Organic Chemistry

A new route for the synthesis of 1,3-diketones

A. S. Zanina, S. I. Shergina, I. E. Sokolov, and R. N. Myasnikova*

Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 3 ul. Institutskaya, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 352 350

A simple route for the synthesis of 1,3-diketones by the reaction of acetylenic ketones with amines followed by hydrolysis of the resulting aminovinylketons is suggested.

Key words: acetylenic ketones; 1,3-diketones; aminovinylketones; synthesis.

1,3-Dicarbonyl compounds serve as key starting reagents in the syntheses of heterocycles.[1—4] In addition, they readily form complexes with metals, which allows them to be used in extraction processes and in processes for synthesizing volatile and thermally stable diketonates used for the preparation of superconducting layers.[5,6]

The most common method for synthesizing 1,3-diketones is the Claisen reaction[7] involving sodium and lithium amides as condensing reagents. It is also known that the acylation of alkynes with acyl chlorides in the presence of Lewis acids results in β-chlorovinylketones, whose hydrolysis gives 1,3-diketones.[8] However, the application of these methods is restricted by the reaction conditions required (low temperatures, dry media) and by the formation of side products, which prevents the synthesis of 1,3-diketones on a large scale.

Previously, we elaborated a convenient method for synthesizing α-alkynylketones by acylating terminal acetylenes in the presence of catalytic amounts of copper salts.[9,10]

$$\mathrm{R{-}C{\equiv}C{-}H + R^1{-}COCl \xrightarrow[Et_3N]{CuCl} R{-}C{\equiv}C{-}CO{-}R^1}$$

This method was also used for obtaining alkynylketones **1** (Scheme 1), which we now describe for the first time (Table 1). Taking into account the high reactivity of acetylenic ketones in reactions with nucleophilic reagents,[11] we elaborated a new route for synthesizing β-dicarbonyl compounds.

Scheme 1

$$\underset{\mathbf{1}}{\mathrm{R{-}C{\equiv}C{-}CO{-}R^1}} \xrightarrow{\mathrm{R^2R^3NH}} \underset{\mathbf{2}}{\mathrm{R{-}C(NR^2R^3){=}CH{-}CO{-}R^1}} \longrightarrow$$

$$\xrightarrow[\mathrm{H_2O}]{\mathrm{H^+}} \underset{\mathbf{3}}{\mathrm{R{-}CO{-}CH_2{-}CO{-}R^1}}$$

The reactions of alkynylketones **1** with amines in alcohols or in dioxane give β-aminovinylketones **2** in 70—93 % yields. For most compounds, the reaction is completed in 0.5—2 h. Alkynylketones with bulky substituents react less readily. For example, the reaction of 6-methoxy-2,2,6,7,7-pentamethyl-4-octyn-3-one (**1**, R = 1-methoxy-1,2,2-trimethylpropyl, R^1 = dimethylethyl) with piperidine and aniline in dioxane takes 30 days.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 710—714, April, 1995.

Table 1. Yields, physicochemical constants, and elemental analysis data for acetylenic ketones **1**

