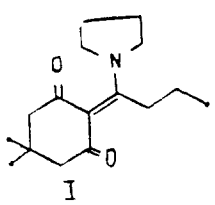
SYNTHESIS OF (±)-ANGUSTIONE BY THE REGIOSELECTIVE ALKYLATION OF ENAMINODIKETONES UNDER THE ACTION OF STRONG BASES

A. A. Zenyuk, A. V. Korchuk,
L. I. Ukhova, and L. G. Lis

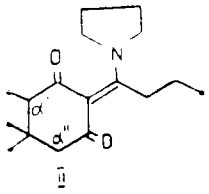
UDC 547.12+547.443.3+547.914.4

The synthesis of (±)-angustione has been carried out on the basis of a method that we have developed for the regio- and stereoselective alkylation of enaminodiketones of the cyclohexane series.

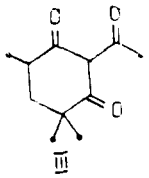
In the course of a study of the alkylation of enaminodiketones of the cyclohexane series (I) by the action of strong bases under conditions analogous to those given in [1], it has been established that methylation takes place with high regioselectivity, giving exclusively the product of α'-methylation (II) with high yield.



I



II



III

(±)-Angustione

In the present work we have considered the possibility of the successive introduction of several alkyl substituents into the cyclic part of the molecule of an enaminodiketone of type (I) and have performed the synthesis of (±)-angustione (III) (scheme), a natural compound isolated from the essential oil of Bakhousia angustifolia [2]. Schemes for the synthesis of angustione known in the literature are distinguished by their multistage nature and the poor availability of the starting materials [3-6].

The treatment with methyl iodide of the monoanion obtained under the action of 1.2 equivalents of lithium diisopropylamide on the enaminodiketone studied did not lead to the formation of alkylation products, either because of inadequate nucleophilicity or because of the formation of unstable OMe ethers which decomposed to the initial enaminodiketones in the course of the working up of the reaction mixture.

The introduction of a methyl group into the α'-position of the enaminodiketone (IV) was achieved by the formation of a dianion under the action of 2.5 equivalents of lithium diisopropylamide followed by treatment with 2.5 equivalents of methyl iodide.

In the working up of the reaction mixture after alkylation, partial hydrolysis of enaminodiketones of type (I) at the pyrrolidine group was observed, which considerably complicated their isolation. The reaction products were therefore subjected to complete hydrolysis with the isolation of the corresponding β-triketones. Subsequent transformation of the β-triketones obtained into enaminodiketones was effected by a known procedure [7].

The compound (VI) (72%) obtained as the result of the above-described reaction was converted into the enaminodiketone (V) with a yield of 71%.

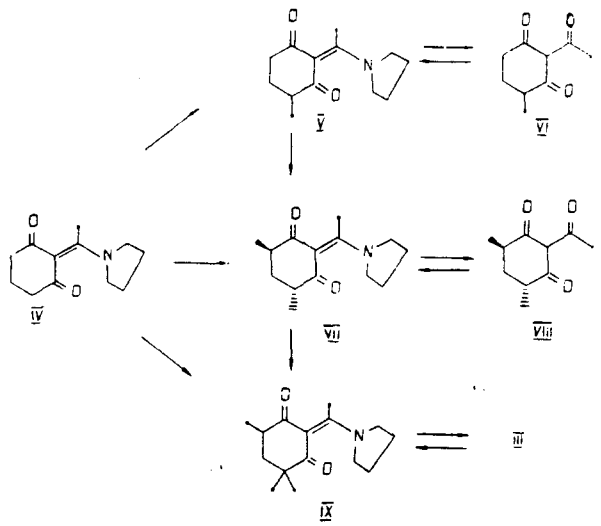
The introduction of a second methyl group into the α"-position of the enaminodiketone (V) was performed by the same method and gave product (VII) with the trans-orientation of the methyl groups. Here the yield of compound (VIII) was 66%, and the stage of its conversion

Institute of Bioorganic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk.
Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 611-617, September-October, 1990. Original article submitted December 12, 1989.

