

## Photochemistry of 3,7-Bis(arylmethylene)bicyclo[3.3.1]nonane Derivatives

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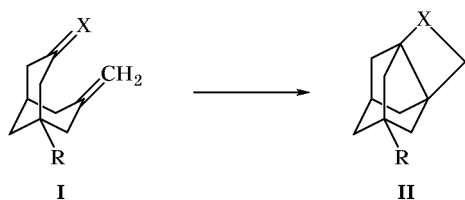
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**Abstract**—UV irradiation of *trans-trans*-3,7-bis(arylmethylene)bicyclo[3.3.1]nonane-2,6-diones leads to their complete or partial transformation into the corresponding *cis-cis* isomers. Irradiation of *trans-trans*-3,7-bis(arylmethylene)bicyclo[3.3.1]nonane-2,6-diol in ether in the presence of CuCl results in intramolecular cyclization involving the exocyclic double bonds and one benzene ring to give *exo-7,endo-10*-dihydroxy-2-phenyl-3,4-benzotetracyclo[4.3.3.1<sup>8,11</sup>.0<sup>1,6</sup>]tridecane.

Interest in the photochemistry of olefinic systems is explained by the fact that electronically excited molecules are capable of undergoing transformations which either cannot occur or are strongly hindered in the ground state. Many strained structures with three- and four-membered rings incorporated into a polycyclic system, which are difficult to obtain by other methods, are formed just in photochemical processes. Intramolecular cycloaddition leading to polycyclic systems becomes possible when an olefinic substrate has an appropriate steric structure ensuring ready formation of a conformer with appropriate distance between the double bonds and their mutual arrangement. Otherwise, the photochemical process will lead to isomerization or polymerization through intermolecular reaction [1].

In the series of bicyclo[3.3.1]nonane derivatives **I** having a *double chair* conformation the exocyclic double bonds in positions 3 and 7 are almost parallel; therefore, photochemical reactions as a rule follow the intramolecular cyclization path with formation of a cyclobutane ring (compounds **II**) [2–4]:



X = CH<sub>2</sub>, O; R = H, CH<sub>2</sub>OH, CH<sub>3</sub>.

In fact, intramolecular photosensitized cycloaddition is a stepwise process where the first step is

$\pi, \pi^*$ -excitation of one of the double bonds [5]. It is important that the reaction can be initiated by unfiltered light of a mercury lamp. The rate of the reaction increases in the presence of CuCl, and the products are formed in nearly quantitative yields (92–97%) [4].

In the present work we studied the behavior of diketones **IIIa–III d** and alcohols **Va–Vd** in photochemical reactions. Intramolecular photocyclization at the C=C bonds in ketone **III** seems to be improbable: According to our data, the structure of compound **IIIa**

