tate, and the extracts were dried over $MgSO_4$. The solvents were evaporated to yield 0.153 g of a crude product, contaminated by impurities (TLC). The raw mixture was chromatographed on a plate (20 × 20 cm) with silica gel L40/100 in a 3:1:1 benzene–hexane–ether system. From the zone with R_f 0.69, 0.11 g (45%) of compound VIII was isolated. IR spectrum ($CHCl_3$): 3590, 3500, 3420, 3310, 1690, 1645, 1608 cm^{-1}. Found, %: C 66.6; H 8.9; N 13.8. $C_{17}H_{27}N_3O_2$. Calculated, %: C 66.9; H 8.9; N 13.8.

Influence of Solvents. The experiments were carried out in absolute solvents at 26 ± 2°C. The experimentally found values (mean of 3-4 measurements) are given for the same degree of the occurrence of the reaction (degree of consumption of the lactone 15 ± 3%). The dependence of log [IVa]/[IIIa] on Ω was calculated by the method of least squares.

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THE CHEMISTRY OF 1,5-DIKETONE DERIVATIVES. 2.* PREPARATION OF 2-HYDROXY-1,3,5-TRIPHENYL-1,5-PENTANEDIONE AND SOME HETEROCYCLE DERIVATIVES

T. V. Moskovkina, V. I. Vysotskii, and M. N. Tilichenko

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The preparation of 2-hydroxy-1,3,5-triphenyl-1,5-pentanedione by the addition of α-hydroxy- or α-acetoxyacetophenone to chalcone is described. The 2-hydroxy-1,5-diketone obtained does not show a tendency to form an intramolecular hemiacetal; instead, an acetate is formed. Reaction with hydroxylamine hydrochloride gives 3-aza-2,8-dioxa-1,4,6-triphenylbicyclo[3.2.1]oct-3-ene, and with ammonium acetate 2,4,6-triphenylpyridine and 3-amino-2,4,6-triphenylpyridine are formed. On reaction with p-toluenesulfonic acid the hydroxydiketone is converted into 3-oxo-2,4,6-triphenyl-2,3-dihydro-4H-pyran.

We have previously described [1] the preparation of 2-hydroxy-1,5-diketones by the oxidation of methoxy derivatives of hexahydrochromene or decahydroxanthene and we found that

*Communication 1, see [1].

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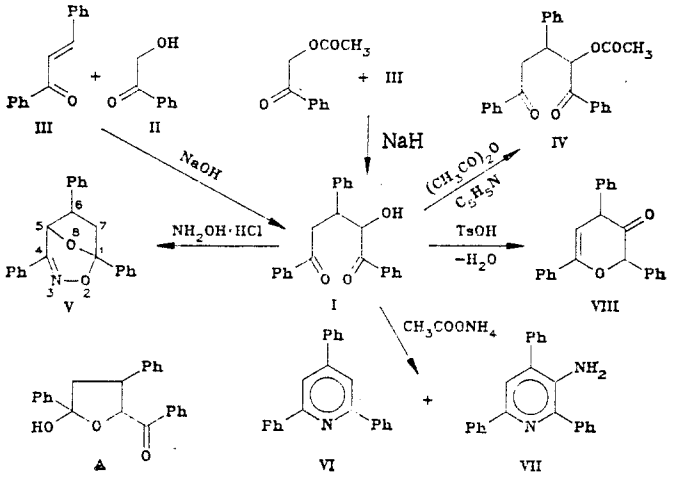
they can exist in both the open form and in the form of a hemiacetal with a five-membered ring.

The present communication describes the preparation of the first example of an aliphatic-aromatic α-hydroxy-1,5-diketone — 2-hydroxy-1,3,5-triphenyl-1,5-pentanedione (I). This compound is formed in 50% yield by the action of α-hydroxyacetophenone (II) with chalcone (III) in the presence of an alcoholic solution of sodium hydroxide, and in 40% yield by condensation of chalcone (III) with α-acetoxyacetophenone in the presence of sodium hydride.



The infrared spectrum of compound (I) shows absorption bands at 3480 (O—H) and 1684 cm^{-1} (C=O). The molecular ion 344 (8)* decomposes with the loss of a molecule of water 326 (26) and then of a benzoyl radical 221 (80). The most intense peak is that of the ion 239, the appearance of which is associated with the loss of a C_6H_5CO particle by the molecular ion. In the proton NMR spectrum, the signal of the hydroxyl group at 3.68 ppm has the form of a doublet (J = 7 Hz) on account of spin-spin interaction with the proton at the $C_{(2)}$ carbon. This signal disappears on the addition of deuteromethanol to the solution. From the form of this hydroxyl signal, one can exclude from consideration the hemiacetal form (A) where this signal would appear as a singlet. This splitting as a result of spin-spin interaction with α-hydrogen atoms is observed in the spectra of acyloins [1, 2]. The signal of the $C_{(2)}$ proton appears on the NMR spectrum as a doublet of doublets at 5.53 ppm (J = 1.5; 7 Hz), and on running the spectrum of a solution of the compound to which deuteromethanol has been added, the signal degenerates to a doublet with J = 1.5 Hz. The methylene group proton signals form an AB-system in the spectrum, each component of which is split into a doublet on account of interaction with the protons of the $C_{(3)}$ atom: H_A = 3.27 ppm (J = 24.0; 9.1 Hz), H_B = 4.15 ppm (J = 24.0; 10.3 Hz). The signal of the benzyl proton at $C_{(3)}$ is overlapped by the H_B proton signal and was not analyzed. The nature of the signals in the proton NMR spectrum points to a rigid spatial structure for compound (I).

