6-benzoquinolines (IIIa-n)

Compounds III	Substituent Ar	IR spectra, cm^{-1}	
		1800—1500	3600—2900
a	H	1705 (55)[a], 1664 (sh), 1624 (22), 1600 (18)	3320, 3199, 3164, 3112, 3074
b	C_6H_5[b]	1681 (84), 1624 (65), 1610 (61)	3345, 3199, 3128, 3106
c	$4\text{-}CH_3OC_6H_4$	1685 (84), 1622 (68), 1601 (sh)	3332, 3207, 3185, 3115
d	$2,4\text{-}(CH_3O)_2C_6H_3$[c]	1680 (80), 1626 (62), 1607 (65)	3342, 3200, 3100, 3075
e	$3,4\text{-}(CH_3O)_2C_6H_3$	1681 (53), 1624 (42), 1587 (41)	3345, 3219, 3203, 3170
f	$3,4\text{-}CH_2O_2C_6H_3$	1684 (39), 1629 (23)	3341, 3203, 3176, 3072
g	$3,4,5\text{-}(CH_3O)_3C_6H_2$	1681 (80), 1630 (57), 1587 (60)	3343, 3223, 3205, 3109
h	$4\text{-}(CH_3)_2NC_6H_4$	1677 (86), 1611 (69), 1560 (40)	3333, 3200, 3186, 3073
i	$4\text{-}(C_2H_5)_2NC_6H_4$	1677 (82), 1622 (sh), 1612 (59)	3332, 3216, 3198, 3162
j	$4\text{-}ClC_6H_4$	1685 (87), 1621 (68), 1601 (14)	3341, 3203, 3186, 3090
k	$2,4\text{-}Cl_2C_6H_3$	1681 (78), 1626 (66), 1580 (53)	3335, 3228, 3200, 3164
l	$2\text{-}O_2NC_6H_4$	1680 (57), 1625 (43)	3335, 3193, 3061
m	$3\text{-}O_2NC_6H_4$	1689 (59), 1660 (sh), 1625 (49)	3317, 3196, 3127, 3100
n	$4\text{-}O_2NC_6H_4$	1679 (80), 1625 (59), 1601 (54)	3205, 3109, 3083

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[a] The absorption in percent is given in parentheses. [b] In the spectrum of a solution in dioxane, these bands are observed at 1699 and 1628 cm^{-1}. [c] In the spectrum of a solution in dioxane, these bands are observed at 1695 and 1630 cm^{-1}.

TABLE 2. Characteristics of 4-Aryl-2-oxo-1,2,3,4-tetrahydro-5,6-benzoquinolines (IIIa-n)

Comp. III	Substituent Ar	Reac. time, h	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
a	H	2	237—239	78,7	5,6	6,9	$C_{13}H_{11}NO$	79,2	5,6	7,1	71
b	C_6H_5	1	263—264	82,9	5,5	4,9	$C_{19}H_{15}NO$	83,5	5,5	5,1	85
c	$4\text{-}CH_3OC_6H_4$	3	238—239	—	—	4,8	$C_{20}H_{17}NO_2$	79,3	5,7	4,6	43
d	$2,4\text{-}(CH_3O)_2C_6H_3$	7	211—212	75,7	5,6	3,9	$C_{21}H_{19}NO_3$	75,7	6,7	4,2	38
e	$3,4\text{-}(CH_3O)_2C_6H_3$	7	214—215	—	—	4,5	$C_{21}H_{19}NO_3$	75,7	5,7	4,2	31
f	$3,4\text{-}CH_2O_2C_6H_3$	7	249—250	75,0	4,6	4,2	$C_{20}H_{15}NO_3$	75,7	4,8	4,4	44
g	$3,4,5\text{-}(CH_3O)_3C_6H_2$	8	226—227	71,3	5,4	3,8	$C_{22}H_{21}NO_4$	72,7	5,8	3,9	33
h	$4\text{-}(CH_3)_2NC_6H_4$	10	285—286	—	—	8,7	$C_{21}H_{20}N_2O$	79,7	6,4	8,9	40
i	$4\text{-}(C_2H_5)_2NC_6H_4$	10	237—238	—	—	8,3	$C_{23}H_{24}N_2O$	80,3	7,0	8,1	35
j	$4\text{-}ClC_6H_4$[a]	0,5	233—234	—	—	4,8	$C_{19}H_{14}ClNO$	—	—	4,6	67
k	$2,4\text{-}Cl_2C_6H_3$[b]	3	267—268	—	—	4,3	$C_{19}H_{13}Cl_2NO$	—	—	4,1	82
l	$2\text{-}O_2NC_6H_4$	0,5	257—258	—	—	8,5	$C_{19}H_{14}N_2O_3$	—	—	8,8	70
m	$3\text{-}O_2NC_6H_4$	1	263—264	—	—	9,0	$C_{19}H_{14}N_2O_3$	71,8	4,4	8,8	62
n	$4\text{-}O_2NC_6H_4$	0,5	265—266	—	—	9,1	$C_{19}H_{14}N_2O_3$	71,8	4,4	8,8	78