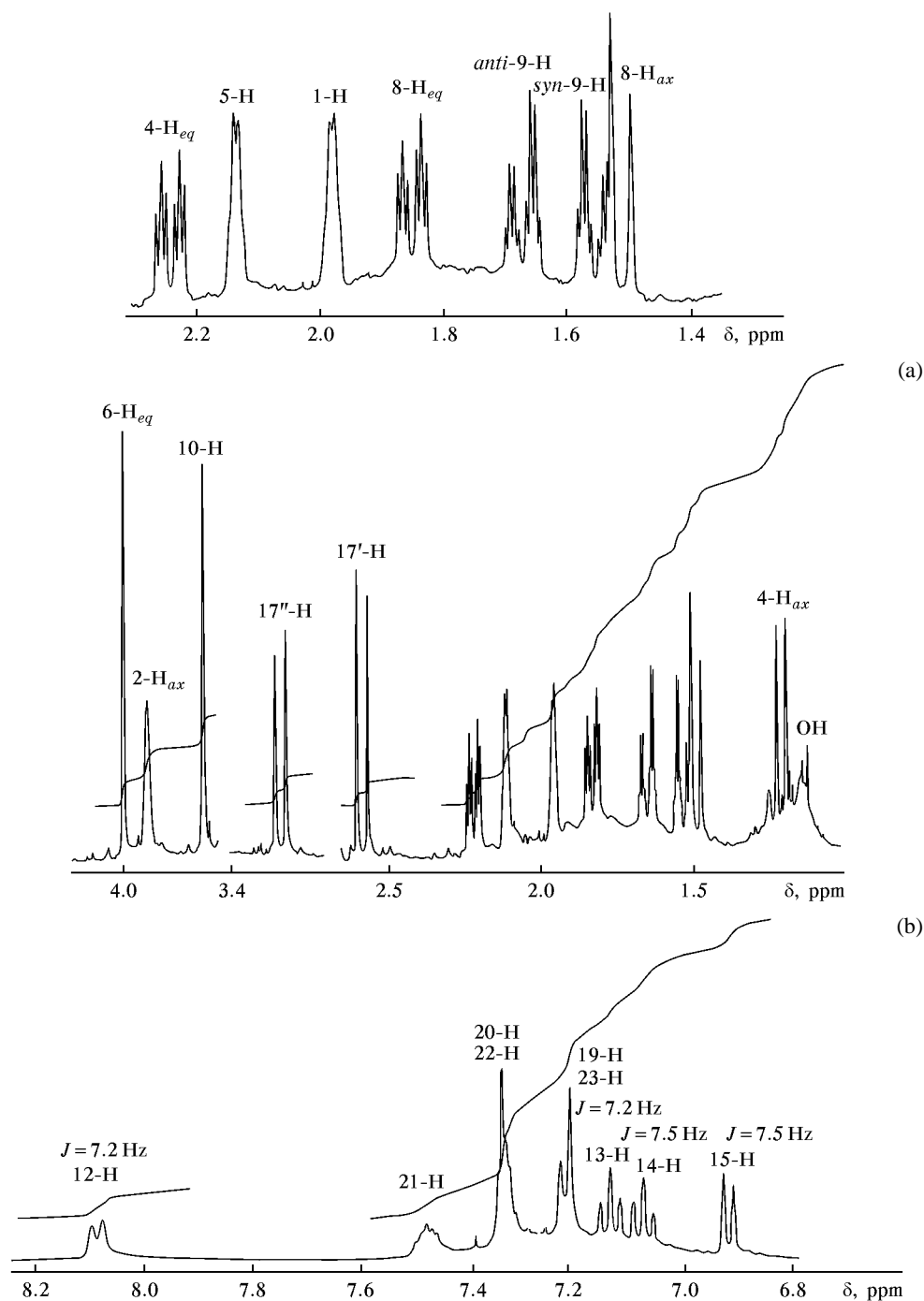
**Table 1.** UV spectra of ketones **III**, alcohols **V**, and products of photochemical reactions

Initial compound	$\lambda_{\max}$ , nm	Product	$\lambda_{\max}$ , nm
<b>IIIa</b>	207, 225, 282	<b>IVa</b>	210, 220 sh
<b>IIIb</b>	208 sh, 229, 325	<b>IVb<sup>a</sup></b>	210 sh, 227, 275 w
<b>IIIc</b>	207, 221, 308	<b>IVc<sup>b</sup></b>	206, 226, 315
<b>III d</b>	213, 245 sh, 360	–	–
<b>Va</b>	209, 247 sh, 270	<b>VI</b>	204, 255 w.sh
<b>Vb</b>	211 sh, 222 sh, 258	<b>VIb<sup>a</sup></b>	211 sh, 228, 280, 285 sh
<b>Vc</b>	208, 225, 258	<b>VIc<sup>a</sup></b>	212, 220
<b>Vd</b>	256 sh, 265, 285 sh	<b>VI d<sup>a</sup></b>	217, 275 w.sh

<sup>a</sup> The spectra were measured after UV irradiation and removal of the solvent.

