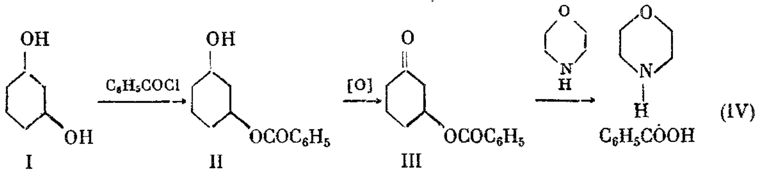
7. E. G. Avvakumov, V. V. Boldyrev, and I. D. Kosobudskii, Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1972, No. 9, Issue 4, 45.
8. V. N. Voitsekhovskii, Zap. Vses. Mineralog. Obshch., 92, No. 5, 587 (1963).
9. W. Gabes and H. Gerding, J. Mol. Struct., 14, 267 (1972).
10. A. Gornu and R. Massot, Compilation of Mass Spectral Data, Heyden and Son, London (1966).
11. T. E. Gallon, J. G. Higginbotham, M. Prutton, and H. Tokutaka, Surf. Sci., 21, 224 (1970).

ALKYLATION OF 3-SUBSTITUTED CYCLOHEXANONE ENAMINES

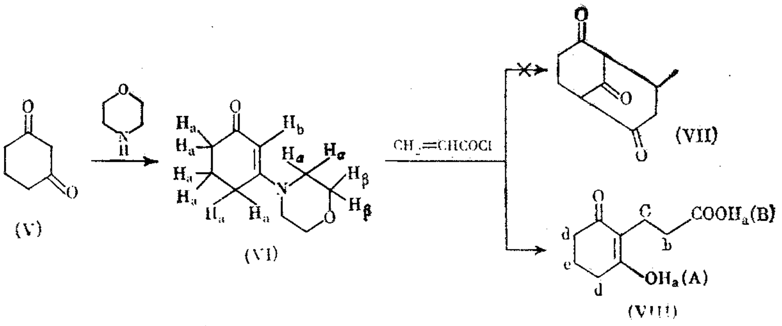
E. N. Aredova, P. A. Krasutskii,
M. M. Krayushkin, S. S. Novikov,
V. V. Sevost'yanova, and A. G. Yurchenko

UDC 66.095.253:547.594.3

The behavior of 4-substituted cyclohexanone enamines when condensed with acryloyl chloride was described in a previous communication [1]. The behavior of cyclohexanones that have a substituent in the 3 position was studied in the present paper. In contrast to 4-benzoylcyclohexanone, 3-benzoylcyclohexanone (III) does not form the enamine when reacted with morpholine. Instead the morpholine salt of benzoic acid (IV) is formed under a wide range of conditions.



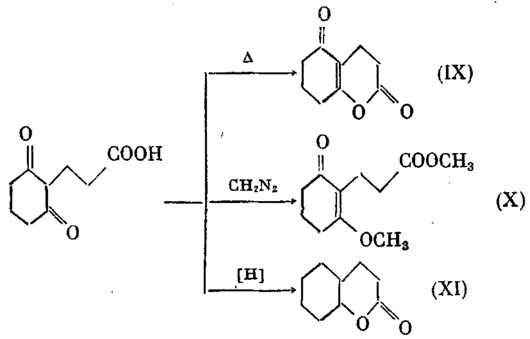
In contrast to 1,4-cyclohexadione, 1,3-cyclohexadione (V) reacts with morpholine to give only the monoenamine (VI).



In contrast to monoketone enamines, 1-morpholinocyclohexen-3-one (VI) is stable, which can be explained by the conjugation of the carbonyl group with the intracyclic double bond. This apparently explains the fact that the alkylation of enamine (VI) with acryloyl chloride leads to the monoalkylation product (VIII) and not the bicyclic product (VII). Probably, due to conjugation with the carbonyl group, in (VI) the isomerization of the double bond in the 6 position is made difficult and alkylation at this center fails to occur. Since in the literature only the melting point is given for (VIII), additional data was needed in order to identify the compound obtained by us. The H_A and H_B protons have acid properties, and acid (VIII) when titrated with 0.1 N alkali solution behaves like a dibasic acid (g-eq = 92, which is half of the molecular weight). The NMR spectrum of (VIII) was taken in pyridine and is easily interpreted as being the spectrum of the pyridinium salt: $12.97 = 2H_a$ (region of acid protons that form an H bond), $2.95 = 2H_b$, $2.86 = 2H_c$, $2.44 = 2H_e$, $1.84 = 2H_d$.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Kiev Polytechnic Institute. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 926-928, April, 1978. Original article submitted March 22, 1977.