Compound	Yield (%)	B.p./°C (*p*/Torr)	n_D (*T*/°C)	Found / Calculated (%) C	Found / Calculated (%) H	Molecular formula
2,2,6-Trimethyl-4-heptyn-6-en-3-one	70.0	85 (15)	1.4715 (20)	79.69 / 79.95	9.43 / 9.39	$C_{10}H_{14}O$
2-Methyl-4-decyn-3-one	77.7	82 (4)	1.4495 (21)	79.22 / 79.46	10.76 / 10.77	$C_{11}H_{18}O$
2-Methyl-2-methoxy-3-nonyn-5-one	61.0	71—72 (2)	1.4490 (19)	72.40 / 72.49	9.93 / 9.96	$C_{11}H_{18}O_2$
4,4-Dimethyl-1-(1-cyclopentene)-1-pentyn-3-one	76.6	93 (3)	1.5100 (21)	82.52 / 81.77	9.09 / 9.15	$C_{12}H_{16}O$
2,2-Dimethyl-4-decyn-3-one	63.5	129 (30)	1.4500 (18)	79.66 / 79.74	11.15 / 11.18	$C_{12}H_{20}O$
4,4-Dimethyl-1-(1-cyclohexene)-1-pentyn-3-one	69.7	104 (2)	1.5112 (20)	81.82 / 82.06	9.35 / 9.54	$C_{13}H_{18}O$
6-Methoxy-2,6,8-trimethyl-4-nonyn-3-one	92.0	142 (27)	1.4485 (22)	74.09 / 74.24	10.54 / 10.54	$C_{13}H_{22}O_2$
4,4-Dimethyl-1-(1-methoxycyclo-hexyl)-1-pentyn-3-one	70.0	145—147 (15)	1.4730 (20)	75.50 / 75.63	10.10 / 9.97	$C_{14}H_{22}O_2$
6-Methoxy-2,2,6,7,7-penta-methyl-4-octyn-3-one	85.0	120 (15)	1.4532 (21)	74.88 / 74.95	10.71 / 10.76	$C_{14}H_{24}O_2$
6-Methoxy-2,2,6,8-tetramethyl--4-nonyn-3-one	79.0	120 (13)	1.4472 (21)	74.73 / 74.95	10.73 / 10.76	$C_{14}H_{24}O_2$
6-Methyl-6-methoxy-4-heptyn-3-one	35.0	55 (2)	1.4452 (22)	70.02 / 70.10	9.04 / 9.15	$C_9H_{14}O_2$
6-Methoxy-2,6,7,7-tetramethyl--4-octyn-3-one	81.0	140 (30)	1.4550 (22)	74.07 / 74.24	10.57 / 10.54	$C_{13}H_{22}O_2$
7-Methyl-7-methoxynona-8-decyn--10-one	36.6	163 (1)	1.4620 (20)	78.02 / 78.09	11.84 / 11.88	$C_{21}H_{38}O_2$

The hydrolysis of β-aminovinylketones **2** gives 1,3-diketones in 70—90 % yields. β-Aminovinylketones can be hydrolyzed without isolation. After the reaction of an amine with ethynylketone is completed (TLC monitoring), the solvent and excess amine are distilled off, and the resulting solution is treated with a solution of HCl in aqueous ethanol (*cf.* Ref. 12). Thus, the addition of amines to alkynylketones and the hydrolysis of the resulting β-aminovinylketones can be performed in one step without diminishing the yield of the target products.

The structures and purity of all compounds obtained for the first time were confirmed by elemental analyses, GLC analyses, and IR spectroscopic data. For example, the data for acetylenic ketones are as follows ($CHCl_3$, CCl_4, ν/cm^{-1}): 2210 (—C≡C—); 1680 (C=O); for β-aminovinylketones (CCl_4): 1630, 1520, 1585 (C=C—C=O, NH_2); 3240, 3400, 3480 (NH, NH_2); for β-anilinovinylketones: 1600 (N—C=C—C=O); 1670 (C=N); 1720 (C=O); 3200 (NH); for dialkyl-substituted aminovinylketones: 1540—1550 (C=C) and 1638—1655 (C=O). The spectra of 1,3-diketones display a broad intense band at 1540—1640 cm^{-1}.

The intermediate compounds, aminovinylketones, are of interest themselves as synthons in organic syntheses and as complex-forming compounds.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer in $CHCl_3$ or CCl_4. GLC analyses and reaction monitoring were performed on a Khrom-5 chromatograph with a flame ionization detector and a 360 × 0.4 cm column with 5 % SE-30 on Inerton AW, using nitrogen as the carrier gas; the thermostat temperature was 90—140 °C for low-boiling compounds and 140—180 °C for high-boiling compounds.

3-Methoxy-3,4,4-trimethyl-1-pentyne (A) and 3-methoxy-3,5-dimethyl-1-hexyne (B) were obtained by a reported procedure[13] in 85.0 and 87.0 % yields, respectively. Data for compound **A**: b.p. 135—136 °C, n_D^{22} 1.4283. Found (%): C, 77.45; H, 11.62. $C_9H_{16}O$. Calculated (%): C, 77.09; H, 11.50. For **B**: b.p. 140 °C, n_D^{22} 1.4200. Found (%): C, 76.89; H, 11.51. $C_9H_{16}O$. Calculated (%): C, 77.09; H, 11.50.

