

- N. K. Davilenko, B. A. Bidzilya, L. P. Golovkova, S. L. Davydova, and K. B. Yatsimirskii, *Teor. Éksp. Khim.*, 3, 404 (1977).
- Kh. Gunther, *Introduction to NMR Spectroscopy* [Russian translation], Mir, Moscow (1984).

NEW SYNTHESIS OF MONOMETHYL ETHERS OF TRIOLS - EXTRACTION AGENTS FOR BORIC ACID

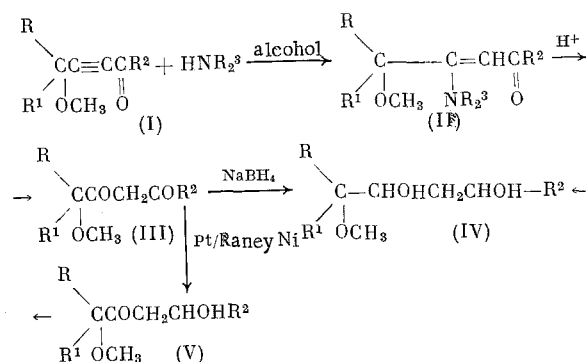
I. L. Kotlyarevskii, A. S. Zanina,
S. I. Shergina, I. E. Sokolov, E. M. Shvarts,
R. T. Ignash, and P. N. Tel'zhenskaya

UDC 542.91:547.424.1:547.385.1:
542.61:546.273.325

β -Diols are good extraction agents for boric acid [1], but methods for synthesizing them have a number of limitations.

We have previously developed a method for the synthesis of methoxyalkynyl ketones (I) and methoxy- β -diketones (III) [2, 3] based on ethers of tertiary mono- and diacetylenic alcohols.

In order to convert ketones (I) to diketones (III) a reaction with amines was used with subsequent hydrolysis of the aminovinyl ketones obtained with mineral acid



Addition of amines to β -methoxyalkynyl ketones (I) was carried out in alcohol at 60°C and γ -methoxy- β -aminoalkenyl ketones (II) were then obtained in 70-96% yield. Ketones (II) were hydrolyzed with dilute HCl in alcohol and γ -methoxy- β -diketones (III) were obtained in quantitative yield. In their IR spectra there is an intense broad band at 1640-1540 cm^{-1} characteristic of β -diketones. Preparation of β -diketones (III) from acetylenic ketones (I) can be carried out in one stage without isolation of aminovinyl ketones (II).

γ -Methoxy- β -diketones (IIIa-g) were reduced with NaBH_4 and γ -methoxy- β -diols (IVa-g) were obtained in 80-90% yield. In their IR spectra there is no trace of the absorption band characteristic of β -diketones and a broad band appears in the region 3600-3300 cm^{-1} .

Hydrogenation of diketones (IIIk-l) in the presence of platinized Raney Ni [4] and 0.1-0.3 ml of 10 N NaOH proceeds initially on the terminal carbonyl group and after absorption of 1 mole of H_2 the reaction products are ketoalcohols (Vk) and (VI). In their IR spectrum there is an intense band at 1700 cm^{-1} (unconjugated CO group) and a broad band at 3600-3500 cm^{-1} . In the PMR spectrum of compounds (Vk, VI) the C-H proton of the secondary alcohol group appears as a multiplet at δ 4.09 ppm, and the terminal CH_3 group is in the form of a doublet at δ 1.17. On prolonged hydrogenation of diketones (IIIj-l) in the presence of freshly platinized Raney Ni, the second carbonyl group is successfully hydrogenated and diols (IVJ-l) are obtained in 80-85% yield.

γ -Methoxy- β -diols are effective extraction agents for $\text{B}(\text{OH})_3$, achieving up to 99.9% extraction of $\text{B}(\text{OH})_3$ in one cycle. They do not alter their properties during extraction and can be used repeatedly [5].

Institute of Chemical Kinetics and Combustion, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Institute of Inorganic Chemistry, Academy of Sciences of the Latvian SSR, Riga. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 3, pp. 621-623, March, 1987. Original article submitted July 1, 1985.