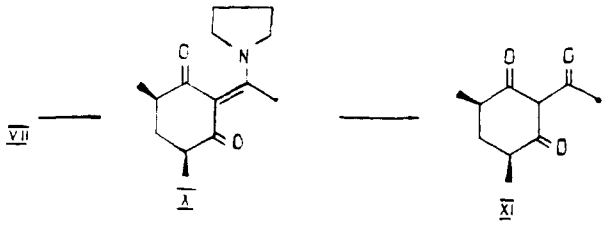
0009-3130/90/2605-0519$12.50

TABLE 1. Results of the Elementary Analysis of Compounds (III-IX)

Compound	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
III	67,23	8,20	—	$C_{11}H_{16}O_3$	67,35	8,16	—
IV	69,21	8,17	6,76	$C_{12}H_{17}NO_2$	69,57	8,21	6,76
V	70,46	8,54	6,30	$C_{13}H_{19}NO_2$	70,59	8,60	6,33
VI	64,06	7,02	—	$C_9H_{12}O_3$	64,29	7,14	—
VII	71,14	9,02	5,99	$C_{14}H_{21}NO_2$	71,49	8,93	5,96
VIII	65,96	7,75	—	$C_{10}H_{14}O_3$	65,94	7,69	—
IX	72,13	9,28	6,01	$C_{15}H_{23}NO_2$	72,29	9,24	5,62



into the enaminodiketone (VII) took place with 84% yield. We established that when the trans-isomer (VII) was left to stand, its partial isomerization into the corresponding cis- isomer (X) took place. After the hydrolysis of this compound, the corresponding β-triketone (XI) with the cis- orientation of the methyl groups was isolated



The multistage nature of the synthesis of compound (VII) impelled us to study the possibility of the direct formation of this compound from the enaminodiketone (IV). For this purpose, (IV) was treated with 2.5 equivalents of lithium diisopropylamide, followed by the addition of 1.2 equivalents of methyl iodide. At the same time, we used an increased amount of solvent (tetrahydrofuran) and a complexing additive (hexamethylphosphoramide). Then 1.2 equivalents of a solution of n-butyllithium in hexane was added with cooling to the monoanion of the enaminodiketone (V) that had formed, taking into account the fact that the diisopropylamine liberated in the first stage was present in the reaction mixture. The subsequent addition of 2.5 equivalents of methyl iodide and the working up of the reaction mixture under hydrolyzing conditions led to the dimethyl-substituted β-triketone (VIII) with a yield of 55%, and the β-triketone (VI) was isolated with a yield of 36%. The formation of the monomethyl-substituted product (VI) can be explained by the fact that in the first alkylation a certain amount of the initial enaminodiketone (IV) that had not taken part in the reaction remained, and this was methylated in the following stage, and also by the incomplete occurrence of the reaction at the stage of introducing a second substituent.

TABLE 2. Physicochemical Properties and Results of Spectral Methods of Analyzing Compounds (III-XI)

