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In the interaction of a series of 1-aryl-3-R-3-(2'-oxo-cycloalkyl)-1-propanones with o-aminophenol and o-phenylenediamine, depending on the structure of the reacting compounds, derivatives of 1,9a-tetra(tri)-methylene-9-oxa(aza)-4a-aza-1,2,4a,9a-tetrahydrofluorene are formed. The interaction of 1-(o-hydroxyphenyl)- and 1-(o-aminophenyl)-3-R-3-(2'-oxocycloalkyl)-1-propanones with o-aminophenol, o-phenylenediamine, ethanolamine, and ethylenediamine leads to the formation of new heterocyclic systems: 2,7-dioxa-5-azatricyclo[4.3.3.0<sup>1,5</sup>]dodecane, 7-oxa-2,5-diazatricyclo[4.3.3.0<sup>1,5</sup>]dodecane, and 2,5,7-triazatricyclo[4.3.3.0<sup>1,5</sup>]dodecane.

The interaction of nonsymm-1,5-diketones with 1,2- and 1,3-diamines and hydroxyamines, leading to closing of hydrogenated azolopyridine structures [1], can proceed along two pathways. In particular, when semicyclic 1,5-diketones — 1-aryl-3-R-3-(2'-oxocycloalkyl)-1-propanones — are used, the azole ring can in principle be closed in the direction both of the aroyl and of the alicyclic fragment of the diketone. The interaction with such nucleophiles of semicyclic diketones possessing a nucleophilic substituent in the ortho-position to the carbonyl group of the aroyl fragment can occur with the participation of this substituent and the formation of a more complex heterocyclic system; for the o-carboxy derivative such participation was demonstrated earlier [2].

In connection with this, we investigated the interaction of semicyclic 1,5-diketones Ia-l with certain 1,2-diamines and 2-hydroxyamines.

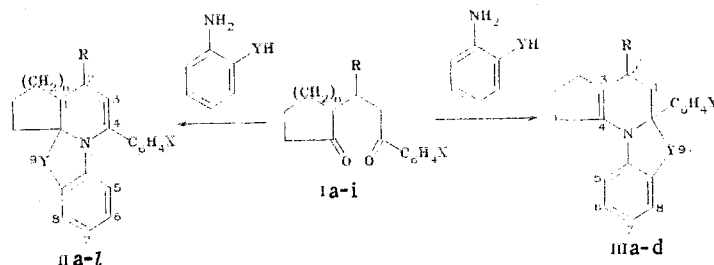
The diketones Ib-d, f-i, and k were produced for the first time, by the addition of cycloalkanones to arylideneacetophenones in the presence of NaOH (Ii), KOH (Ih), CH<sub>3</sub>ONa (If), diethylamine (Ic, d), or by the Michael thermal reaction [3] between the Mannich phase of the substituted acetophenone and the cycloalkanone (Ib, g, k). The diketone Il was produced by reduction of the diketone Ig with SnCl<sub>2</sub>.

In the IR spectra of the newly synthesized diketones, the absorption bands of the carbonyl group in the interval 1650-1730 cm<sup>-1</sup> are observed. In the spectra of the o-hydroxysubstituted diketones Ii, k there is also a broad absorption band of a chelated OH group in the region of 2800-3200 cm<sup>-1</sup>, and in the spectrum of the o-aminosubstituted diketone Il a doublet at 3360 and 3510 cm<sup>-1</sup> (NH<sub>2</sub>). According to the data of the mass spectra, the sizes of the molecular ions correspond to those calculated; fragmentation of the molecular ions is observed according to a scheme of retro-Michael cleavage.

The interaction of o-aminophenol and o-phenylenediamine with p-substituted diketones Ie, f, as well as with o-nitrosubstituted diketones Ig, h, including a cyclohexanone fragment, occurs regiospecifically with closing of the azole ring in the direction of an alicyclic fragment of the diketone and the formation of compounds II f-j. Earlier such a course of the reaction was noted for a semicyclic diketone unsubstituted in the ring with a cyclohexanone fragment [1].