<sup>b</sup> Yield 30% (according to the <sup>1</sup>H NMR data).

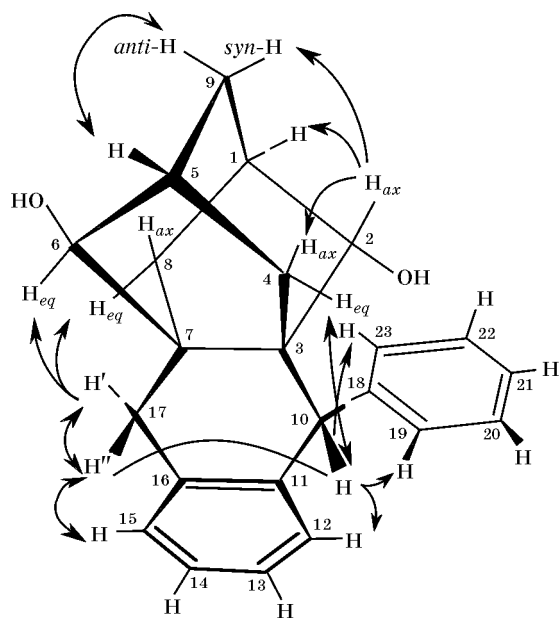




**Fig. 1.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of photocyclization product **VI**: (a) protons at the skeletal carbon atoms and (b) aromatic fragment.

After irradiation of a solution of diketone **IIIa** in ethanol for 20 h, the isolated oily product was a mixture of at least five compounds. By chromatography on silica gel we isolated 3 enriched fractions which showed in the IR spectra absorption bands belonging to hydroxy groups ( $3500\text{--}3400\text{ cm}^{-1}$ ) and uncon-

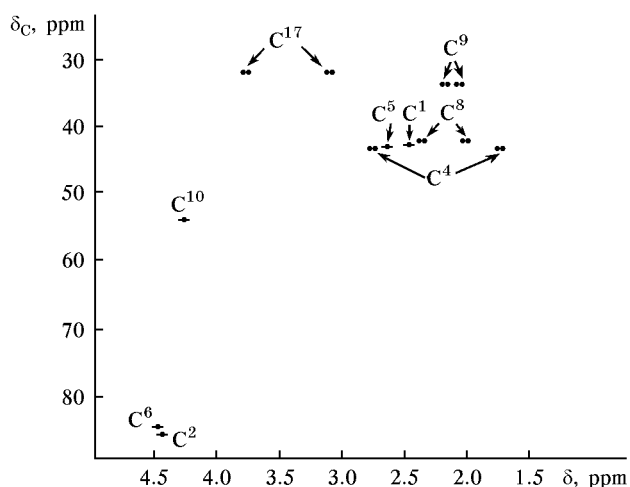
jugated carbonyl groups ( $1740$ ,  $1735$ , and  $1725\text{ cm}^{-1}$ ). The  $\text{ArCH=}$  signals almost disappeared from the  $^1\text{H}$  NMR spectra, whereas new signals appeared at  $\delta$  3 to 4.2 ppm. We can conclude that the photolysis is sensitized by  $\text{C=O}$  groups and that it involves  $\text{C=C}$  bonds and the alcohol taken as solvent [9]. Changes



**Fig. 2.** Structure of product **VI** with atom numbering; some results of the NOE experiment are also shown.

in the UV spectra of the reaction mixtures obtained by irradiation of compounds **Va–Vd** in ether are typical of intramolecular photochemical cyclizations with participation of double bonds [1] (Table 1).