TABLE 1. Properties of γ -Methoxy- β -aminoalkenyl Ketones, γ -Methoxy- β -diketones, and γ -Methoxy- β -diols

Compound	Yield, %	bp, °C (p, mm Hg); mp, °C	n_D^{20} (T° C)	Found Calculated, %			Empirical formula
				C	H	N	
3-Amino-4-methyl-4-methoxy-1-phenyl-2-penten-1-one (IIa)	92.4	97-98 (alcohol)	-	71.21	7.60	6.60	C ₁₃ H ₁₇ NO ₂
3-Amino-4-methyl-4-methoxy-1-phenyl-2-octen-1-one (IIb)	96.0	167 (1)	1.5805 (24)	71.21	7.81	6.32	C ₁₆ H ₂₃ NO ₂
				73.54	8.64	5.40	
3-Amino-4-methyl-4-methoxy-1-phenyl-2-decen-1-one (IIc)	91.7	195-196 (2)	1.5645 (21)	74.90	9.34	4.74	C ₁₈ H ₂₇ NO ₂
				74.70	9.40	4.84	
3-Amino-3-(1-methoxycyclohexyl)-1-phenyl-2-propen-1-one (IIId)	90.5	108 (alcohol)	-	74.27	8.14	5.33	C ₁₆ H ₂₁ NO ₂
				74.10	8.16	5.40	
5-Amino-2,6-dimethyl-6-methoxy-4-hepten-3-one (IIe)	90.9	95.5 (2.5)	1.5021 (20)	64.72	10.18	7.69	C ₁₀ H ₁₉ NO ₂
5-Amino-2,6-dimethyl-6-methoxy-4-dodecen-2-one (IIIf)	70.1	153.5 (4)	1.4930 (20)	64.83	10.34	7.54	C ₁₅ H ₂₉ NO ₂
				70.55	11.16	5.40	
5-Amino-6-methoxy-2,2,6-trimethyl-4-dodecen-3-one (IIg)	89.4	158 (3)	1.4890 (20)	70.54	11.45	5.48	C ₁₆ H ₃₁ NO ₂
				71.14	11.58	5.37	
2,6-Dimethyl-5-diethylamino-6-methoxy-4-dodecen-3-one (IIh)	87.5	135-137 (1)	1.4919 (20)	71.33	11.60	5.20	C ₁₉ H ₃₇ NO ₂
				73.01	11.87	4.58	
5-Diethylamino-6-methoxy-2,2,6-trimethyl-1-4-dodecen-3-one (IIi)	61.1	127 (2)	1.4860 (21)	73.26	11.97	4.50	C ₂₀ H ₃₉ NO ₂
				73.99	11.98	4.08	
4-Methyl-4-methoxy-1-phenyl-1,3-pentanedione (IIIa)	70	125-126 (1.5)	1.5681 (22)	73.79	12.08	4.23	C ₁₃ H ₁₆ O ₃
				70.52	7.31	-	
4-Methyl-4-methoxy-1-phenyl-1,3-octanedione (IIIb)	90.5	138-140 (1)	1.5510 (21)	70.89	7.30	-	C ₁₆ H ₂₂ O ₃
				73.27	8.39	-	
4-Methyl-4-methoxy-1-phenyl-1,3-dodecanedione (IIIc)	90.7	153 (1)	1.5430 (20)	73.25	8.45	-	C ₁₈ H ₂₆ O ₃
				74.44	9.03	-	
3-(1-Methoxycyclohexyl)-1-phenyl-1,3-propanedione (IIIId)	86.7	47-48 (CH ₃ OH)	-	74.49	8.81	-	C ₁₆ H ₂₆ O ₃