In the case of the diketone with a cyclopentanone fragment (diketones Ia-d), however, both possible directions of heterocyclization can occur; the result depends on the nature of the substituent in the aroyl fragment of the diketone and on the nature of the nucleophile. The reaction of the diketone Ia, unsubstituted in the ring, with o-aminophenol proceeds analogously with closing of the diketone and the formation of compound IIa. On the contrary, the reaction

of this diketone with *o*-phenylenediamine leads to the formation of a mixture of compounds IIb and IIIa in a 3:7 ratio. The reaction of *p*-methoxy-substituted diketone Ic with *o*-aminophenol leads to a mixture of compounds IId and IIId in a 1:2 ratio, while the reaction of the same diketone with *o*-phenylenediamine gives virtually only compound IIId. In contrast to this, the interaction of the *p*-nitrosubstituted diketone Id with *o*-phenylenediamine leads to the formation only of compound IIe (the product of the reaction of the diketone Id with *o*-aminophenol could not be isolated, but, judging by the spectral data, it also has a structure of the type of II). Finally, the *p*-methoxysubstituted, 1,5-diketone Ib, which contains no substituent in the 3-position, reacts with *o*-aminophenol to form compound IIc and with *o*-phenylenediamine to form IIId.



I a  $n=1$ ,  $R=C_6H_5$ ,  $X=H$ ; b  $n=1$ ,  $R=H$ ,  $X=p-OCH_3$ ; c  $n=1$ ,  $R=C_6H_5$ ,  $X=p-OCH_3$ ; d  $n=1$ ,  $R=C_6H_5$ ,  $X=p-NO_2$ ; e  $n=2$ ,  $R=C_6H_5$ ,  $X=p-OCH_3$ ; f  $n=2$ ,  $R=C_6H_5$ ,  $X=p-NO_2$ ; g  $n=2$ ,  $R=H$ ,  $X=o-NO_2$ ; h  $n=2$ ,  $R=C_6H_5$ ,  $X=o-NO_2$ ; i  $n=2$ ,  $R=C_6H_5$ ,  $X=o-OH$ . II a  $n=1$ ,  $R=C_6H_5$ ,  $X=H$ ,  $Y=O$ ; b  $n=1$ ,  $R=C_6H_5$ ,  $X=H$ ,  $Y=NH$ ; c  $n=1$ ,  $R=H$ ,  $X=n-OCH_3$ ,  $Y=O$ ; d  $n=1$ ,  $R=C_6H_5$ ,  $X=p-OCH_3$ ,  $Y=O$ ; e  $n=1$ ,  $R=C_6H_5$ ,  $X=p-NO_2$ ,  $Y=NH$ ; f  $n=2$ ,  $R=C_6H_5$ ,  $X=p-OCH_3$ ,  $Y=O$ ; g  $n=2$ ,  $R=C_6H_5$ ,  $X=p-OCH_3$ ,  $Y=NH$ ; h  $n=2$ ,  $R=C_6H_5$ ,  $X=p-NO_2$ ,  $Y=NH$ ; i  $n=2$ ,  $R=H$ ,  $X=o-NO_2$ ,  $Y=NH$ ; j  $n=2$ ,  $R=C_6H_5$ ,  $X=o-NO_2$ ,  $Y=NH$ ; k  $n=2$ ,  $R=C_6H_5$ ,  $X=o-OH$ ,  $Y=O$ ; l  $n=2$ ,  $R=C_6H_5$ ,  $X=o-OH$ ,  $Y=NH$ ; III a  $R=C_6H_5$ ,  $X=H$ ,  $Y=NH$ ; b  $R=H$ ,  $X=p-OCH_3$ ,  $Y=NH$ ; c  $R=C_6H_5$ ,  $X=p-OCH_3$ ,  $Y=O$ ; d  $R=C_6H_5$ ,  $X=p-OCH_3$ ,  $Y=NH$