The photolysis of compound **Va** was carried out on a preparative scale. A solution of **Va** in dry ether was irradiated for 22 h in the presence of a catalytic amount of CuCl in an inert atmosphere. We observed disappearance of the initial compound and formation of several products (see Experimental). By column chromatography on silica gel (benzene–ethyl acetate,



**Fig. 3.**  $^1\text{H}$ – $^{13}\text{C}$  heteronuclear correlation spectrum of compound **VI**.

2:1) we isolated a product ( $R_f$  0.62) which showed in the IR spectrum no C=C absorption ( $1658\text{ cm}^{-1}$  for **Va**). The mass spectrum of this product contained the molecular ion peak  $[M^+]$  with  $m/z$  332 (35%); the base peak was  $[M-\text{H}_2\text{O}]^+$ ,  $m/z$  314 (100%). The presence of ion peaks with  $m/z$  296 ( $[314-\text{H}_2\text{O}]$ , 26%) and 255 ( $[M-\text{Ph}]$ , 46%) indicates that the molecule contains two hydroxy groups and a phenyl group (for the other ion peaks, see Experimental). In the  $^{13}\text{C}$  NMR spectrum signals from 23 carbon atoms were present; this means that the molecule has no symmetry elements. In addition, signals from three quaternary aromatic carbon atoms were observed at  $\delta_{\text{C}}$  141.38, 137.73, and 138.50 ppm. These data led us to presume that the photochemical cyclization involves one phenyl ring in a way similar to the known photochemical transformation of styrene into phenanthrene [10].

In the aromatic region of the  $^1\text{H}$  NMR spectrum ( $\delta$  6–8 ppm) we observed two doublet and two triplet signals with an intensity ratio of 1:1:1:1. This pattern obviously corresponds to an *ortho*-phenylene group. Also, there were three multiplet signals at  $\delta$  7.2–7.5 ppm with an intensity ratio of 2:2:1, which are typical of a monosubstituted benzene ring (Fig. 1b). A broadened upfield signal at  $\delta$  1.12–1.19 ppm (Fig. 1a) was assigned to hydroxy proton. The latter disappears on treatment with  $\text{D}_2\text{O}$ , and at low temperature ( $-35^\circ\text{C}$ , sample temperature  $-50^\circ\text{C}$ ) it is split into two broadened singlets with  $\delta$  1.16 and 1.19 ppm. These findings indicate different orientations (*exo* and *endo*) of the hydroxy groups in molecule **VI**. Table 2 contains  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts and  $^1\text{H}$ – $^1\text{H}$  coupling constants of product **VI**. The phenyl group gives signals in the  $^{13}\text{C}$  NMR spectrum at  $\delta$  138.50, 128.54, 126.67, 126.86, 126.31, and 125.37 ppm ( $\text{C}^{18}$ – $\text{C}^{23}$ , Fig. 2). Signals of the other aromatic carbon atoms are given in Table 2.

Taking into account the above data, the isolated product can be assigned the structure of either *exo*-7,*endo*-10-dihydroxy-2-phenyl-3,4-benzotetracyclo-[4.3.3.1<sup>8,11</sup>.0<sup>1,6</sup>]tridecane (**VI**) or its *endo*-7,*exo*-10-dihydroxy isomer **VII** [6] (Scheme 2). The choice of structure **VI** was made on the basis of NOE DIF experiments (Fig. 2). Signals in the  $^{13}\text{C}$  NMR spectrum were assigned using APT sequence, calculations by the ACD Lab.  $^{13}\text{C}$  program, and  $^1\text{H}$ – $^{13}\text{C}$  heteronuclear correlation technique (Fig. 3). The  $^1\text{H}$  signals were assigned by the double resonance technique with selective irradiation of 1-H, 5-H, 4- $\text{H}_{\text{eq}}$ , 8- $\text{H}_{\text{eq}}$ , *anti*-9-H, and 17''-H. In the latter case we observed only transformation of the 17'-H doublet at  $\delta$  2.56 ppm