To study the chemical properties of the hydroxydiketone I we carried out a series of functional reactions. Reaction with acetic anhydride in pyridine results in the formation of the acetate IV. The absorption band for the hydroxy group is absent from the IR spectrum of the acetate and there are bands at 1748 (C=O in an ester), 1690, and 1686 cm^{-1} (ketone C=O).

In the mass spectrum of compound IV, in the region of the greatest m/z values, a peak at 344 corresponds to the loss of a $CH_2{=}C{=}O$ fragment by the molecular ion. The most intense peak in the spectrum is that of the ion $[M - CH_3COOH, -COC_6H_5]^+$ 221 and there are also ion peaks $[M - CH_3COOH]^+$ 326 (65), $[M - C_6H_5CO]^+$ 281 (50), and $[M - C_6H_5]$ 309 (11). Thus, compounds I and IV undergo complex fragmentation on electron impact.

The proton NMR spectrum shows a signal for the $C_{(2)}$ proton in the form of a doublet at 6.40 ppm (J = 4.1 Hz). The signal of the benzyl proton at position 3 gives a multiplet centered at 4.21 ppm. The protons of the methylene group form an AB system in the spectrum, each component of which is split into a doublet on account of interaction with the proton of the $C_{(3)}$ atom: H_A = 3.35 ppm (J = 18.0; 5.0 Hz), H_B = 3.81 ppm (J = 18.0; 9.0 Hz).

*Notation is: m/z (% of maximum peak).

TABLE 1. 2-Hydroxy-1,3,5-triphenyl-1,5-pentanedione and Sóme Heterocycle Derivatives

Compound	mp, °C from EtOH	Found, %			Empirical formula	Calculated, %			Yield %
		C	H	N		C	H	N	
I	132—133	80,52	5,83	—	$C_{23}H_{20}O_3$	80,23	5,80	—	52
IV	103—105	77,90	5,50	—	$C_{25}H_{22}O_4$	77,72	5,70	—	98
V	146—147	80,90	5,60	4,25	$C_{23}H_{19}NO_2$	80,94	5,57	4,15	40
VII	136—137	85,80	5,50	8,85	$C_{23}H_{28}N_2$	85,70	5,43	8,68	31
VIII	126—128	83,00	5,70	—	$C_{23}H_{18}O_2$	82,82	5,52	—	37

By reacting compound I with hydroxylamine hydrochloride, we obtained 3-aza-2,8-dioxa-1,4,6-triphenylbicyclo[3.2.1]oct-3-ene (V) in addition to the expected 3-hydroxy-2,4,6-triphenylpyridine. The structure of compound V was confirmed by the following results: in its IR spectrum, functional group bands were absent; there was only a small-intensity band at 1606 cm^{-1} due to a C=N group. In the proton spectrum, there were signals at 2.80 (7-H, J = 10.0; 14.2 Hz), 3.20 (7-H, J = 10.0, 14.2 Hz), 5.30 ppm (5-H, J = 10.0 Hz). A signal for the benzyl proton in the form of a multiplet was found at 4.1 ppm. In the mass spectrum of (V), the molecular ion peak at 341 (33) corresponds to the calculated molecular weight, and its breakdown included loss of a C_6H_5CNO fragment, peak 222 (66). One possible route to the formation of compound (V) is through an oxime of a hemiacetal of structure A with subsequent dehydration.

Ammonium acetate in acetic acid reacted with compound I to form two products: the known 2,4,6-triphenylpyridine (VI) and 3-amino-2,4,6-triphenylpyridine (VII). The latter showed a band in its IR spectrum due to an amino group in the 3570-3400 cm^{-1} region; in the mass spectrum, the molecular ion peak 322 (100) corresponded to the calculated molecular weight. The protons of the amino group were represented in the proton spectrum by a singlet at 4.0 ppm which disappeared on addition of deuteromethanol to the sample solution; there were also signals from the aromatic protons.