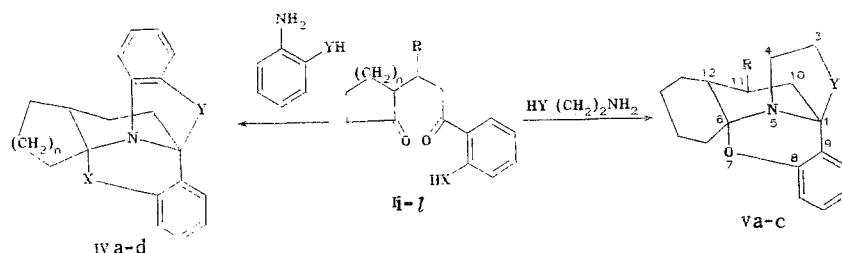
Mixtures of the structural isomers IIb-IIIa and IId-IIId could not be separated; the possibility remains that they are equilibrium mixtures, and the interconversion of the isomers occurs with opening and subsequent reclosing of the azole ring through an intermediate dihydropyridine compound; earlier it was shown that analogous derivatives of azolinotetrahydropyridines can react as derivatives of 1,4-dihydropyridine [1].

The facts cited permit us to note two tendencies pertaining to 1,5-diketones with a cyclopentanone fragment: in the first place, in their interaction with *o*-phenylenediamine, a more appreciable tendency for closing of the azole ring in the direction of the aroyl fragment of the diketone (i.e., for the formation of compounds III) is observed than in the interaction with *o*-aminophenol. This is evidently explained by the fact that compounds II with  $Y=NH$  are somewhat less stable than with  $Y=O$ , since in compounds II the  $Y$  group experiences shielding stress, while the conformational energy of the  $NHR$  group is somewhat higher than for  $OR$ . In the second place, the introduction of donor groups into the aromatic ring of the diketone increases the tendency for the formation of compounds III, whereas the introduction of an acceptor group directs the reaction toward the formation of compounds II.

As for diketones with a cyclohexanone fragment, they react with the formation only of compounds II most likely because the latter are more stable than the alternative structures at  $n=2$ , since compounds II contain a conjugated  $C=C$  bond in the absence of shielding stress.

Interaction of bifunctional nucleophiles with diketones II-7, containing nucleophilic substituents  $OH$  and  $NH_2$  in the ortho-position to the carbonyl group, proceeds in most cases with their participation. The conversions that occur can be represented in such a way that the azole ring is closed in the direction of the aroyl fragment of the diketone; the ortho-substituent is then added at the  $C=C$  bond of an intermediate compound of type III. As a result, derivatives of new heterocyclic systems are formed: 2,7-dioxa-5-azatricyclo[4.3.3.0<sup>1,5</sup>]-dodecane (IVb, Va, b), 7-oxa-2,5-diazatricyclo[4.3.3.0<sup>1,5</sup>]dodecane (IVa, c, Vc), and 2,5,7-triazatricyclo[4.3.3.0<sup>1,5</sup>]dodecane (IVd). We should note that in the previously described [2] interaction of the *o*-carboxysubstituted semicyclic 1,5-diketone with *o*-aminophenol and *o*-phenylenediamine there is an alternative scheme of cyclization, i.e., the formation of an intermediate product of type II is formally assumed. An exception to the scheme described above is the interaction of the diketone IIi with *o*-aminophenol and *o*-phenylenediamine: in these

cases complete cyclization does not occur, and compounds IIk,l are formed. The cause of the difference in the behavior of the diketone II and of the other 1,5-diketones with nucleophilic o-substitutions, in particular, the diketone IIj, from which it differs only in a phenyl substituent in the 3-position, is still unclear: an examination of the models shows that the latter does not prevent the formation of structure IV, all the more in that in the interaction of the diketone II with ethanolamine and ethylenediamine there is a complete cyclization, and compounds Vb and c are formed.



