EXPERIMENTAL

Electron impact mass spectra, DADI spectra, and defocusing spectra in the first field-free space were obtained on a Varian MAT-112. Electron ionization energies were 70 and 12 eV. Ionization chamber temperature was 180°. Samples were introduced into the mass spectrometer through a Varian Aerograph 1440 chromatograph. Column, 3% SE-30 on Chromosorb W (180 cm × 2 mm), He at 20 ml/min, T_{inj} = 220°, T_{sep} = 230°, T_{col} = 120-230° (10°/min).

Esters II-V were synthesized by the Darzens method [4], viz., the reaction of benzaldehyde or acetophenone with monochloroacetate or 2-bromopropionate esters. In all cases, esters were obtained as a 1:1 mixture of E- and Z-isomers. E- and Z-isomers were separated during mass spectral photography by introduction of the samples into the mass spectrometer through the chromatograph. Retention times: E-, Z-II 6'30" and 4'50"; E-, Z-III 5'20" and 3'50"; E-, Z-IV 7'50" and 5'00"; E-, Z-V 4'40" and 4'00", respectively.

Acid E-I was obtained by hydrolysis of the mixture of E- and Z-II esters [8].

LITERATURE CITED

1. M. S. Malinovskii, Hydroxyolefins and Their Derivatives [in Russian], Goskhimizdat, Moscow (1961), pp. 130, 398.
2. P. V. Zimakov (ed.), Ethylene Oxide [in Russian], Khimiya, Moscow (1967), p. 57.
3. R. A. Kuroyan, A. I. Markosyan, A. P. Engoyan, and S. A. Vartanyan, Zh. Org. Khim., 19, 1947 (1983).
4. R. Adms (ed.), Organic Reactions [Russian translation], Coll. Vol. 5, Inostr. Lit., Moscow (1951), p. 319.
5. J. Baldas and Q. N. Porter, Austral. J. Chem., 20, 2655 (1967).
6. R. K. Bansal, K. Sethi, and F. W. Bachelor, Indian J. Chem., 19B, 515 (1980).
7. A. V. Shchelkunov (ed.), Structure of Ethylene Oxide Derivatives [in Russian], Nauka, Alma Ata (1973), pp. 17, 31.
8. A. I. Bokanov, I. V. Persianova, and V. I. Shvedov, Zh. Org. Khim., 18, 1122 (1982).

PHOTOCHEMISTRY OF UNSATURATED LACTONES.

2.* PHOTOANNELATION OF 2-ACETYL-3,4,4-TRIMETHYL-2-BUTEN-4-OLIDE BY TERMINAL ALKYNES

A. A. Avetisyan, A. Kh. Margaryan, G. K. Nalbandyan,
and T. V. Avetisyan

UDC 547.314.217.1'728:514.14:
543.422'51

The photochemical cycloaddition of 2-acetyl-3,4,4-trimethyl-2-buten-4-olide to 1-heptyne and 1-chloro-2-propyne was carried out. The reaction gives isomeric cycloadducts of the "head to head" and "head to tail" types. The influence of solvent on the directivity of the reaction was investigated. The possibility was shown of using the cycloadducts obtained in the synthesis of difficulty available polyfunctionally substituted butanolides and heterocyclic compounds containing a spirocyclobutene fragment.

The use of α,β-unsaturated lactones in their photoannelation reaction by alkynes has been dealt with in only one paper by Japanese authors [2]. To broaden the field of application of this reaction, we studied the photocycloaddition of 2-acetyl-3,3,4-trimethyl-2-buten-4-olide (I) to 1-heptyne (IIa) and 1-chloro-2-propyne (IIb).

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*For Communication 1, see [1].