Alkynylketones **1** were synthesized by the known procedures.[9,10] The physicochemical constants of α-ethynylketones, which we transformed into β-diketones **3**, have been determined previously.[9,10] The yields, physicochemical constants, and elemental analysis data are presented in Table 1.

3-Diethylamino-3-phenyl-1-*p*-tolyl-2-propen-1-one (2, R = Ph, R^1 = *p*-tolyl, R^2 = R^3 = Et). 3-Phenyl-1-*p*-tolyl-2-propyn-1-one (6.5 g, 0.03 mol) in ethanol (100 mL) was placed in a three-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. Diethylamine (2.2 g, 31 mmol) was added, and the mixture was stirred for 2 h at 65 °C. The ethanol was distilled off, and the product was purified by recrystallization from ethanol to give 8.6 g (95.5 %)

Table 2. Yields, physicochemical constants, and elemental analysis data for aminovinylketones **2**

Aminovinylketone	Yield (%)	B.p./°C / p/Torr or m.p./°C (solvent)	n_D (T/°C)	Found/Calculated (%) C	H	N	Molecular formula
5-Amino-2,2,6-trimethyl-4,6-heptadien-3-one	87.0	50—51 (petroleum ether)	—	71.85 / 71.81	10.33 / 10.25	8.31 / 8.37	$C_{10}H_{17}NO$
5-Anilino-2-methyl-4-decen--3-one	88.8	180 / 3	1.5600 (22)	78.79 / 78.72	9.66 / 9.71	5.57 / 5.40	$C_{17}H_{25}NO$
3-Anilino-2-methyl-2-methoxy-3-nonen-5-one	92.0	177 / 3	1.4620 (20)	74.24 / 74.14	8.92 / 9.15	5.14 / 5.09	$C_{17}H_{25}NO_2$
1-Anilino-4,4-dimethyl-1-(1-cyclopentene)-1-penten-3-one	60.0	98.5 (ethanol)	—	80.35 / 80.25	8.48 / 8.60	5.51 / 5.40	$C_{18}H_{23}NO$
4,4-Dimethyl-1-piperidino--1-(1-cyclopentene)-1-penten-3-one	72.6	73—74 (petroleum ether)	—	78.05 / 78.11	10.25 / 10.41	5.16 / 5.35	$C_{17}H_{28}NO$
5-Anilino-2,2-dimethyl--4-decen-3-one	78.2	185 / 6	1.5530 (21)	79.32 / 79.07	9.93 / 9.95	5.20 / 5.12	$C_{18}H_{27}NO$
1-Anilino-4,4-dimethyl-1-(1-cyclohexene)-1-penten-3-one	59.4	67—68 (hexane)	—	80.60 / 80.52	8.78 / 8.89	4.85 / 4.94	$C_{19}H_{25}NO$
1-*N,N*-Diethylamino-4,4-dimethyl-1-(1-cyclohexene)-1-penten-3-one	93.2	145 / 3	1.5273 (22)	77.71 / 77.41	11.09 / 10.96	5.31 / 5.45	$C_{17}H_{29}NO$
4,4-Dimethyl-1-piperidino-1-(1-cyclohexene)-1-penten-3-one	93.5	76—77 (petroleum ether)	—	78.36 / 78.49	10.56 / 10.61	5.33 / 5.09	$C_{18}H_{29}NO$