IIj n=1, R=H, X=O; k n=2, R=H, X=O; l n=2, R=H, X=NH; IV a n=1, X=O, Y=NH; b n=2, X=Y=O; c n=2, X=O, Y=NH; d n=2, X=Y=NH; V a R=H, Y=O; b R=C<sub>6</sub>H<sub>5</sub>, Y=O; c R=C<sub>6</sub>H<sub>5</sub>, Y=NH

In the IR spectra of compounds II (Table 1), an absorption band of the C=C bond conjugated with the aromatic ring is observed in the region of 1630-1645 cm<sup>-1</sup>, whereas in the spectra of compounds III an absorption band of an unconjugated bond is observed in the region of 1660-1675 cm<sup>-1</sup>. In the spectra of compounds IV and V there is no absorption of the C=C bonds. For compounds II and III when Y = O, as well as compounds IV and V, there is no absorption of the OH group. For compounds IIk,l (X = o-OH), there is no absorption of the OH group.

In the PMR spectra of compounds II, the signals (1H) of the vinyl protons in the region of 5.0-5.6 ppm, as well as doublets, usually in the region of 5.6-5.8 ppm, which belong to the aromatic protons 5-H, are characteristic: a strong-field shift of the signal of one aromatic proton in analogous structures was noted earlier [1]. In the presence of an acceptor o-substituent in the shielding ring (IIIi, j), the signal is shifted into an even stronger field - to 5.3 ppm, while in the presence of a donor o-substituent (IIk) it is shifted into a weaker field, to 6.0 ppm. In the spectra of compounds III-V these signals are absent. In mixtures of isomeric compounds (IIb + IIIa and IId + IIIc) the relative content of the isomer II is determined according to the intensity of these signals. We might also mention the presence of two signals of the OCH<sub>3</sub> group for a mixture of IId + IIIc; the relative intensity of the weaker-field signal corresponds to the content of the isomer IId.

In the <sup>13</sup>C NMR spectra of compounds IIl, IVc, and Vc there is a signal in the region of 80 ppm (82.2 ppm for IIl, 79.2 ppm for IVc, 79.6 ppm for Vc); it belongs to C(9a) for IIl and to C(1) for IVc and Vc; this value of the chemical shift is characteristic of the signal of the angular carbon atom (C(8a)) in the spectra of derivatives of hydrogenated 8a-aryl-1-aza-indolizine [4]. In the spectra of compounds IVc and Vc there is also a signal in the region of 90 ppm (90.1 for IVc and 93.7 ppm for Vc); it belongs to the angular atoms C(6) bonded to nitrogen and oxygen atoms; in the spectrum of compound IIl the signal in this region is absent.

Compounds IV and V, when heated with aqueous solutions of mineral acids for several hours, break down to the original 1,5-diketones and amines.

#### EXPERIMENTAL

The IR spectra of the synthesized compounds were recorded on a Specord IR-75 spectrometer in liquid petrolatum and chloroform. The NMR spectra were recorded on a Bruker HX-90E instrument; the PMR spectra in deuteriochloroform, the <sup>13</sup>C NMR spectra in deuterodimethyl sulfoxide; the internal standard was TMS. The course of the reactions and the purity of the compounds obtained were monitored by thin-layer chromatography on plates of Silufol; solvent system hexane-ethyl acetate (from 8:1 to 1:1).