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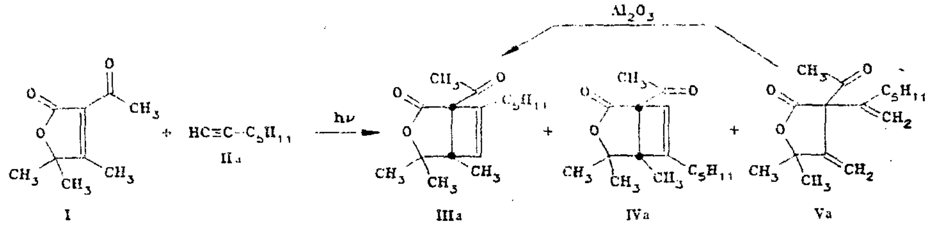
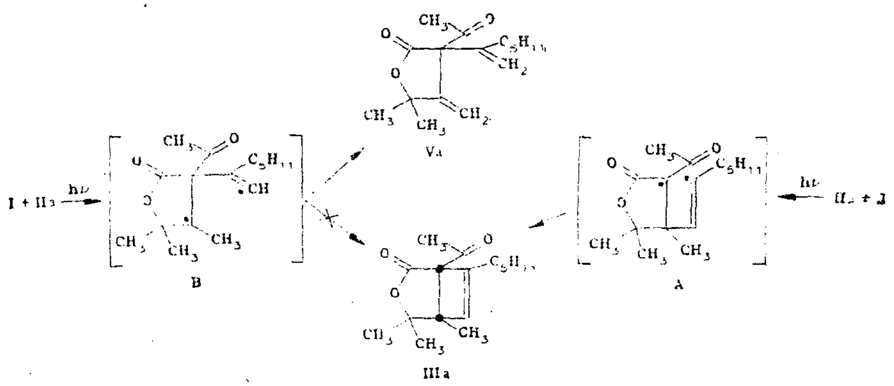
Irradiation of a solution of compounds I and IIa in benzene in a nitrogen atmosphere leads to a mixture of three reaction products IIIa-Va in a yield of 68-70% in a ratio of 10:12:13, which was determined by GLC at the end of photolysis.



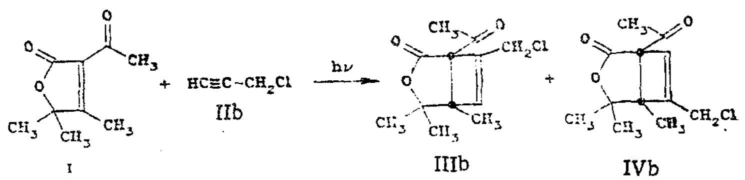
Thus, the structural directivity of the reaction is weakly expressed, and the content of the type "head to head" (HH, IIIa) isomer and the type "head to tail" (HT, IVa) isomer in the reaction mixture is approximately the same. According to the data of PMR and IR spectra, the predominating isomer Va is not a cycloadduct, but 2-acetyl-2-(2'-heptenyl)-3-methylene-4,4-dimethylbutan-4-olide. In particular, in the IR spectra of compound Va there are characteristic absorption bands of the stretching vibrations of the C=C bonds at 1650 and 1695 cm^{-1}, and in the PMR spectrum, the methylene group protons in the heptenyl radical resonate in the form of multiplets, while the protons of the exocyclic methylene group at the 3-position of the butanolide resonate in the form on an AB-spin system.

An indirect proof for the correct assignment of the structure of compound Va is the fact of its quantitative isomerization into isomer IIIa, when its chloroform solution is left to stand over Al_2O_3 at 20°C for several days. It could be assumed that compounds IIIa and Va are formed via a common 1,4-biradical intermediate A.

However, experiments with a variety of solvents in the photocycloaddition reaction of lactone I to 1-heptyne show that a low degrees of conversion, the ratio of the reaction products IIIa and Va depends on the polarity of the solvent. Isomer Va predominates in weakly polar solvents (hexane, benzene), while isomer IIIa predominates in more polar solvents (acetone, acetonitrile). These data indicate that different intermediates precede the reaction products IIIa and Va. The formation of cycloadduct IIIa, possibly proceeds via 1,4-biradical intermediate of type A.



The addition of lactone I to compound IIb under standard conditions leads to isomeric cycloadducts IIIb and IVb in a yield of 30-32% in a ratio of 11:2. The yield of cycloadducts decreases because of the formation of a polymeric film on the walls of the reactor, which hinders the UV irradiation.