5-Anilino-6-methoxy-2,6,8-trimethyl-4-nonen-3-one	84.0	180 / 13	1.5120 (20)	75.39 / 75.24	9.50 / 9.57	4.54 / 4.62	$C_{19}H_{29}NO_2$
1-Anilino-4,4-dimethyl-1-(1-methoxycyclohexyl)-1-penten-3-one	92.0	174 / 2	1.5332 (22)	76.00 / 76.15	9.04 / 9.27	4.72 / 4.44	$C_{20}H_{29}NO_2$
6-Methoxy-2,2,6,7,7-pentamethyl-5-piperidino-4-octen-3-one	87.0	136 / 3	1.5041 (21)	73.62 / 73.74	11.33 / 11.40	4.63 / 4.53	$C_{19}H_{35}NO_2$
5-Anilino-6-methoxy-2,2,6,8-tetramethyl-4-nonen-3-one	93.7	182—184 / 13	1.5109 (20)	75.72 / 75.67	9.69 / 9.84	4.50 / 4.41	$C_{20}H_{31}NO_2$
3-*p*-Nitrophenyl-1-piperidino-1-phenyl-1-propen-3-one	93.7	154 (benzene+acetone)	—	71.27 / 71.41	5.97 / 5.99	8.22 / 8.22	$C_{20}H_{20}N_2O_3$
1-Anilino-3-*p*-nitrophenyl-1-phenyl-1-propen-3-one	88.2	165—166 (ethanol)	—	73.31 / 73.46	4.62 / 4.40	7.94 / 8.16	$C_{21}H_{15}N_2O_3$
3-*N,N*-Diethylamino-1-*p*-nitrophenyl-3-phenyl-3-propen-1-one	89.6	130 (ethanol+pentane)	—	70.32 / 70.35	6.16 / 6.21	8.47 / 8.64	$C_{19}H_{20}N_2O_3$
3-Morpholino-1-*p*-nitrophenyl-3-phenyl-3-propen-1-one	91.0	155 (ethanol+pentane)	—	67.39 / 67.44	5.35 / 5.36	8.15 / 8.28	$C_{19}H_{18}N_2O_4$
3-Anilino-1-*p*-tolyl-3-phenyl-3-propen-1-one	76.7	141—142 (ethanol)	—	84.30 / 84.31	6.15 / 6.11	4.43 / 4.47	$C_{22}H_{19}NO$
3-*N,N*-Diethylamino-1-*p*-tolyl-3-phenyl-3-propen-1-one	95.5	79—80 (ethanol)	—	81.80 / 81.87	7.92 / 7.90	4.77 / 4.63	$C_{20}H_{23}NO$
3-Piperidino-1-*p*-tolyl-3-phenyl-3-propen-1-one	89.0	117—119 (ethanol)	—	82.47 / 82.58	7.69 / 7.59	4.71 / 4.59	$C_{21}H_{23}NO$
3-Amino-3-(1-methoxycyclohexyl)-1-*m*-tolyl-2-propen-1-one	80.0	71—72 (ethanol)	—	74.53 / 74.69	8.41 / 8.48	5.24 / 5.22	$C_{17}H_{23}NO_2$
3-Amino-4-methyl-4-methoxy-1-*m*-tolyl-2-penten-1-one	92.0	57—58 (hexane)	—	72.05 / 72.07	8.16 / 8.21	6.19 / 6.00	$C_{14}H_{19}NO_2$
1-Anilino-4,4-dimethyl-1-phenyl-1-penten-3-one	90.0	93—94 (petroleum ether)	—	81.66 / 81.68	7.80 / 7.58	4.80 / 5.01	$C_{19}H_{21}NO$
3-Amino-4-methyl-4-methoxy-1-*m*-tolyl-2-octen-1-one	84.0	187—190 / 2	1.5675 (22)	74.01 / 74.14	9.18 / 9.15	5.25 / 5.09	$C_{17}H_{25}NO_2$
5-Anilino-2,2-dimethyl-4-nonen-3-one	87.0	170 / 5	1.5588 (23)	78.70 / 78.72	9.62 / 9.71	5.55 / 5.40	$C_{17}H_{25}NO$

Table 2. (Continued)