				73.85	7.73	-	
2,6-Dimethyl-6-methoxy-3,5-heptanedione (IIIe)	87.3	98 (25)	1.4610 (20)	73.82	7.74	-	C ₁₀ H ₁₈ O ₃
				64.42	9.68	-	
2,6-Dimethyl-6-methoxy-3,5-dodecanedione (IIIIf)	77.9	110-111 (1)	1.4650 (21.5)	64.49	9.74	-	C ₁₅ H ₂₈ O ₃
				70.17	10.96	-	
6-Methoxy-2,2,6-trimethyl-3,5-dodecanedione (IIIg)	90.7	127 (3)	1.4670 (20)	70.27	11.01	-	C ₁₆ H ₃₀ O ₃
				71.21	11.18	-	
4-Methyl-4-methoxy-1-phenyl-1,3-pentane-1,3-diol (IVa)	89.7	161 (1.5)	1.5200 (22)	71.07	11.08	-	C ₁₄ H ₂₀ O ₃
				69.55	9.02	-	
4-Methyl-4-methoxy-2-phenyl-1,3-octane-1,3-diol (IVb)	86.2	153 (1)	1.5184 (24)	69.61	8.99	-	C ₁₆ H ₂₆ O ₃
				71.90	9.47	-	
4-Methyl-4-methoxy-1-phenyl-1,3-dodecane-1,3-diol (IVc)	90.1	180 (1)	1.5075 (24)	72.14	9.88	-	C ₁₈ H ₃₀ O ₃
				73.36	10.01	-	
3-(1-Methoxycyclohexyl)-1-phenyl-1,3-propane-1,3-diol (IVd)	85.8	47-48 (alcohol)	-	73.43	10.03	-	C ₁₆ H ₂₆ O ₃
				73.85	7.73	-	
2,6-Dimethyl-6-methoxy-3,5-heptane-1,3-diol (IVe)	85.1	107 (3)	1.4500 (24)	73.82	7.74	-	C ₁₀ H ₂₂ O ₃
				62.93	11.55	-	
2,6-Dimethyl-6-methoxy-3,5-dodecane-1,3-diol (IVf)	80.4	145 (1)	1.4600 (20)	63.13	11.65	-	C ₁₅ H ₃₂ O ₃
				69.15	12.21	-	
6-Methoxy-2,2,6-trimethyl-3,5-dodecane-1,3-diol (IVg)	85.2	134 (1)	1.4570 (24)	69.18	12.39	-	C ₁₅ H ₃₄ O ₃
				70.13	12.58	-	
5-Methyl-5-methoxy-2,4-hexane-1,3-diol (IVj)	79.2	79-80 (1)	1.4598 (16)	70.02	12.49	-	C ₈ H ₁₈ O ₃
				59.01	11.00	-	
5-Methyl-5-methoxy-2,4-nonane-1,3-diol (IVk)	81.2	115-117 (2)	1.4585 (17)	59.23	11.18	-	C ₁₁ H ₂₄ O ₃
				64.50	11.80	-	
5-Methyl-5-methoxy-2,4-undecane-1,3-diol (IVl)	83.6	145 (5)	1.4570 (23)	64.66	11.84	-	C ₁₃ H ₂₈ O ₃
				67.00	12.03	-	
5-Methyl-5-methoxy-4-nonane-1,3-diol (IVk)	84.9	99 (2.5)	1.4480 (22)	67.19	12.15	-	C ₁₁ H ₂₂ O ₃
				64.88	10.38	-	
5-Methyl-5-methoxy-4-undecane-1,3-diol (IVl)	71.4	102 (2)	1.4495 (20)	65.31	10.96	-	C ₁₃ H ₂₆ O ₃
				67.72	11.36	-	
				67.78	11.38		