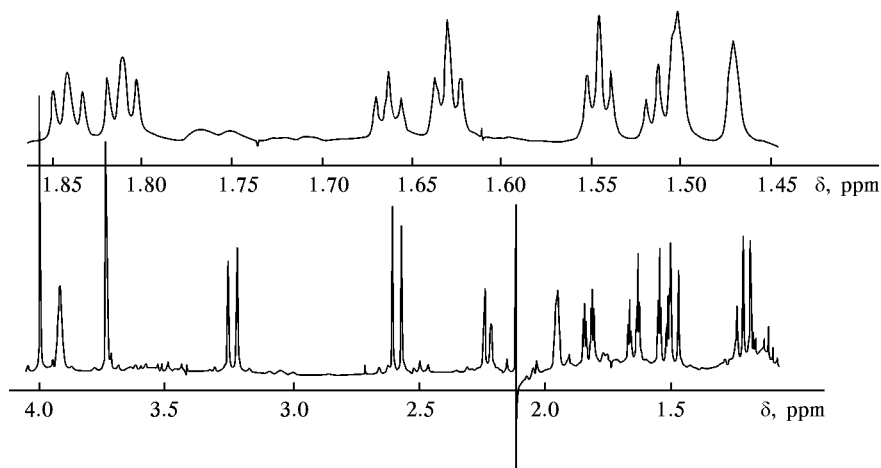


Fig. 4. Double resonance  $^1\text{H}$  NMR spectrum of compound VI with irradiation of the 5-H proton.

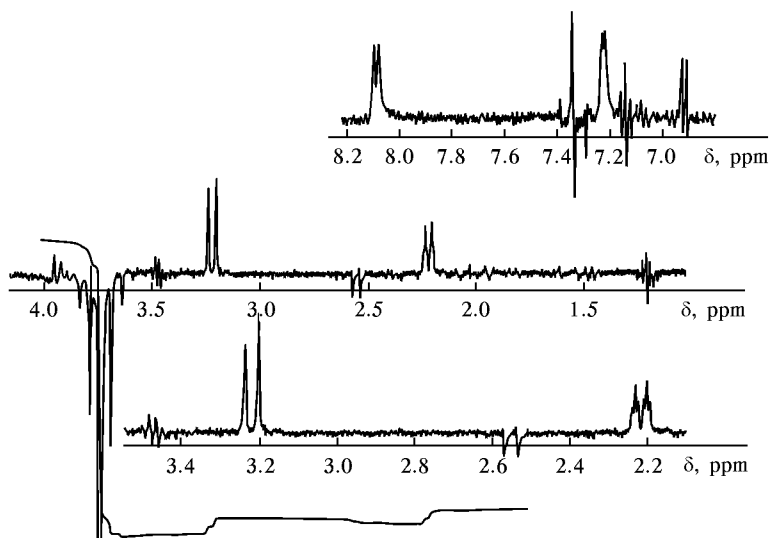


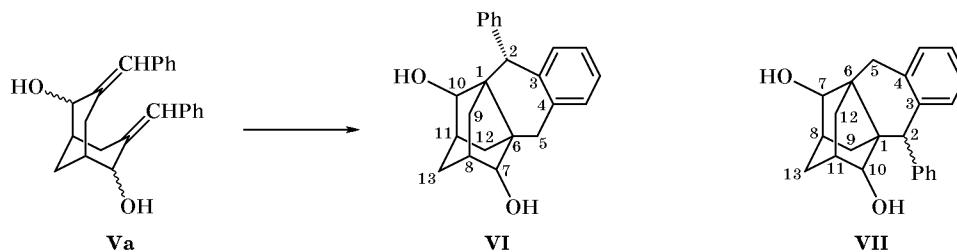
Fig. 5.  $^1\text{H}$  NOE spectrum of compound VI with irradiation of the 10-H proton.