1-(p-Methoxyphenyl)-3-(2'-oxocyclopentyl)-1-propanone (Ib) and 1-(o-Hydroxyphenyl)-3-(2'-oxocyclohexyl)-1-propanone (Ik). A mixture of 0.05 mole of the Mannich base of the corresponding substituted acetophenone and 0.15 mole of the corresponding cyclanone (130-150°C)

TABLE 1. Data of the IR and PMR Spectra of Compounds II-V

| Compound  | IR spectrum, $\text{cm}^{-1}$             | PMR spectrum, ppm (SSCC, Hz), intensity (assignment)   |
|-----------|---|--|
| IIa       | 1643                                      | 5,81 d (7), 1H (5-H); 5,35 d (3), 1H (3-H)   |
| IIc       | 1645                                      | 5,70 d (7), 1H (5-H); 5,21 qu, 1H (3-H); 3,84 s, 3H (OCH <sub>3</sub> )  |
| IIe       | 1631, 3376                                | 5,63 d (7), 1H (5-H); 5,53 d (3), 1H (3-H); 4,00 s, 1H (9-H); 3,17 qu (10,5; 3), 1H (2-H)  |
| IIf       | 1635                                      | 5,75 d (8), 1H (5-H); 5,28 d (3), 1H (3-H); 3,80 s, 3H (OCH <sub>3</sub> )   |
| IIg       | 1640, 3392                                | 5,70 d (7), 1H (5-H); 5,16 d (3), 1H (3-H); 4,20 a.s., 1H (9-H); 3,82 s, 3H (OCH <sub>3</sub> ); 3,60 qu 1H (2-H)                                |
| IIh       | 1640, 3403                                | 5,63 (7), 1H (5-H); 5,57 d (3), 1H (3-H); 4,28 a.s., 1H (9-H); 3,70 qu (10; 3), 1H (2-H)   |
| IIi       | 1645, 3400                                | 5,29 d (8), 1H (5-H); 5,09 qu, 1H (3-H); 4,15 a.s., 1H (9-H)   |
| IIj       | 1645, 3410                                | 5,34 d (8), 1H (5-H); 5,00 d (3), 1H (3-H); 4,18 a.s., 1H (9-H); 3,70 qu (11; 3), 1H (2-H)   |
| IIk       | 1640, 3300-3400                           | 7,9 s, 1H (OH); 6,00 d (7), 1H (5-H); 5,31 d (2), 1H (3-H); 3,70 qu (10,5; 2), 1H (2-H)  |
| IIl       | 1643, 3100-3200, 3368                     | —  |
| IIlb      | 1672, 3390                                | 3,94 a.s., 1H (9-H); 3,76 s, 3H (OCH <sub>3</sub> );   |
| IIId      | 1660, 3390                                | 3,90 a.s., 1H (9-H); 3,79 s, 3H (OCH <sub>3</sub> )  |
| IIb+IIla  | 1640, 1668, 3380                          | 5,69 d (7), 0,3H (IIb, 5-H); 5,31 d (3), 0,3H (IIb, 3-H); 3,98 a.s., 1H (9-H)  |
| IIId+IIlc | 1633, 1670                                | 5,82 d (7), 0,33H (IIId, 5-H); 5,19 d (3), 0,33H (IIId, 3-H); 3,82 s, 1H (IIId, OCH <sub>3</sub> ); 3,79 s, 2H (IIlc, OCH <sub>3</sub> )         |
| IVa       | 3400                                      | 7,30-6,56 m 8H (arom); 4,18 a.s., 1H (2-H)   |
| IVb       | Absence of bands of the C=C and OH groups | 7,19-6,56 m, 8H (arom)   |
| IVc       | 3400                                      | 7,22-6,57 m, 8H (arom); 4,21 a.s., 1H (2-H)  |
| IVd       | 3430                                      | 7,22-6,56 m, 8H (arom); 4,28 a.s., 2H (2-H, 7-H)   |
| Va        | Absence of bands of the C=C and OH groups | 7,35-6,80 m, 4H (arom); 4,12 qu (10; 9), 1H (3-H); 3,87 t, d (10; 10; 4), 1H (3-H'); 3,29 t, d (10; 10; 4), 1H (4-H); 2,87 qu (10; 9), 1H (4-H') |
| Vb        | Absence of bands of the C=C and OH groups | 7,32-6,76 m, 8H (arom); 4,09 qu (9; 8), 1H (3-H); 3,80 t, d, (9; 9; 4), 1H (3-H'); 3,22 t, d (9; 9; 4), 1H (4-H); 2,82 qu (9; 8), 1H (4-H')      |
| Vc        | 3400                                      | 7,40-6,75 m, 8H (arom); 3,26-2,67 m, 4H (3-H, 4-H)   |

was boiled until no appreciable amount of the dimethylamine product was evolved (30 min in the case of Ib, 4 h for Ik). The excess cyclanone was distilled off at reduced pressure, and the residue crystallized.