The mass spectrometric data were found to be particularly informative in the assignment of structures of the isomeric cycloadducts of the HH type (IIIa, b) and HT type (IVa, b). Thus, the M^+ of the structural isomers IIIa, b undergo under electron impact a McLafferty

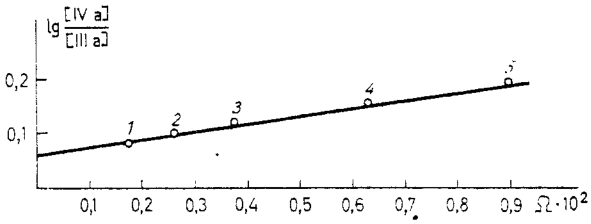


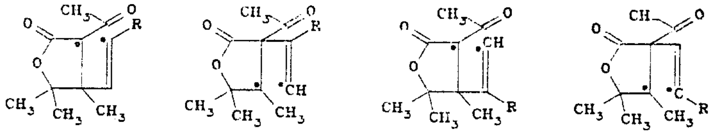
Fig. 1. Influence of aprotic solvents on the ratio of cycloadducts corresponding to type "head to tail" (IVa) and "head to head" (IIIa) addition. The concentration of the starting reagents I and IIa is the same in all solvents and equals to 0.16 and 1.60 M, respectively. Solvents: 1) cyclohexane, 2) benzene, 3) ethyl acetate, 4) acetone, 5) acetonitrile.

type rearrangement with hydrogen transfer from the substituent at the $C_{(7)}$ atom to the lactone ring carbonyl group according to a coordinate six-membered mechanism, followed by splitting off of an allenic radical [3]. The peak intensity of the ion formed as a result of this process (m/z 169) in the mass spectra of isomers IIIa, b is high and equal to 100 and 45%, respectively, while in the mass spectra of isomers IVa, b this peak is practically absent.

The differences in the IR and PMR spectra of the isomeric cycloadducts lead us to expect that they could be used in the assignment of structures in the photocycloaddition reactions of acetylenes to α,β-unsaturated lactones. Thus, in the IR spectra of isomers IVa, b, the frequency of the absorption band of the lactone carbonyl is 8-10 cm^{-1} higher than in the spectra of isomers IIIa, b. In the PMR spectra of isomers IVa, b, the olefinic proton resonates in a weaker field than in isomers IIa, b, the difference being up to 0.15 ppm.

During the photocycloaddition of lactone I to monosubstituted acetylenes IIa, b, comparable amounts of type HH and HT adducts are obtained, which cannot be correctly interpreted by taking into account the influence of polarization of the π-electronic cloud in the unsaturated substrate on the structural directivity of the photoannelation (the Corey hypothesis [4]).

If we take as a basis the currently accepted suppositions on the intermediate formation of 1,4-biradicals in the photoannelation reaction [5, 6], the formation of HH (IIIa, b) and HT (IVa, b) cycloadducts is possible from the intermediately formed alternative biradical intermediates A, B (HH) and C, D (HT).



A B C D

$R=C_5H_{11}$, CH_2Cl

It was shown that biradical B does not contribute to the formation of type HH cycloadducts (see above). The absence of the contribution of an intermediate biradical D to the formation of the type HT cycloadduct indicates the absence in the reaction mixture of a possible product with an exocyclic double bond in the 3-position and a 1-heptenyl radical in the 2-position of the butanolide [7].

Thus, during the photoannelation of compound I by alkynes IIa, b, the isomeric cycloadducts are apparently formed via the intermediate biradicals A and C, which are the most stable of those alternatively possible, and the structure of which is determined by an initial binding of the unsaturated substrate with the lactone C(β) atom.

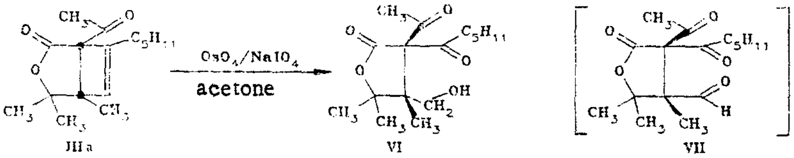
In the absence of specific interactions between the reagents and the solvent, and with an equal mechanism of formation of the isomeric cycloadducts, their ratio is determined by the Kirkwood—Onsager parameter Ω, which is characteristic for reactions with the participation of electrically neutral, but polar molecules [8-12]

$$\Omega=\frac{\varepsilon-1}{\varepsilon+1}\cdot\frac{\rho}{M},$$

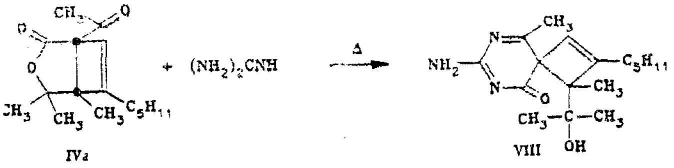
where ε is the dielectric constant, ρ is density and M is molecular weight of the solvent.