Compound	Yield, %	mp, °C (solvent)	IR (1500-1700) cm^{-1}	Mass spectrum, M^+	PMR, solvent, δ, ppm, J, Hz
III	45	Oil	1573 1675 Film	196	$CDCl_3$ (two tautomeric forms in a ratio of ~45 55): 1,17s (6H, 4-CH_3); 1,18d (3H, 6-CH_3, J CH_3 6H 6,0); 1,27 s (3H, 4-CH_3); 1,28d (3H, 6-CH_3, J CH_3 6H 6,0); 1,34s (3H, 6-CH_3); 1,63m (2H, 5-H_a); 1,75 m (2H, 5-H_B); 2,55 m (1H, 6-CH); 2,58 s (3H, CH_3CO); 2,59s (3H, CH_3CO); 2,85m (1H, 6-CH); 18,48s (1H, OH); 18,49s (1H, OH)
V	71	120--122 (benzene–hexane)	1535 1575 1625	221	C_6D_6: 1,03m (4H, 3-CH_2 pyrrolidine); 1,38 d (3H, 4-CH_3, J CH_3 4H_{ax} 6,3); 1,58m (1H, 5-CH_{ax} J 5H_{ax}/5H_{eq} 13,0, J 5H_{ax}/4H_{ax} 12,0, J 5H_{ax}/6H_{ax} 12,0, J 5H_{ax}/6H_{eq} 5,0); 1,79 dq (1H, 5-CH_{eq}, J 13,0, J 5H_{eq} 4H_{ax} 5,0, J 5H_{eq}/6H_{ax} 5,0, J 5H_{eq} 6H_{eq} 5,0); 2,21s (3H, CH_3CN); 2,35 m (1H, 4-CH_{ax}, J 12,0, J 6,3, J 5,0); 2,45m (2H, α-CH_2–pyrrolidine); 2,47m (1H, 6-CH_{ax}, J 6H_{ax} 6H_{eq} 17,0, J 12,0, J 5,0); 2,64dt (1H, 6-CH_{eq}, J 17,0, J 5,0, J 5,0); 3,30m (2H, α'-CH_2–pyrroline)
VI	72	Oil	1565 1665 Film	168	$CDCl_3$ (two tautomeric forms in a ratio of ~45 55): 1,19 d (3H, 4-CH_3, J CH_3 4CH 6,7); 1,31d (3H, 4-CH_3, J CH_3 4CH 6,7); 1,70 m (2H, 5-CH_a); 2,03m (2H, 5-CH_B); 2,41 m (2H, 4-CH); 2,57m (1H, 6-CH); 2,58 s (6H, CH_3CO); 2,69m (3H, 6-CH_2); 18,09s (1H, OH); 18,45s (1H, OH)
VII	84	111—113 (benzene–hexane)	1545 1580 1620	235	C_6D_6: 1,04m (4H, β-CH_2-pyrrolidine); 1,38d (6H; 4-CH_3, 6-CH_3, J CH_3 4H 6,6l, J CH_3 6H 6,6); 1,76t (2H, 5-CH_2, J CH_2 4H 6,6, J CH_2 6H 6,6); 2,21s (3H, CH_3CN) 2,51m (2H, α-CH_2–pyrrolidine); 2,64 hex. (2H, 4-CH, 6-CH, J 4H CH_3 6,6, J 4H 5CH_2 6,6, J 6H CH_3 6,6, J 6H 5CH_2 6,6); 3,32m (2H, α'-CH_2–pyrrolidine)
III*	66 55	Oil	1560 1665 Film	182	$CDCl_3$: 1,20d (3H, 4-CH_3, J CH_3/4H 7,0); 1,37d (3H, 6-CH_3, J CH_3/6H 7,0); 1,84m (2H, 5-CH_2); 2,58 m (1H, 6-CH); 2,80 m (1H, 4-CH); 18,25s (1H, OH)
IX	80	135—136 (benzene–hexane)	1553 1585 1625	249	$CDCl_3$: 1,14s (3H, 4-CH_3); 1,17d (3H, 6-CH_3, J CH_3 6H_{ax} 7,0); 1,19 s (3H, 4-CH_3); 1,60 t (1H, 5-CH_{ax}, J 5H_{ax} 5H_{eq} 12,5, J 5H_{ax}/6H_{ax} 12,5); 1,73 dd (1H, 5-CH_{eq}, J 12,5, J 5H_{eq} 6H_{ax} 5,0); 1,95 pent (2H, β-CH_2–pyrrolidine J βCH, β'CH_2 6,8, J βCH/αCH 6,8); 2,12pent (2H, β'-CH_2–pyrrolidine, J 6,8, J 6,8); 2,46 s (3H, CH_3CN); 2,55m (1H, 6-CH_{ax}, J 12.5, J 7,0, J 5,0); 3,58 t (2H, α-CH_2–pyrrolidine, J 6,8); 3,71t (2H, α'-CH_2–pyrrolidine, J 6,8)
X	—	121—123 (benzene–hexane)	1560 1627	235	C_6D_6: 1,07m (4H, β-CH_2-pyrrolidine); 1,45q (1H 5-CH_{ax}, J 5H_{ax}/5H_{eq} 12,0, J 5H_{ax} 6H_{ax} 12,0, J 5H_{ax} 4H_{ax} 12,0); 1,47 d (6H, 4-CH_3, 6-CH_3, J CH_3/6H 6,0, J CH_3 4H 6,0); 1,83dt (1H, 5-CH_{eq}, J 5H_{eq}/5H_{ax} 12,0, J 5H_{eq} 4H_{ax} 4,5, J 5H_{eq} 6H_{ax} 4,5) 2,26c (3H, CH_3CN); 2,44m (2H, 4-CH, 6-CH, J 12,0, J 6,0, J 4,5); 2,52t (2H, α-CH–pyrrolidine J αCH_2/α'CH_2 6,0); 3,33t (2H, α'-CH_2–pyrrolidine J 6,0)
XI	95	Oil	1560 1665 Film	182	$CDCl_3$; 1,18d (3H, 4-CH_3, J CH_3 4CH 7,0); 1,28d (3H, 6-CH_3, J CH_3 6CH 7,0); 1,47q (1H, 5-CH_{ax}, J 5H_{ax}/5H_{eq} 12,5, J 5H_{ax}/4H_{ax} 12,5, J 5H_{ax}/6H_{ax} 12,5); 2,04dt (1H, 5-CH_{eq}, J 12,5, J 12,5, J 5H_{eq} 4H_{ax} 4,0, J 5H_{eq} 6H_{ax} 4,0); 2,41 m (1H, 6-CH_{ax}, J 12,5, J 7,0, J 4,0); 2,60s (3H, CH_3CO); 2,78m (1H, 4-CH_{ax}, J 12,5, J 7,0, J 4,0)