1-(o-Nitrophenyl)-3-(2'-oxocyclohexyl)-1-propanone (Ig). A mixture of 0.01 mole of the hydrochloride of the Mannich base of o-nitroacetophenone, 0.015 mole of dimethylaniline, and 0.05 mole of cyclohexanone was heated with mixing in a stream of argon at 150°C until a homogeneous solution was obtained, cooled, acidified with 10% HCl, extracted with ether, the extract washed with water, dried, the solvent evaporated, the residue triturated with ether, and the diketone Ig filtered off.

1-(p-Methoxyphenyl)-3-phenyl-3-(2'-oxocyclopentyl)-1-propanone (Ic) and 1-(p-Nitrophenyl)-3-phenyl-3-(2'-oxocyclopentyl)-1-propanone (Id). A mixture of 0.1 mole of the corresponding chalcone, 0.3 mole of cyclopentanone, and 6 ml of diethylamine was allowed to stand at room temperature (in the case of Id several times the mixture was heated to 60°C for brief periods). After seven days in the case of Ic or 10 days in the case of Id, the precipitated crystalline reaction product was filtered off and washed with ethanol. When the mother liquor was allowed to stand for three days, a supplementary amount of the diketone precipitated.

1-(p-Nitrophenyl)-3-phenyl-3-(2'-oxocyclohexyl)-1-propanone (If). We dissolved 0.7 g (0.03 mole) of sodium in 40 ml of methanol and added 2.5 g (0.01 mole) of 4'-nitrochalcone and 3 ml (0.03 mole) cyclohexanone. The mixture was mixed vigorously until the chalcone dissolved completely (1 h) and left at room temperature for 18 h. The diketone If was filtered off, washed with ethanol and with water.

1-(o-Hydroxyphenyl)-3-phenyl-3-(2'-oxocyclohexyl)-1-propanone (Ii). To a solution of 2.3 g (0.01 mole) of the 2-hydroxychalcone and 4 ml (0.04 mole) cyclohexanone in 25 ml of ethanol we added 2 ml of a 30% solution of NaOH. After 24 h of standing at room temperature, the mixture was acidified with cooling with 5% HCl; the diketone Ii was filtered off, washed with ethanol, and with water.