For five aprotic solvents, a linear dependence was observed between the logarithm of a ratio of concentrations of cycloadducts IVa and IIIa and the Kirkwood—Onsager parameter (Fig. 1): $\log [IVa]/[IIIa] = 0.06 + \tan \varphi \cdot \Omega \cdot 10^2$, where $\tan \varphi = 0.132$ (correlation coefficient $r = 0.95$).

Because of the high preparative yield of the cycloadducts in the addition reaction of lactone I to 1-heptyne IIa and the ease of isomerization of compound Va into cycloadduct IIIa, they can be used as the starting compounds in the synthesis of difficultly available polyfunctionally substituted butanolides, as well as heterocyclic compounds containing a spirocyclobutene fragment. Thus, the reaction of cycloadduct IIIa with OsO_4 in 80% aqueous acetone, followed by the decomposition of the osmatecomplex by $NaIO_4$ leads to 2-acetyl-2-hexanoyl-3-hydroxymethyl-3,4,4-trimethylbutane-4-olide (VI) in a yield of 64%.



When the reaction is carried out in 99% acetone, according to the PMR spectral data (9.5 ppm — the aldehyde proton), not only compound VI is formed, but also a small amount of 4-formyl derivative VII. Judging from the integral curve in the PMR spectrum of the mixture, the ratio of products VI and VII is approximately 3:1. The reaction of cycloadduct IVa with guanidine in an alcoholic solution of sodium ethylate leads to spiro[5,3]none-2-amino-4,8-dimethyl-7-pentyl-8-hydroxyisopropyl-1,3-diaza-1,3,6-triene (VIII) in a 45.5% yield.



The transformation products of the cycloadducts were isolated by preparative TLC on silica gel, and were characterized by PMR, IR spectra, and elemental analysis. Thus, the photocycloaddition products of 2-acetyl-3,4,4-trimethyl-2-buten-4-olide to monosubstituted alkynes, are by themselves of interest as starting materials in the synthesis of difficultly available organic compounds.

EXPERIMENTAL

The irradiation of the solution of lactone I with monosubstituted alkynes IIa, b in benzene was carried out in a flat-bottomed reactor at 20°C in a nitrogen atmosphere. A PRK-2M lamp (375 W), mounted horizontally on the bottom of a mirror-like illuminating tray at a distance of 20 cm from the bottom of the apparatus, served as the UV radiation source. The purity of the reagents and reaction end products was verified by GLC on a LKhM-8MD apparatus (catharometer), using a 3 m × 3 mm metallic column with OV-17 (5%) filler, on a Chromaton N-AW HMDS carrier (0.16-0.20 mm) at a flow rate of helium of 40 ml/min. The overall yield of the reaction products was determined from peak areas on the chromatograms by the internal standard method (n-eicosane). The IR spectra were run on UR-20 spectrophotometer (CCl_4, $CHCl_3$) and the PMR spectra on a Perkin-Elmer R-20B spectrometer (60 MHz), at a 10-12% sample concentration, using TMS as internal standard, while the mass spectra were measured on an MX-1303 mass spectrometer at a temperature of 110-115°C, and at an ionizing voltage of 50 eV.

Preparative Separation of Adducts IIIa, IVa, and Va. A solution of 2 g (0.01 mole) of acetolactone I, 8.4 g (0.15 mole) of 1-heptyne IIa in 9.6 g of benzene were placed in a photolysis reactor. After 28 h from the beginning of the irradiation, the volatile products were distilled on a rotary evaporator at 55°C (33 gPa), and the residue, a yellow oil containing the reaction products and unreacted starting lactone, was preparatively separated on a glass column (1 m × 25 mm) filled with 120 g of a brand L40/100 silica gel. The reaction products (given in order of emergence from the column) were isolated by elution with a 20:10:1 hexane—benzene—ethyl acetate mixture.