Aminovinylketone	Yield (%)	B.p./°C *p*/Torr or m.p./°C (solvent)	n_D (*T*/°C)	Found / Calculated (%) C	H	N	Molecular formula
3-Amino-4-methyl-4-methoxy-1-*m*-tolyl-2-decen-1-one	76.0	200—203 1	1.5623 (22)	75.25 75.21	9.47 9.63	4.75 4.67	$C_{19}H_{29}NO_2$
3-Anilino-4-methyl-4-methoxy-1-(1-furfuryl)-2-decen-1-one	93.8	218 1	1.5850 (22)	74.36 74.33	8.14 8.22	3.96 3.94	$C_{22}H_{29}NO_3$
3-Anilino-2-methyl-2-methoxy-3-undecen-5-one	77.0	174 2	1.5110 (19)	75.16 75.20	9.62 9.63	4.63 4.62	$C_{19}H_{29}NO_2$
3-Anilino-2-methyl-2-methoxy-3-tridecen-5-one	73.6	165—167 1	1.5130 (19)	76.02 76.09	9.96 10.03	4.11 4.22	$C_{21}H_{33}NO_2$

Table 3. Yields, physicochemical constants, and elemental analysis data for 1,3-diketones **3**

1,3-Diketone	Yield (%)	B.p./°C *p*/Torr or m.p./°C (solvent)	n_D (*T*/°C)	Found / Calculated (%) C	H	Molecular formula
2,2,6-Trimethyl-6-heptene-3,5-dione	87.2	91—92 13	1.4877 (21)	71.14 71.39	9.57 9.59	$C_{10}H_{16}O_2$
2-Methyldecane-3,5-dione	96.0	92—93 6	1.4628 (21)	71.43 71.69	10.79 10.94	$C_{11}H_{20}O_2$
2-Methyl-2-methoxynonane-3,5-dione	71.0	85 1	1.4620 (20)	64.62 64.66	11.88 11.84	$C_{11}H_{20}O_3$
4,4-Dimethyl-1-(1-cyclopentene-1)-pentane-1,3-dione	89.8	116 5	1.5270 (31)	74.08 74.19	9.32 9.33	$C_{12}H_{18}O_2$
2,2-Dimethyldecane-3,5-dione	84.2	98 5	1.4620 (20)	72.49 72.68	11.01 11.19	$C_{12}H_{22}O_2$
4,4-Dimethyl-1-(1-cyclohexene-1)-pentane-1,3-dione	80.3	130 2	1.5280 (23)	74.87 74.96	9.41 9.67	$C_{13}H_{20}O_2$
6-Methoxy-2,6,9-trimethylnonane-3,5-dione	70.0	122—124 15	—	68.33 68.38	10.71 10.59	$C_{13}H_{24}O_3$
4,4-Dimethyl-1-(1-methoxycyclohexyl)pentane-1,3-dione	89.5	95 1	1.4925 (19)	70.14 69.96	10.02 10.07	$C_{14}H_{24}O_3$
6-Methoxy-2,2,6,9-tetramethylnonane-3,5-dione	87.5	140—141 15	1.4630 (21)	69.52 69.38	10.76 10.81	$C_{14}H_{26}O_3$
3-*p*-Nitrophenyl-1-phenylpropane-1,3-dione*	97.5	167 (benzene+acetone)	—	66.85 66.91	4.30 4.12	$C_{15}H_{11}O_4$
3-*p*-Tolyl-1-phenylpropane-1,3-dione	75.0	83—84 (ethanol+pentane)	—	80.65 80.64	5.95 5.92	$C_{16}H_{14}O_2$
3-(1-Methoxycyclohexyl)-1-*p*-tolylpropane-1,3-dione	76.0	188—192 2	1.5782 (19)	74.42 74.63	8.08 7.95	$C_{17}H_{22}O_3$
4-Methyl-4-methoxy-1-*m*-tolylpentane-1,3-dione	92.8	145—147 2	1.5585 (22)	71.74 71.77	7.77 7.74	$C_{14}H_{18}O_3$
4,4-Dimethyl-1-phenylpentane-1,3-dione	72.0	127—128 2	1.5634 (24)	76.54 76.44	7.94 7.90	$C_{19}H_{16}O_2$
4-Methyl-4-methoxy-1-*m*-tolyloctane-1,3-dione	70.0	178—180 2	1.5501 (19)	73.88 73.66	8.75 8.58	$C_{17}H_{24}O_3$
2,2-Dimethylnonane-3,5-dione	80.7	85.5 6	1.4625 (20)	71.42 71.69	10.85 10.94	$C_{11}H_{20}O_2$
4-Methyl-4-methoxy-1-*m*-tolyldecane-1,3-dione	90.0	168—172 2	1.5415 (22)	75.14 74.96	9.06 9.27	$C_{19}H_{28}O_3$
4-Methyl-4-methoxy-1-furyl-decane-1,3-dione	50.7	174—176 5	1.5300 (21)	68.54 68.42	8.56 8.63	$C_{16}H_{24}O_4$
2-Methyl-2-methoxyundecane-3,5-dione	87.0	113 2	1.4630 (20)	68.38 68.47	10.59 10.71	$C_{13}H_{24}O_3$