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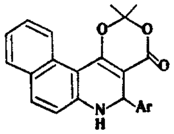
[a] Found: Cl 11.4%. Calculated: Cl 11.5%. [b] Found: Cl 20.5%. Calculated: Cl 20.8%.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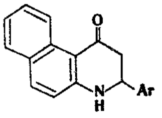
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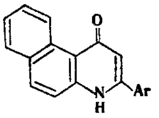
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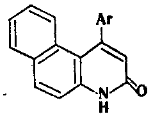
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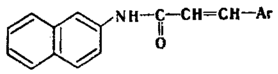
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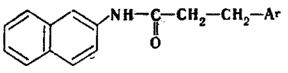

IX

compound obtained from I and IIb (Fig. 1). This indicates the presence of a CH_2CH fragment in the molecule and excludes the formation of VI-IX. It is difficult to distinguish III and V only on the basis of the IR and PMR spectral data.

It is known that 4-oxo-1,2,3,4-tetrahydroquinoline [3] and 4-oxo-1,2,3,4-tetrahydro-6,7- (or 7,8-)benzoquinolines [4-6] react with aldehydes at the methylene group and with phenylhydrazine at the carbonyl group.

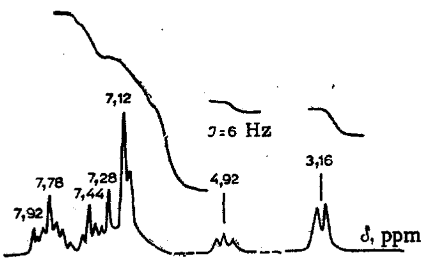
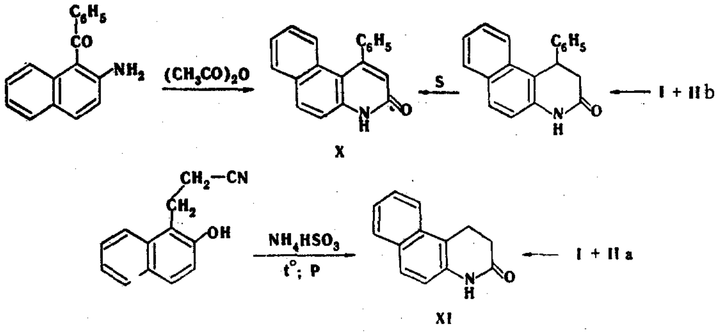


Fig. 1. PMR spectrum of the compound obtained from isopropylidene malonate (I) and N-benzylidene-2-naphthylamine (IIb).

The compounds that we obtained did not react either with aldehydes or phenylhydrazine. This constitutes evidence for the formation of substances with the III structure.

The structures of the compounds that we obtained were established unambiguously by means of two alternative syntheses. Thus 1,2-dihydro-2-oxo-4-phenyl-5,6-benzoquinoline (X) [7] was found to be identical to the compound obtained by sulfur dehydrogenation of the product of the reaction of I with IIb, and 2-oxo-1,2,3,4-tetrahydro-5,6-benzoquinoline (XI) [8] was found to be identical to the product of the reaction of I and IIa.

Thus there is no doubt that precisely III are formed in the reaction of I and II.