2-Acetyl-2-(2'-heptenyl)-3-methylene-4,4-dimethylbutan-4-olide (Va), yellow oil. GLC: T_{column} 225°C, t_{ret}* 5.5. IR spectrum (CCl_4): 3090, 1770, 1720, 1685, 1650, 915 cm^{-1}. PMR spectrum (CCl_4): 0.66-1.60 (15H, m); 1.80-2.26 (5H, m); 4.85 (H_A, d), 5.10 (H_B, d, J_{AB} = 1 Hz); 5.40-5.60 ppm (2H, m).

1-Acetyl-4,4,5-trimethyl-7-pentyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (IIIa), yellow oil. GLC: T_{column} 225°C, t_{ret} 6.0. IR spectrum (CCl_4): 3050, 1752, 1708, 1630 cm^{-1}. PMR spectrum (CCl_4): 0.62-1.62 (18H, m); 1.90-2.37 (5H, m); 5.95 ppm (1H, t, J = 1.5 Hz). Mass spectrum, m/z, %: M^+ 264 (17), 205 (44), 178 (75), 177 (46), 169 (100), 166 (45), 163 (48), 149 (48), 135 (65), 122 (46), 121 (79), 107 (45), 93 (41), 91 (38), 79 (38), 77 (38), 55 (43).

1-Acetyl-4,4,5-trimethyl-6-pentyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (IVa), yellow oil. GLC: T_{column} 225°C, t_{ret} 8.5. IR spectrum (CCl_4): 3055, 1760, 1708, 1630 cm^{-1}. PMR spectrum (CCl_4): 0.62-1.62 (18H, m); 1.77-2.35 (5H, m); 6.10 ppm (1H, t, J = 1.5 Hz). Mass spectrum, m/z, %: M^+ 264 (21), 205 (43), 178 (47), 177 (53), 163 (47), 149 (55), 122 (44), 121 (100), 107 (33), 93 (23), 91 (23), 79 (21), 77 (21), 57 (23), 55 (25).

Preparative Separation of Adducts IIIb and IVb. A solution of 2 g (0.01 mole) of acetolactone I, 11.2 g (0.15 mole) of propargyl chloride IIb in 6.8 g of benzene is placed in a photolysis reactor. After 22 h from the beginning of irradiation, the volatile products were distilled on a rotary evaporator at 40-45°C (33 gPa), and the residue, a brown viscous mass containing the desired end products was clarified by treatment with activated carbon in chloroform. Chloroform was evaporated and the residue was separated by preparative column chromatography on a glass column (3 m × 25 mm), filled with 100 g of brand L40/100 silica gel. The reaction products were isolated (in the order of emergence from the preparative column) by elution with a 30:1 benzene—chloroform mixture.

1-Acetyl-4,4,5-trimethyl-7-chloromethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (IIIb), yellow oil. GLC: T_{column} 200°C, t_{ret} 6.1. IR spectrum (CCl_4): 3050, 1758, 1712, 1608 cm^{-1}. PMR spectrum (CCl_4): 1.20 (3H, s); 1.33 (3H, s); 1.14 (3H, s); 2.16 (3H, s); 3.41 and 5.06 (2H, quartet, A- and B-parts of ABX system, J_{AB} = 15 Hz); 6.23 ppm (1H, t, X-parts of ABX system, $J_{AX} = J_{BX}$ = 2 Hz). Mass spectrum, m/z, %: 242 (15), 207 (19), 185 (18), 184 (29), 183 (30), 169 (45), 163 (16), 158 (16), 156 (43), 149 (34), 147 (32), 121 (41), 120 (100).

1-Acetyl-4,4,5-trimethyl-6-chloromethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (IV), yellow oil. GLC: T_{column} 200°C, T_{ret} 9.15. IR spectrum (CCl_4): 3050, 1770, 1712, 1610 cm^{-1}. PMR spectrum (CCl_4): 1.24 (3H, s); 1.32 (6H, s); 2.27 (3H); 4.00 (2H, d, J = 1.6 Hz); 6.35 ppm (1H, t, J = 1.6 Hz). Mass spectrum, m/z, %: M^+ 242 (12), 184 (32), 183 (20), 182 (83), 163 (29), 158 (18), 156 (47), 149 (68), 121 (98), 120 (100), 105 (57).