into a singlet, while the other proton signals remained unchanged. On irradiation of 1-H ( $\delta$  1.95 ppm) the following responses were obtained: the 8- $\text{H}_{eq}$  signal (doublet of triplets) was converted into a doublet of doublets, and the *anti*-9-H and *syn*-9-H signals (doublets of quartets) were converted into doublets of triplets. Likewise, irradiation of 5-H ( $\delta$  2.08 ppm; Fig. 4) resulted in transformation of the 4- $\text{H}_{eq}$  signal from doublet of triplets to doublet of doublets, and of the *anti*-9-H and *syn*-9-H signals, to doublets of triplets. Irradiation of 4- $\text{H}_{eq}$  ( $\delta$  2.22 ppm) changed the 5-H signal from broadened doublet to a broadened singlet (the enhanced signal looks like a triplet), and the *anti*-9-H signal (doublet of quartets) was converted into a doublet of triplets. A response at 4- $\text{H}_{ax}$  was also observed: it changed from doublet to singlet.

An analogous pattern is typical of irradiation of 8- $\text{H}_{eq}$  ( $\delta$  1.82 ppm): the doublets from 1-H and 8- $\text{H}_{ax}$  are converted to singlets, and the doublet of quartets from *syn*-9-H ( $\delta$  1.51 ppm) becomes a doublet of triplets. The largest number of responses of protons in the bicyclononane fragment is produced by irradiation at a frequency corresponding to the *anti*-9-H signal ( $\delta$  1.63 ppm). In this case, signals from the 4- $\text{H}_{eq}$ , 1-H, 5-H, 8- $\text{H}_{eq}$ , and *syn*-9-H protons change their multiplicity (collapse).

The NOE responses at 8- $\text{H}_{ax}$  and 8- $\text{H}_{eq}$  ( $\delta$  1.47 and 1.82 ppm, respectively) on irradiation of 17'-H ( $\delta$  2.56 ppm) indicate that the 17'-H proton is oriented toward  $\text{C}^8$ . The response at 19-H with the same sign may be the result of double secondary polarization through 17''-H (strongly polarized) and 10-H;

Scheme 2.



a weak response at the latter is observed with the opposite sign ( $\delta$  3.73 ppm). An analogous explanation may be given to weak responses with the same sign of 12-H and 19-H on irradiation of 2- $H_{ax}$  [through polarization of 4- $H_{ax}$  (strong) and 10-H], and a very weak response at 4- $H_{eq}$  with the opposite sign may be attributed to secondary polarization through 4- $H_{ax}$ . On irradiation of 17"-H the response of 19-H has the opposite sign due to secondary polarization only through 10-H. An analogous secondary polarization of the 17"-H signal (with the opposite sign) through 17"-H (strong response) is observed on irradiation of 10-H (Fig. 5).

Thus, all NMR experiments support structure VI (Fig. 2) assigned to the product of photochemical cyclization of *endo*-2,*exo*-6-dihydroxy-3,7-dibenzylidenebicyclo[3.3.1]nonane (Va) in ether solution in the presence of CuCl (Scheme 2).

## EXPERIMENTAL

The progress of reactions was monitored by TLC on Silufol UV-254 plates with fixed layer of silica gel; preparative column chromatography was performed on Silpearl silica gel. The IR spectra were recorded on a UR-20 spectrometer. The UV spectra were measured on a Cary 219 spectrophotometer. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Varian VXR-400 instrument from solutions in  $\text{CDCl}_3$ ; the chemical shifts were measured relative to tetramethylsilane as internal reference. The mass spectra were run on a Hewlett-Packard HP-5985 mass spectrometer coupled with a gas chromatograph.

For qualitative monitoring of the photochemical processes, the UV spectra of ketones III and alcohols V were recorded from solutions in alcohol with a concentration of  $(1-6) \times 10^{-4}$  M (Table 1).

The reaction mixtures were irradiated with a PRK-7 immersible mercury lamp (237–398 nm) in a quartz reactor under argon on cooling with water (irradiation time 8–30 h).