Table 3. (Continued)

1,3-Diketone	Yield (%)	B.p./°C / p/Torr or m.p./°C (solvent)	n_D (T/°C)	Found / Calculated (%) C	H	Molecular formula
2-Methyl-2-methoxytridecane-3,5-dione	92.8	126 / 2	1.4660 (19)	70.26 / 70.27	10.96 / 11.01	$C_{15}H_{28}O_3$
2-Methoxy-2,6,6-trimethyl-heptane-3,5-dione	96.0	102 / 30	1.4605 (22)	66.35 / 65.97	10.06 / 10.07	$C_{11}H_{20}O_3$
2,6-Dimethyl-2-methoxydecane-3,5-dione	86.0	127—130 / 13	1.4634 (20)	68.38 / 68.32	10.59 / 10.47	$C_{13}H_{24}O_3$
4-Methyl-4-methoxy-1-*p*-methoxy-phenylpentane-1,3-dione	86.0	178—183 / 13	1.5782 (19)	67.18 / 67.26	7.25 / 7.08	$C_{14}H_{18}O_4$
2-Methyl-2-methoxydodecane-3,5-dione	86.0	120 / 1	1.4640 (21)	69.37 / 69.38	10.78 / 10.81	$C_{14}H_{26}O_3$
4-Methyl-4-methoxy-1-α-naphthylpentane-1,3-dione	81.0	49—51 (subl.)	—	75.76 / 75.53	6.74 / 6.71	$C_{17}H_{18}O_3$
5-Methyl-1-methoxyhexane-2,4-dione	87.0	52 / 2	1.4590 (20)	60.52 / 60.74	8.83 / 8.92	$C_8H_{14}O_3$
3-(1-Methoxycyclohexyl)-1-*p*-nitrophenylpropane-1,3-dione**	75.4	81—82 (ethanol)	—	62.92 / 62.94	6.30 / 6.27	$C_{16}H_{19}NO_5$
4-Methyl-1-(1-methoxycyclo-hexyl)propane-1,3-dione	83.3	110—111 / 2	1.4900 (20)	68.90 / 68.99	9.86 / 9.80	$C_{13}H_{22}O_3$
4-Methyl-4-methoxy-1-*p*-methoxy-phenyldecane-1,3-dione	73.0	145—149 / 1	1.5583 (19)	71.30 / 71.22	8.73 / 8.81	$C_{19}H_{28}O_4$
4-Methyl-4-methoxy-1-*p*-nitro-phenyldecane-1,3-dione***	88.0	230 / 3	1.5690 (19)	64.46 / 64.25	7.51 / 7.34	$C_{18}H_{25}NO_5$
4-Methyl-4-methoxy-1-*p*-tolyl-decane-1,3-dione	84.0	168—172 / 2	1.5415 (22)	74.96 / 75.14	9.27 / 9.06	$C_{19}H_{28}O_3$

* N, Found/calculated (%): 4.99/5.20; ** 4.51/4.59; *** 4.11/4.17.

of aminovinylketone **2** (R = Ph, R^1 = *p*-tolyl, R^2 = R^3 = Et), m.p. 79—80 °C. The other aminovinylketones **2** were obtained in a similar way. The yields, physicochemical constants, and elemental analysis data are presented in Table 2.