Dehydration of compound I by p-toluenesulfonic acid led to the formation of 3-oxo-2,4,6-triphenyl-2,3-dihydro-4H-pyran (VIII) together with the expected 2-benzoyl-3,5-diphenyl-2,3-dihydrofuran (the product of the dehydration of structure A). The value of m/z for the molecular ion in the mass spectrum was in agreement with the molecular weight calculated for VIII — 326 (38). In the IR spectrum there were bands at 1706 (C=O), and 1676 cm^{-1} (C=C). The proton spectrum showed a signal for a vinyl proton in the form of a doublet at 6.30 ppm (J = 5.0 Hz), and for a benzyl proton on the $C_{(2)}$ atom, a doublet at 5.55 ppm (J = 1.5 Hz, long-range interaction with the proton at position 4); there was also a signal from the $C_{(4)}$ proton at 4.65 ppm (J = 1.5; 5.0 Hz).

EXPERIMENTAL

Infrared spectra were run on a Specord 75-IR instrument, either in chloroform solution or as nujol mulls. Bruker HX-90E and Bruker WH-250 spectrometers (90 and 250 MHz) were used for the NMR spectra with solutions in $CDCl_3$. Mass spectra were determined on an LKB-9000S instrument at 70 V. The individual substances were monitored by TLC on Silufol UV-254 plates using petroleum ether/ethyl acetate (7:3) and petroleum ether/diethyl ether (1:1). Development was effected in UV light or by iodine vapor. Identification of substances prepared by different routes was established by mixed melting points, comparison of the thin-layer chromatograms, and by their IR spectra.

2-Hydroxy-1,3,5-triphenyl-1,5-pentanedione (I). A.* To a solution of 10.4 g (0.05 mole) chalcone and 6.8 g (0.05 mole) hydroxyacetophenone in 80 ml ethanol 10 ml 10% alcoholic NaOH was added dropwise with stirring at 20°C. A precipitate appeared after 2 h. The mixture was kept at 20°C for 24 h and the precipitate then filtered off and washed with EtOH (2 × 20 ml), water (2 × 20 ml), and again with EtOH (10 ml) after which it was dried to yield compound I.

B. Sodium hydride (0.6 g) was suspended in 15 ml dry ether. In one procedure, 1.8 g (0.01 mole) α-acetoxyacetophenone was added and stirred 3 h and then a solution of 2.1 g

*With the participation of E. S. Karaulov and N. N. Gnitetskaya.

(0.01 mole) chalcone in 20 ml dry ether added. The mixture was stirred 1 h and then the absence of starting materials established by TLC. The reaction mixture was washed with water and the ether layer dried over $MgSO_4$. The ether was evaporated and the residue dissolved in 20 ml of a 10% solution of NaOH in MeOH. After 4 h the precipitated solid was separated, yielding 1.4 g (40%) compound I.

2-Acetoxy-1,3,5-triphenyl-1,5-pentanedione (IV). To a mixture of 6 ml dry pyridine and 6 ml acetic anhydride was added 2 g compound I and the mixture left to stand for 24 h. It was diluted with water and left until the oil which deposited solidified and crumbled to a powder. The reaction product was filtered off, washed with water, and dried. Yield, 2.2 g compound IV.

3-Aza-2,8-dioxa-1,4,6-triphenylbicyclo[3.2.1]oct-3-ene (V). To a hot solution of 3.44 g (0.01 mole) hydroxydiketone I in 90 ml EtOH a solution of 1.4 g (0.02 mole) hydroxylamine hydrochloride in 5 ml water was added dropwise over 5 min. The mixture was heated at bp for 4 h, 0.4 g (0.005 mole) hydroxylamine hydrochloride added and again heated at bp for 3 h. It was cooled to 20°C, and the crystals which deposited were filtered off to yield 1.2 g compound V. The mother liquor was concentrated to half volume and after cooling and filtering a further 0.25 g compound V was obtained.

2,4,6-Triphenylpyridine (VI) and 3-Amino-2,4,6-triphenylpyridine (VII). To 2.0 g (0.006 mole) compound I was added 3 g ammonium acetate and 15 ml acetic acid. The reaction mixture was heated for 1 h on a boiling water bath, cooled, and 2,4,6-triphenylpyridine (VI) filtered off, yielding 0.2 g, mp 137.5°C [3]. The mother liquor was neutralized with Na_2CO_3 and the oil which separated extracted with ether. Evaporation of the ether yielded 1.5 g of an oily product which TLC showed to contain two components. This mixture was divided by preparative TLC on Grade II alumina in 7:3 petroleum ether/ethyl acetate, the chromatography being carried out twice. From the zone with R_f 0.75, 0.4 g 2,4,6-triphenylpyridine VI was eluted with diethyl ether and from the R_f 0.65 zone, 1 g of the aminopyridine VII which was recrystallized from ethanol.

3-Oxo-2,4,6-triphenyl-2,3-dihydro-4H-pyran (VIII). Compound I (1.8 g, 0.005 mole) was dissolved in 50 ml dry benzene and 10-15 g p-toluenesulfonic acid added and the mixture heated to boiling in the flask of a Dean–Stark apparatus and refluxed for 9 h. After cooling, the solid which separated was filtered off. Yield, 0.6 g compound VIII.

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