TABLE 2. Characteristics of the Synthesized Compounds

| Compound  | mp, °C               | Found, % |     |      | Gross formula   | Calculated, % |     |      | Yield, % |
|-----------|----------------------|----------|-----|------|---|---------------|-----|------|----------|
|           |                      | C        | H   | N    |   | C             | H   | N    |          |
| Ib        | 75-76 <sup>a</sup>   | 73.4     | 7.5 | —    | C <sub>15</sub> H <sub>18</sub> O <sub>3</sub>                | 73.2          | 7.3 | —    | 82       |
| Ic        | 102-103              | 78.3     | 6.7 | —    | C <sub>21</sub> H <sub>22</sub> O <sub>3</sub>                | 78.5          | 6.7 | —    | 73       |
| Id        | 125-126              | 71.7     | 5.7 | 4.4  | C <sub>20</sub> H <sub>19</sub> NO <sub>4</sub>               | 71.7          | 5.6 | 4.2  | 69       |
| If        | 137-139              | 71.6     | 6.2 | 4.1  | C <sub>21</sub> H <sub>21</sub> NO <sub>4</sub>               | 71.8          | 5.9 | 4.0  | 66       |
| Ig        | 78-79 <sup>a</sup>   | 65.4     | 6.3 | 5.3  | C <sub>15</sub> H <sub>17</sub> NO <sub>4</sub>               | 65.5          | 6.2 | 5.1  | 74       |
| Ih        | 158-159              | 71.9     | 6.1 | 4.0  | C <sub>21</sub> H <sub>21</sub> NO <sub>4</sub>               | 71.8          | 5.9 | 4.0  | 92       |
| Ii        | 124-125 <sup>b</sup> | 78.2     | 6.5 | —    | C <sub>21</sub> H <sub>22</sub> O <sub>3</sub>                | 78.2          | 6.8 | —    | 60       |
| Ik        | 91-92 <sup>b</sup>   | 73.7     | 7.7 | —    | C <sub>15</sub> H <sub>18</sub> O <sub>3</sub>                | 73.2          | 7.3 | —    | 55       |
| Il        | 102-103 <sup>c</sup> | 73.2     | 7.9 | 5.5  | C <sub>15</sub> H <sub>19</sub> NO <sub>2</sub>               | 73.5          | 7.8 | 5.7  | 56       |
| Ila       | 162-164              | 86.0     | 6.4 | 4.0  | C <sub>26</sub> H <sub>23</sub> NO                            | 85.5          | 6.3 | 3.9  | 42       |
| Ilc       | 120-122              | 79.1     | 6.8 | 5.1  | C <sub>21</sub> H <sub>21</sub> NO <sub>2</sub>               | 79.0          | 6.7 | 4.5  | 22       |
| Ile       | 166-167              | 76.1     | 5.8 | 10.1 | C <sub>26</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub> | 76.5          | 5.4 | 10.2 | 45       |
| Ilf       | 181-182 <sup>d</sup> | 82.2     | 6.6 | 3.4  | C <sub>28</sub> H <sub>27</sub> NO <sub>2</sub>               | 82.2          | 6.6 | 3.4  | 80       |
| Ilg       | 197-200 <sup>c</sup> | 82.3     | 6.5 | 7.3  | C <sub>28</sub> H <sub>28</sub> N <sub>2</sub> O              | 82.4          | 6.8 | 6.8  | 80       |
| Ilh       | 232-234 <sup>c</sup> | 76.8     | 6.2 | 10.1 | C <sub>27</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub> | 76.7          | 5.9 | 10.0 | 57       |
| Ili       | 174-175              | 72.1     | 5.8 | 11.7 | C <sub>21</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub> | 72.6          | 6.0 | 12.1 | 35       |
| Ilj       | 203-204              | 76.6     | 6.1 | 10.2 | C <sub>27</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub> | 76.6          | 5.9 | 9.9  | 41       |
| Ilk       | 196-197              | 81.9     | 5.9 | 3.7  | C <sub>27</sub> H <sub>25</sub> NO <sub>2</sub>               | 82.0          | 6.3 | 3.5  | 31       |
| Ilj       | 236-237              | 81.8     | 6.8 | 7.1  | C <sub>27</sub> H <sub>26</sub> N <sub>2</sub> O              | 82.2          | 6.6 | 7.1  | 73       |
| IIb       | 132-133              | 79.2     | 7.1 | 8.9  | C <sub>21</sub> H <sub>22</sub> N <sub>2</sub> O              | 79.2          | 6.9 | 8.8  | 35       |
| IIId      | 137-138 <sup>b</sup> | 81.9     | 6.7 | 7.2  | C <sub>27</sub> H <sub>26</sub> N <sub>2</sub> O              | 82.4          | 6.4 | 7.1  | 74       |
| IIb+IIla  | 134-137 <sup>c</sup> | 85.4     | 6.9 | 8.0  | C <sub>26</sub> H <sub>24</sub> N <sub>2</sub>                | 85.7          | 6.6 | 7.7  | 58       |
| IIId+IIlc | 123-127              | 82.2     | 6.5 | 3.4  | C <sub>27</sub> H <sub>25</sub> NO <sub>2</sub>               | 82.2          | 6.3 | 3.5  | 76       |
| IVa       | 133-135 <sup>e</sup> | 79.4     | 6.8 | 8.9  | C <sub>20</sub> H <sub>20</sub> N <sub>2</sub> O              | 78.9          | 6.6 | 9.2  | 35       |
| IVb       | 123-126              | 79.2     | 6.4 | 4.5  | C <sub>21</sub> H <sub>21</sub> NO <sub>2</sub>               | 79.0          | 6.6 | 4.4  | 28       |
| IVc       | 127-130              | 78.8     | 6.9 | 8.4  | C <sub>21</sub> H <sub>22</sub> N <sub>2</sub> O              | 79.2          | 6.9 | 8.8  | 20       |
| IVd       | 136-138              | 79.7     | 7.5 | 13.0 | C <sub>21</sub> H <sub>23</sub> N <sub>3</sub>                | 79.5          | 7.3 | 13.2 | 40       |
| Va        | 134-136              | 75.8     | 7.8 | 5.2  | C <sub>17</sub> H <sub>21</sub> NO <sub>2</sub>               | 75.3          | 7.7 | 5.2  | 51       |
| Vb        | 177-178              | 79.6     | 7.3 | 4.1  | C <sub>23</sub> H <sub>25</sub> NO <sub>2</sub>               | 79.5          | 7.2 | 4.0  | 83       |
| Vc        | 167-168              | 79.3     | 7.6 | 8.3  | C <sub>23</sub> H <sub>26</sub> N <sub>2</sub> O              | 79.8          | 7.5 | 8.1  | 46       |