*Compound (VIII) was obtained by two methods.

On the successive introduction of three methyl groups with the isolation of the intermediate products, the yield of the desired compound (IX) proved to be low because of the occurrence of a side reaction involving alkylation in the side chain. The enaminodiketone (IX) was therefore obtained by the methylation of compound (VII). After hydrolysis of the reaction product (IX), the corresponding triketone (III) – (±)-angustione – was obtained with a yield of 45%. The melting point of the copper complex obtained from the triketone (III) corresponded to that given in the literature for the copper complex of (±)-angustione [5].

The structures of the β-triketones obtained (III, VI, VIII, and XI) and of the corresponding enaminodiketones (V, VII, IX, and X) followed from the results of physicochemical analysis. Thus, the mass spectra of all these compounds exhibited the peaks of the molecular ions, while the elementary analyses of compounds (III-IX) confirmed their empirical formulas. In their UV spectra, absorption bands characteristic for enaminodiketones and β-triketones were observed in the 1500-1700 cm^{-1} region (Tables 1 and 2). The PMR and also the ^{13}C NMR spectra (Tables 2 and 3) contain the signals of all the fragments of the molecules of these compounds.

Analysis of the PMR spectra of the enaminodiketones obtained (V, VII, IX, and X) permitted certain conclusions to be drawn concerning the stereochemistry and conformational mobility of their molecules. Thus, the values of the SSCCs of the methylene protons at C-5 with the methine protons at C-4 and C-6 of the case of the enaminodiketones (V) and (X) unambiguously showed the pseudoequatorial position of the methyl substituents in the ring and, correspondingly, the cis- orientation of the methyl groups in the case of the enaminodiketone (X). The values of the SSCCs of the 5-CH_2 with the methine proton at C-6 for the enaminodiketone (IX) likewise showed the pseudoequatorial position of the 6-CH_3 group. At the same time, in the place of the enaminodiketone (VII) the observed SSCCs of the 5-CH_2 protons with the methine protons at C-4 and C-6 were the same, at 6.6 Hz, in connection with which it must be mentioned that the axial and equatorial protons at C-5 had identical chemical shifts. An analogous situation arises in relation to the methine protons at C-4 and C-6 of this compound. The observed averaging of the SSCCs is probably the result of a rapid inversion of the cyclohexane ring and shows the trans- orientation of the methyl groups at C-4 and C-6. This was confirmed by the fact that the sum of the SSCCs of the methine protons at C-4 and C-6 and of the methylene protons at C-5 for the enaminodiketone (X) amounted to 33 Hz (12 Hz × 2 + 4.5 Hz × 2), while the same sum for the enaminodiketone (VII) was 26.4 Hz (6.6 Hz × 4); consequently, one of the methine protons of compound (VII) had the pseudoequatorial orientation, which means that one of the methyl groups of the ring was pseudoaxial.