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument in CCl_4 or as a thin layer. PMR spectra were recorded on a Bruker AM-250 spectrometer in CCl_4 relative to HMDS. GLC was conducted on a Khrom-4 chromatograph using a 120×0.4 cm column with 0.5% PEGA on glass (0.25-0.22 mm), carrier gas N_2 . Acetylenic ketones were obtained according to [2], β -diketones (IIIj-m) were obtained according to [3].

3-Amino-4-methyl-4-methoxy-1-phenyl-2-octen-1-one (IIb). Ammonia was passed into a solution of 43 g of 4-methyl-4-methoxy-1-phenyl-2-octyn-1-one (Ib) in 100 ml of alcohol at 60°C for 3-6 h, the alcohol was distilled off, and the residue was distilled under vacuum. (IIb) was obtained. Aminovinyl ketones (IIa-j) were obtained similarly (Table 1).

Hydrolysis of 3-Amino-4-methoxy-1-phenyl-2-octen-1-one (IIb). To a new solution of 44 g (0.614 mole) of (IIb) in 100 ml of alcohol was added 15 ml of HCl and 15 ml of water; the mixture was agitated for 3 h at 60°C , cooled, and extracted with ether. The extract was washed with water and dried with MgSO_4 . After distillation 40 g of 4-methyl-4-methoxy-1-phenyl-1,3-octanedione was obtained, yield 90.5%. β -Diketones (IIIa-j) were synthesized in the same way.

γ -Methoxy- β -diketones from Acetylenic Ketones. 87 g (1 mole) of morpholine was added to 238.3 g (1 mole) of ketone (If) in 250 ml of alcohol; the mixture was agitated for 5 h at 75°C , cooled, supplemented with 100 ml of HCl and 100 ml of water, and agitated for 3 h at 60°C . It was then treated as described above. After distillation 233.6 g at 60°C . It was then treated as described above. After distillation 233.6 g of 2,6-dimethyl-6-methoxy-3,5-dodecanedione (IIIf) was obtained, yield 90.5%.

2,6-Dimethyl-6-methoxy-3,5-dodecanediol (IVf). To a solution of 40 ml of water and 70 ml of MeOH was added with agitation several KOH granules, 11.4 g of NaBH_4 , and 51.5 g of (IIIf) in 150 ml of MeOH. The mixture was maintained for 4 h at $50-60^\circ\text{C}$. The mixture was evaporated, and the residue was boiled for 2 h with a solution of 20% KOH, cooled, extracted with ether, and the extract was dried with MgSO_4 . After distillation (IVf) was obtained, yield 80.4%. The yields and constants for diols (IVa-j) are given in Table 1.

Hydrogenation of 5-Methyl-5-methoxy-2,4-hexanedione (IIIj). 4 g of Raney Ni was shaken for 1 min with 25 ml of water in a long-necked flask, and 1 g of H_2PtCl_6 in 3 ml of water was added. The aqueous solution was decanted, the catalyst was washed with 15 ml of alcohol, then 9.9 g of diketone (IIIj) in 30 ml of alcohol was added, followed by 0.1 ml of a 10 N solution of NaOH; hydrogenation was carried out until the calculated quantity of hydrogen had been absorbed. The alcoholic solution was decanted, saturated with NaCl, and extracted with ether. The extract was washed with a saturated solution of NaCl, dried with MgSO_4 , and distilled. 8 g of diol (IVj) was obtained, yield 79.2%. Diols (IVk, l) and ketoalcohols (Vk, l) were obtained similarly (see Table 1).

CONCLUSIONS

A new method for the synthesis of monomethyl ethers of triols starting from acetylenic ketones has been developed.

LITERATURE CITED

1. E. M. Shvarts, R. T. Ignash, M. M. Balode, P. N. Tel'zhenskaya, and A. F. Ievin'sh, *Izv. Akad. Nauk LatvSSR*, No. 3, 268 (1975).
2. S. I. Shergina, I. E. Sokolov, A. S. Zanina, and I. L. Kotlyarevskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 689 (1984).
3. A. S. Zanina, S. I. Shergina, G. N. Khabibulina, I. E. Sokolov, A. A. Kirchanov, R. N. Myasnikova, and I. L. Kotlyarevskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2781 (1977).
4. J. M. Sprague and H. Adkins, *J. Am. Chem. Soc.*, **56**, 2669 (1934).
5. I. L. Kotlyarevskii, A. S. Zanina, E. M. Shvarts, R. T. Ignash, S. I. Shergina, I. E. Sokolov, and G. N. Ivacheva, German Patent No. 3,110,126; *Chem. Abs.*, **98**, 16284e (1983).