Compounds III are strongly associated in the solid state by intermolecular hydrogen bonds, as indicated by the shift of the $\nu_{C=O}$ (amide I) absorption band of the stretching vibrations of the carbonyl group to higher frequencies in dioxane solution (Table 1).

EXPERIMENTAL

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 of the compounds at 2900-3600 cm^{-1} were recorded with an IK-14A spectrometer with an LiF prism. The PMR spectra were recorded with a Perkin–Elmer R-12A spectrometer (60 MHz); the chemical shifts of the protons are presented relative to the cyclohexane internal standard on the δ scale.

4-Aryl-2-oxo-1,2,3,4-tetrahydro-5,6-benzoquinolines (IIIa-n) (see Table 2). The N-arylidene-2-naphthylamines (II) were not isolated in pure form but were obtained directly during the reaction from 2-naphthylamine and the appropriate aldehyde. A mixture of 0.01 mole of 2-naphthylamine, 0.01 mole of the appropriate aldehyde, and 5 ml of ethanol was refluxed for 10-15 min, after which 0.01 mole of I was added to the hot solution of naphthylamine II, and the mixture was refluxed (see Table 2). The benzoquinolines (III) that precipitated during the reaction or after the mixture was cooled were removed by filtration, washed with ethanol, and crystallized: IIIa from dioxane, IIb-d, h-k from dioxane and water, IIIe-g from ethanol and dioxane, and IIIl-n from acetic acid and water. The products were white or light-yellow crystalline substances that were only slightly soluble in ethanol, benzene, and chloroform but more soluble in dioxane and DMF.

4-Phenyl-2-oxo-1,2-dihydro-5,6-benzoquinoline (X). A mixture of 0.005 mole of IIIa and 0.0025 mole of sulfur was heated at 270° for 2-3 h (the end of hydrogen sulfide evolution was monitored with lead tetraacetate), after which it was worked up to give 1.2 g (89%) of X with mp 305-307° (from acetic acid and water). IR spectrum: 1665 (84), 1635 (sh), 1601 (31), 3048, and 2674 cm^{-1}. Found: C 84.5; H 4.9; N 5.3%. $C_{19}H_{13}NO$. Calculated: C 84.2; H 4.8; N 5.2%.

LITERATURE CITED

1. N. S. Kozlov, V. D. Pak, and Z. Z. Nugumanov, Khim. Geterotsikl. Soedin., No. 2, 194 (1970).
2. I. É. Lielbriedis, V. V. Chirkova, and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 2, 251 (1968).
3. G. Clemo and W. Perkin, Jr., J. Chem. Soc., 125, 1608 (1924).
4. A. F. Bekhli, N. P. Kozyreva, and E. M. Peresleni, Khim. Geterotsikl. Soedin., No. 6, 798 (1970).
5. A. F. Bekhli and N. P. Kozyreva, Khim. Geterotsikl. Soedin., No. 6, 802 (1970).
6. S. I. Kutkevichus and V. A. Darashkaite, Khim. Geterotsikl. Soedin., No. 9, 1224 (1972).
7. K. Dziewonski, L. Kwiecinski, and L. Sternbach, Bull. Int. Acad. Polon. Sci. Letters, Ser. A, 1934, p. 329, Krakau Univ., C, 1, 1704 (1935).
8. N. A. Amon, German Patent No. 2,495,048 (1950); Chem. Zentralblatt, 2, 1055 (1950).

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

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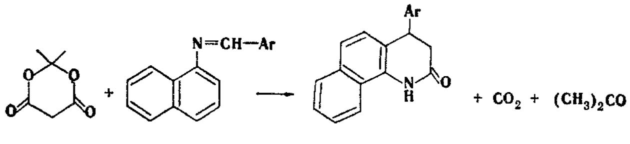
4-Aryl-2-oxo-1,2,3,4-tetrahydro-7,8-benzoquinolines were obtained by reaction of isopropylidene malonate with N-arylidene-1-naphthylamines. It is shown that the products are associated in the solid state by intermolecular hydrogen bonds. The IR and PMR spectral data are presented.

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 IIa-m IIIa-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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