The predominantly pseudoequatorial position of the methyl substituents in the ring correlates well with the results of conformational analysis concerning the energetic advantageousness of the equatorial position of voluminous methyl substituents in a cyclohexane ring. The fact that on the repeated alkylation of the enaminodiketone (V) the trans- isomer (VII) with the axial orientation of one of the methyl groups was formed predominantly is explained by the occurrence of the reaction under the conditions of kinetic control. The lower thermodynamic stability of this isomer was confirmed by the partial isomerization of compound (VII) into compound (X) on standing.

EXPERIMENTAL

PMR spectra were taken on a Bruker WM-360 instrument with a working frequency of 360 MHz using TMS as internal standard. Chemical shifts are given in ppm on the δ scale, and spin-spin coupling constants (SSCCs) are given in Hz. ^{13}C NMR spectra were taken on a Bruker WM-360 instrument at a working frequency of 90 MHz with TMS as internal standard and $CDCl_3$ as solvent. IR spectra were obtained on a UR-20 instrument in KBr tablets if not otherwise stated. Mass spectra were obtained on a Varian MAT-311 spectrometer. Reactions were performed in THF, which was redistilled over lithium tetrahydroaluminate and was stored over metallic sodium. Hexamethylphosphoramide was redistilled over calcium oxide and was stored over 4 Å molecular sieves. Methyl iodide was redistilled over P_2O_5 and was stored over 4 Å molecular sieves and drops of mercury. Diisopropylamine was redistilled and was stored over KOH. n-Butyllithium was used in the form of a 1.48 N solution in hexane. The occurrence of the reaction and the individuality of the compounds were monitored by the TLC method on Silufol UV-254 plates (Kavalier, Czechoslovakia). Column chromatography was conducted on silica gel L 40/100 (Lachema–Chemapol) under pressure. Lithium diisopropylamide (LDA) was prepared by mixing in THF at −15°C for 15 min equimolar amounts of n-butyllithium in hexane and diisopropylamine in an atmosphere of argon. Hexamethylphosphoramide was used as complexing additive in an amount equivalent to the amount of base employed.

α'Alkylation of Enaminodiketones of the Cyclohexane Series. General Procedure. To a solution of LDA in THF cooled to −75°C was added 10 mmole of an enaminodiketone in 30 ml of THF at −(70-75)°C. The mixture was stirred at this temperature for 1 h, and methyl iodide was added. The resulting solution was stirred for 2 h and was poured into 100 ml of a 1 N solution of NaOH which, after 4 h, was acidified with concentrated HCl and extracted with ether (5 × 60 ml). The combined extracts were dried over Na_2SO_4, the solvent was driven off in vacuum, and the residue was chromatographed on silica gel (with ether–hexane as eluent).

2-[1'-(N-pyrrolidyl)ethylidene]cyclohexane-1,3-dione (IV). When 0.1 mole of 2-acetylcyclohexane-1,3-dione and an equimolar amount of pyrrolidine were boiled with a Dean-Stark trap by the method of [7], 16.5 g (80%) of compound (IV) was obtained.

2-Acetyl-4-methylcyclohexane-1,3-dione (VI). When 25 mmole of LDA in 30 ml of THF was used in the above-given alkylation procedure, 10 mmole of compound (IV) and 25 mmole of methyl iodide yielded 1.2 g (72%) of the triketone (VI).