**Photochemical isomerization of ketone IIIa.** A suspension of 330 mg (1 mmol) of ketone IIIa in

100 ml of dry ether was irradiated for several hours under stirring with a magnetic stirrer until the precipitate completely dissolved. The solution was filtered through a layer of silica gel, the solvent was distilled off under reduced pressure, and the transparent oily residue was analyzed. The yield of compound IVa was 67%. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1690 (C=O), 1610 (C=C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 7.22 (5H, Ph), 6.45 (1H, =CH), 3.3–2.72 m (3H), 2.41–2.43 m (1H). Found, %: C 84.25; H 6.20.  $\text{C}_{23}\text{H}_{20}\text{O}_2$ . Calculated, %: C 84.12; H 6.14.

**Photochemical cyclization of 3,7-dibenzylidenebicyclo[3.3.1]nonane-2,6-diol (Va).** A mixture of 400 mg (1.2 mmol) of diol Va and 20 mg of CuCl in 300 ml of dry ether was irradiated for 22 h while stirring on a magnetic stirrer. The mixture was evaporated to a volume of 25–30 ml and filtered through a layer of aluminum oxide (Brockmann activity grade II), the sorbent was washed with 10 ml of ether, and the solvent was removed under reduced pressure. According to the TLC data, the residue (300 mg) was a mixture of at least five products,  $R_f$  0.84, 0.62, 0.52, 0.41, and 0.21 (benzene–ethyl acetate, 2:1). A fraction enriched with a substance with  $R_f$  0.62 was evaporated under reduced pressure to obtain 0.28 g of a colorless solid with mp 65°C. Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 332 [ $M$ ] $^+$  (35), 314 [ $M-H_2O$ ] $^+$  (100), 296 (26), 255 [ $M-Ph$ ] $^+$  (46), 241 (26.8), 215 (19.7), 217 (18.5), 202 (16.3), 179 (16.9), 178 (19.6), 165 (20.1), 115 (15.2), 91 (26). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3600–3200 (OH), 1600 v.w. For  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data, see Fig. 1 and Table 2. Found %: C 82.64; H 7.60.  $\text{C}_{23}\text{H}_{24}\text{O}_2$ . Calculated, %: C 83.10; H 7.30.

## REFERENCES

1. Greiving, H., Hopf, H., Jones, P.G., Desvergne, J.P., and Bonas-Laurent, H., *J. Chem. Soc., Chem. Commun.*, 1994, pp. 1075–1076.
2. Mori, T., Kimoto, K., Kawanisi, M., and Nozaki, H., *Tetrahedron Lett.*, 1969, p. 3653.

3. Mori, T., Yang, K., Kimoto, K., and Nozaki, H., *Tetrahedron Lett.*, 1970, pp. 2419–2423.
4. Yurchenko, A.G., Veroshchenko, A.T., and Stepanov, F.N., *Zh. Org. Khim.*, 1970, vol. 6, no. 1, pp. 189–194.
5. Sventon, D.S., *J. Chem. Educ.*, 1969, vol. 47, no. 7, p. 803.
6. Averina, N.V., Borisova, G.S., and Gubin, A.V., *Vestn. Mosk. Gos. Univ.*, 2000, vol. 41, no. 3, pp. 192–194.
7. Hassner, A. and Mead, T.C., *Tetrahedron*, 1964, vol. 20, pp. 2201–2210.
8. Kevill, D.N., Weiler, E.D., and Cromwell, N.H., *J. Org. Chem.*, 1964, vol. 29, pp. 1276–1278.
9. *Einführung in die Photochemie*, Becker, H.G.O., Ed., Berlin: Wissenschaften, 1976. Translated under the title *Vvedenie v fotokhimiya organicheskikh soedinenii*, Leningrad: Khimiya, 1976, p. 232.
10. Moor, W.M., Morgan, D.D., and Stermitz, F.R., *J. Am. Chem. Soc.*, 1963, vol. 85, pp. 829–830.