3-Phenyl-1-*p*-tolyl-1,3-propanedione (3, R = Ph, R^1 = *p*-tolyl). Dilute HCl (1 : 1, 15 mL) was added to a solution of aminovinylketone **2** (15.0 g, 50 mmol; R = Ph, R^1 = *p*-tolyl, R^2 = R^3 = Et) in MeOH (100 mL). The reaction mixture was stirred for 2 h at 60—65 °C. After cooling, the precipitate was filtered off and washed with water until a neutral pH was attained. Crystallization from an ethanol—pentane mixture gave 8.8 g (75 %) of 1,3-diketone **3** (R = Ph, R^1 = *p*-tolyl), m.p. 83—84 °C. The other β-diketones **3** were obtained similarly. The yields, physicochemical constants, and elemental analysis data are presented in Table 3.

2-Methoxy-2,6-dimethyl-3,5-decanedione (3, R = 2-methoxyprop-2-yl, R^1 = hex-2-yl) (without isolation of the intermediate products). Triethylamine (175.0 g, 1.75 mol) was added to a suspension of CuCl (15.0 g, 0.15 mol) in benzene (1 L). The mixture was stirred for 10 min under a stream of nitrogen, and the methyl ether of dimethyl(ethynyl)carbinol (147 g, 1.5 mol) was added. 2-Methylhexanoyl chloride (223 g, 1.5 mol) was added over a period of 30 min at 55—60 °C. The mixture was kept for 1 h and then washed with dilute HCl (1 : 3, 500 mL) and water until a neutral pH was attained. The benzene was partially distilled off (~400 mL) in the vacuum of a water-aspirator pump. MeOH (100 mL) and aniline (140.0 g, 1.5 mol) were added to the benzene solution of α-ethynylketone. The mixture was stirred at 60 °C for 2 h, and the resulting anilinovinylketone was hydrolyzed with 25 % HCl (300 mL). The mixture was extracted with benzene, washed with water, and dried with $CaCl_2$. The solvent was distilled off, and the residue was distilled *in vacuo* to give 228.0 g (80.0 %) of diketone **3** (R = 2-methoxyprop-2-yl, R^1 = hex-2-yl).

References

1. O. Attanasi, P. Filipone, A. Mei, and F. Serra-Zanetti, *Synthetic Commun.*, 1986, **16**, 343.
2. G. Zvilichovsky, *Tetrahedron*, 1967, **23**, 353.
3. D. Olliero and G. Solladie, *Synthesis*, 1975, 246.
4. M. S. Manhas, S. G. Amin, and V. V. Rao, *Synthesys*, 1977, 309.
5. G. A. Marinkina, A. S. Zanina, S. I. Shergina, I. E. Sokolov, and I. L. Kotlyarevskii, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1304 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1015 (Engl. Transl.)].
6. A. R. Kaul', *Zh. Vsesoyuz. Khim. Obshch.*, 1989, **34**, 492 [*Mendeleev Chem. J.*, 1989, **34** (Engl. Transl.)].
7. K. P. Kopecky, D. C. Nonhbel, G. Morris, and G. S. Hammond, *J. Org. Chem.*, 1962, **27**, 1036.
8. A. E. Pohland and W. R. Benson, *Chem. Rev.*, 1966, **66**, 161.
9. A. S. Zanina, S. I. Shergina, I. E. Sokolov, and I. L. Kotlyarevskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990,

2551 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2307 (Engl. Transl.)].

10. A. S. Zanina, S. I. Shergina, I. E. Sokolov, and I. L. Kotlyarevskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 855 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 777 (Engl. Transl.)].
11. L. I. Vereshchagin, L. D. Gavrilova, E. I. Titova, *et al.*, *Zh. Org. Khim.*, 1975, **11**, 286 [*J. Org. Chem. USSR*, 1975, **11** (Engl. Transl.)].
12. Ya. F. Freimanis, in *Khimiya Enaminoketonov, Enaminoiminov, Enaminotiolov* [*Chemistry of Enaminoketones, Enaminoimines, and Enaminothioles*], Zinatne, Riga, 1974, 222—232 (in Russian).
13. I. E. Sokolov and I. L. Kotlyarevskii, *Izv. Akad. Nauk SSSR, Ser. Khim*, 1980, 202 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29**, No. 1 (Engl. Transl.)].

Received August 10, 1994;
in revised form December 30, 1994