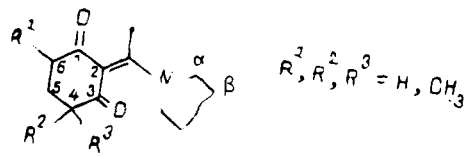
4-Methyl-2-[1'-(N-pyrrolidyl)ethylidene]cyclohexane-1,3-dione (V). When 7 mmole of 2-acetyl-4-methylcyclohexane-1,3-dione (VI) and an equimolar amount of pyrrolidine were boiled in benzene with a Dean–Stark trap, 1.1 g (71%) of compound (V) was obtained.

trans-2-Acetyl-4,6-dimethylcyclohexane-1,3-dione (VIII). Method A. When 12 mmole of LDA in 15 ml of THF was used, 5 mmole of compound (V) and 12 mmole of methyl iodide yielded 0.6 g (66%) of the triketone (VII) and 0.2 g of the triketone (VI).

Method B. At −(70-75)°C, a solution of 10 mmole of 2-[1'-(N-pyrrolidyl)ethylidene]cyclohexane-1,3-dione (IV) was added to a solution of 25 mmole of LDA prepared from 16.9 ml of a 1.48 N solution of n-butyllithium, 3.5 ml of diisopropylamine, and 6 ml of hexamethylphosphoramide in 60 ml of THF. The mixture was stirred at the same temperature for 1 h, and 0.7 ml of methyl iodide was added. After 1 h, 8.1 ml of butyllithium was added, and after 1 hour's stirring, an additional 1.6 ml of methyl iodide. The solution was stirred for 2 h and was then poured into 100 ml of a 1 N solution of NaOH and, after 4 h, the mixture was acidified with concentrated HCl and extracted with ether (5 × 60 ml). The combined extracts were dried over Na_2SO_4, the solvent was driven off in vacuum, and the residue was chromatographed on silica gel. This gave 1.0 g (55%) of compound (VIII) and 0.6 g (36%) of compound (VI).

trans-4,6-Dimethyl-2-[1'-(N-pyrrolidyl)ethylidene]cyclohexane-1,3-dione (VII). From 5 mmole of 2-acetyl-4,6-dimethylcyclohexane-1,3-dione and an equimolar amount of pyrrolidine, by boiling in benzene with a Dean–Stark trap, 1.0 g (84%) of compound (VII) was obtained.

TABLE 3. Details of the ^{13}C NMR Spectra of the Enaminodiketones



Carbon atom	IV	V	VII	IX
C-1	193,00 s	195,60 s	195,56 s	197,73 s
C-2	112,63 s	111,93 s	110,87 s	110,60 s
C-3	193,00 s	192,63 s	195,56 s	194,83 s
C-4	38,18 t	40,77 d	37,84 d	40,91 s
C-5	21,59 t	28,54 t	35,72 t	43,88 t
C-6	38,18 t	36,73 t	37,84 d	37,06 d
CH_3-CN	24,21 q	24,24 q	24,36 q	24,43 q
α-CH_2-pyrr.	51,50 t	51,86 t	51,86 t	51,82 t
	55,37 t	55,24 t	55,13 t	55,97 t
β-CH_2-pyrr.	24,54 t	24,56 t	24,57 t	24,61 t
	25,04 t	25,04 t	25,04 t	25,04 t
C—N	178,17 s	178,34 s	178,68 s	178,92 s
CH_3	—	16,54 q	17,02 q	16,78 q
	—	—	17,02 q	25,14 q
	—	—	—	26,97 q

2-Acetyl-4,4,6-trimethylcyclohexane-1,3-dione – (±)-Angustione (III). When 10 mmole of LDA in 15 ml of THF was used, 4 mmole of 4,6-dimethyl-2-[1'-(N-pyrrolidyl)ethylidene]cyclohexane-1,3-dione (VII) and 10 mmole of methyliodide gave 0.35 g (45%) of compound (III).