<sup>a</sup>From petroleum ether. <sup>b</sup>From heptane. <sup>c</sup>From a mixture of ethanol and dimethylformamide. <sup>d</sup>From acetone. <sup>e</sup>From methanol. The remaining compounds were recrystallized from ethanol.

1-(o-Nitrophenyl)-3-phenyl-3-(2'-oxocyclohexyl)-1-propanone (Ih). To a suspension of 2.5 g (0.01 mole) 2'-nitrochalcone in 50 ml of ethanol we added 3 ml (0.03 mole) of cyclohexanone and 2 ml of a 30% solution of KOH. The mixture was mixed vigorously; after 30 min the diketone Ih was filtered off, and washed with ethanol and with water.

1-(o-Aminophenyl)-3-(2'-oxocyclohexyl)-1-propanone (Il). Into a solution of 7.6 g SnCl<sub>2</sub> in 15 ml conc. HCl we introduced 2 g (0.007 mole) of the diketone Ig, mixed the mixture until a transparent solution was obtained, poured out into a 30% NaOH solution, extracted with ether the extract washed with water, dried, the ether evaporated, the residue covered with 15 ml of ethanol, and the diketone Il filtered off.

Interaction of 1,5-Diketones with o-Aminophenol and o-Phenylenediamine. A solution of 0.01 mole of the diketone, 0.01-0.012 mole of the amine, 50 mg p-toluenesulfonic acid in 50 ml xylene was boiled with a Dean-Stark trap until the liberation of water ceased (3-8 h). According to the data of thin-layer chromatography, the reaction mixture contains only the corresponding reaction product, an excess of the amine, and sometimes small amounts of the unreacted diketone. Xylene was distilled off at reduced pressure, the residue treated with 15-20 ml of ethanol, and after several hours the reaction product was filtered off and washed with ethanol.

Interaction of 1,5-Diketones with Ethanolamine and Ethylenediamine. To a solution of 0.01 mole of the diketone in 20-30 ml of ethanol we added 0.02 mole of the amine; the mixture was left at room temperature and the reaction product was filtered after three days. The properties and yields of the synthesized compounds are cited in Table 2.

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