2-Acetyl-2-hexanoyl-3-hydroxymethyl-3,4,4-trimethylbutan-4-olide (VI). A solution of 0.18 g (0.68 mole) of compound IIIa in 16 ml of acetone is placed in a 100 ml three-necked flask, and 40 mg of OsO_4 are added with stirring. After 1 h, the solution acquired a brown color (due to the formation of an osmate complex). The reaction mixture was left to stand overnight. A 4 ml portion of water was added to the dark solution, and then 0.36 g (1.36 mmole) of $NaIO_4 \cdot 3H_2O$ was added, with ice-cooling, in portions, in the course of 8 h. Stirring was continued for 24 h. The reaction mixture was filtered through a column with silica gel (5 g), the filtrate was evaporated in vacuo, the residue was extracted by ether, and the extract was dried over $MgSO_4$. Ether was evaporated, and the residue (154 mg) was chromatographed on a plate (20 × 20 cm) with silica gel L40/100 (layer thickness 1.5 mm) in a 2:2:1 hexane—benzene—acetone system. From the zone with R_f 0.36, 130 mg (64%) of butanolide VI were isolated. IR spectrum ($CHCl_3$): 3595, 3470, 1770, 1715, 1060 cm^{-1}. PMR spectrum ($CDCl_3$): 0.62-1.65 (18H, m); 2.0-2.75 (6H, m, CH_3C—, —CH_2C—, OH); 4.07 ppm (2H, d, J = 3.75 Hz).

Spiro[5,3]non-2-amino-4,8-dimethyl-7-pentyl-8-hydroxyisopropyl-1,3-diaza-1,3,6-triene (VIII). A 5 ml portion of absolute ethanol and 0.088 g (0.16 mmole) of metallic sodium were placed in a three-necked flask fitted with a stirrer with a mercury seal and reflux condenser and 0.086 g (0.9 mmole) guanidine hydrochloride was added with stirring. Stirring was continued for another 30 min at 20°C and 0.22 g (0.83 mmole) of compound IVa, dissolved in 1 ml of absolute alcohol, was added. The mixture was stirred at the boiling point of the solution for 14 h. Alcohol was distilled off in a weak vacuum, 5 ml of water were added to the residue, and the mixture was acidified by HCl. The mixture was extracted by ether and ethyl ace-

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*t_{ret} — retention time in the GLC column, min.

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.

LITERATURE CITED

1. A. A. Avetisyan, A. Kh. Margaryan, and A. O. Gukasyan, Zh. Org. Khim., 19, 586 (1983).
2. Hiroshi Kosugi, Shizuo Sekiguchi, Ryu-ichi Sekita, and Hisashi Uda, Bull. Chem. Soc. Japan, 49, 520 (1976).
3. É. P. Serebryakov, S. D. Kulomzina, A. Kh. Margaryan, and O. S. Chizhov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1798 (1977).
4. E. G. Corey, J. D. Bass, R. le Mahieu, and R. B. Mitra, J. Am. Chem. Soc., 86, 5570 (1964).
5. P. G. Bauslaugh, Synthesis, 2, 287 (1970).
6. P. de Mayo, Acc. Chem. Res., 4, 41 (1971).
7. A. Kh. Margaryan, É. P. Serebryakov, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 408 (1978).
8. I. M. Hartmann, W. Hartmann, and G. O. Schenk, Chem. Ber., 100, 3146 (1967).
9. B. D. Challand and P. de Mayo, Chem. Comm., 16, 982 (1968).
10. G. Mark, F. Mark, and O. E. Plansky, Annalen, 719, 151 (1968).
11. G. Mark, H. Matthaus, F. Mark, J. Leitich, and D. Henneberg, Monatsh. Chem., 102, 37 (1971).
12. S. D. Kulomzina, É. P. Serebryakov, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim. No. 12, 2739 (1975).

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

UDC 547.422.5.04'811'829.07:
543.422

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

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*Communication 1, see [1].

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