4,4,6-Trimethyl-2-[1'-(N-pyrrolidyl)ethylidene]cyclohexane-1,3-dione (IX). From 1 mmole of 2-acetyl-4,4,6-trimethylcyclohexane-1,3-dione (III) and an equimolar amount of pyrrolidine, by boiling in benzene with a Dean–Stark trap, 0.2 g (80%) of compound (IX) was obtained.

Copper Complex of the Diketone (III). A solution of 1 mmole of 2-acetyl-4,4,6-trimethylcyclohexane-1,3-dione (III) in 5 ml of ether was stirred with 5 ml of saturated copper acetate solution for 30 min. The organic layer was separated off and the aqueous layer was extracted with ether (3 × 10 ml). The combined extracts were dried over Na_2SO_4. The solvent was driven off in vacuum. The residue was crystallized from hexane. This gave 0.11 g of the copper complex. mp 201-202°C; according to the literature, mp 201-202°C [5].

LITERATURE CITED

1. N. M. Berry, M. C. P. Parey, and L. M. Harwood, Synthesis, No. 6, 476 (1986).
2. A. R. Penfold, J. Proc. Roy. Soc., N. S. Wales, 57, 300 (1924).
3. W. R. Chan and C. H. Hassall, J. Chem. Soc., No. 8, 2860 (1955).
4. J. C. Bardham and R. N. Adhya, J. Chem. Soc., No. 7, 219 (1956).
5. G. R. Ensor and W. Wilson, J. Chem. Soc., No. 11, 4068 (1956).
6. A. Groot and B. J. M. Jansen, J. Royal Netherland Chem. Soc. 95, No. 4, 81 (1976).
7. A. A. Akhrem, A. M. Monseenkov, and E. A. Meshcheryakova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1348 (1968).

BROMINATION OF EMODIN

R. A. Muzychkina and L. N. Pribytkova

UDC 547.673.6:542.944

Using emodin as an example, it has been shown that in the bromination of hydroxyanthraquinones the qualitative composition and quantitative ratio of the reaction products depend on the nature of the brominating agent and the solvent, the ratio of the reactants, and the temperature regime. In order to obtain bromo-3-methyl-1,6,8-trihydroxyanthraquinone it is recommended to use dioxane dibromide in acid solution as the brominating agent, and to obtain 5-bromo-3-methyl-1,6,8-trihydroxyanthraquinone the same reagent in dioxane solution. The optimum conditions for obtaining 3-bromomethyl-1,6,8-trihydroxyanthraquinone by the methods of initiated bromination and photobromination have been selected.

Halogen derivatives of hydroxyanthraquinones are promising intermediates in the synthesis of biologically active compounds [1]. Depending on the conditions, halogenation is possible in the side chains and in the aromatic nucleus (α- or β-position); however, it is impossible to achieve a strictly selective process [2]. Because of the dissimilar reactivities of the rings, in an excess of halogenating agent up to eight α-, β-, and α,β-bromo-substituted derivatives have been observed, the separation of which was effected by chromatographic methods. This makes the use of individual compounds difficult and requires the selection of the optimum conditions for obtaining particular products [3]. The bromination of emodin (I) was first performed in 1888, but the structures of the mono- and dibromoderivatives obtained were not shown [4]. There are no later applications in the literature on the bromination of emodin.

In the present paper we describe the bromination of emodin by dioxane dibromide in CH_3COOH and dioxane solutions, by bromine in acidic (CH_3COOH, H_2SO_4) and organic (C_2H_4OH, $CHCl_3$, CCl_4, $C_4H_8O_2$) media, and also in the presence of initiators – benzoyl peroxide and UV light. The emodin/bromine ratio was varied from 1:1 to 1:10 in a temperature regime from 5°C to the

S. M. Kirov Kazakh State University, Alma-Ata.

Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 618-621, September-October, 1990. Original article submitted November 24, 1989.

0009-3130/90/2605-0524$12.50