A number of transformations was run in order to confirm the structure of (VIII) chemically.



Structures (IX)-(XI) are in agreement with the physicochemical and elemental analysis data.

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument, while the NMR spectra were taken on a Varian A-60DA spectrometer (60 MHz). The mass spectra were obtained on a Varian CH-6 MAT GmbH instrument using the following conditions: direct insertion of the sample into the ion source, energy of ionizing electrons 70 eV, emission current 100 μA, accelerating voltage 1.75 kV, and temperature of ion source 180°C.

3-Benzoylcyclohexanone (III) was synthesized as described in [2, 3]. Morpholine salt of benzoic acid (IV) [4], mp 121-122° (from water). The IR spectrum resembles the spectrum of benzoic acid. Based on the mixed melting point and IR spectrum, the salt obtained by counter synthesis is identical with the salt isolated from the reaction.

1-Morpholinocyclohexen-3-one (VI) was obtained as described in [4] and has mp 92-94°, cf. [5]. Infrared spectrum (ν, cm^{-1}): 1640 (C=O), 1580 (C=C). PMR spectrum (δ, ppm): 1.97-2.5 m ($6H_a$), 3.21-3.27 q ($4 H_\alpha$), 3.65-3.81 q ($4 H_\beta$), 5.25 s ($1 H_b$). Mass spectrum (m/e): 181($M^{+\cdot}$), 153($M^{+\cdot}$ – CO), 125($M^{+\cdot}$ – 2CO), 95($M^{+\cdot}$ – C_4H_8ON).

1-(Cyclohexa-1',3'-dion-2'-yl)-3-propanoic Acid (VIII). The alkylation with acryloyl chloride was run as described in [6]. The imonium salt was decomposed by refluxing with water for 1 h to give (VIII) in 32% yield, mp 179-180°, cf. [7]. Infrared spectrum (ν, cm^{-1}): 1700 (COO), 1580, 1610 (C=O), 1645 $\left(\overset{O}{\overset{/\!/}{C}}-C=\right)$ 3250-3280 (OH).

Lactone of 1-(Cyclohexa-1',3'-dion-2'-yl)-3-propanoic Acid (IX). Acid (VIII) was sublimed twice at 180° (10 mm) to give the lactone (IX) in 90% yield, mp 48-50°. Infrared spectrum (ν, cm^{-1}): 1600 (C=C–C=O), 1660 (C=C), 1700 (C=O), 1285 (=C–O), 1040, 1090 (–C–O). Mass spectrum (m/e): 166 ($M^{+\cdot}$), 138 ($M^{+\cdot}$ – CO), 110 ($M^{+\cdot}$ – 2CO), 82 ($M^{+\cdot}$ – 3CO). Found: C 65.42; H 6.01%. $C_9H_{10}O_3$. Calculated: C 65.65; H 6.07%.

Dimethyl Ester of 1-(Cyclohexa-1',3'-dion-2'-yl)-3-propanoic Acid. The esterification was run as described in [8]. Removal of the solvent gave a viscous oil, which was purified on Al_2O_3 (I activity). Infrared spectrum (ν, cm^{-1}): 1200, 1170 ($-C-OCH_3$), 1250 (=C–O), 1090 ($O-CH_3$), 1615 (C=C), 1740 (C=O).

Perhydrocoumarin (XI). Amalgamated Zn dust was obtained by stirring a mixture of 15 g of Zn dust, 1 g of $HgCl_2$, 0.8 ml of conc. HCl, and 5 ml of water for 5 min. Then the aqueous layer was decanted, 25 ml of conc. HCl, 25 ml of water, and 1.9 g of acid (VIII) were added, the mixture was refluxed for 10 h, and then 25 ml of the solution was distilled off, another 25 ml of conc. HCl was added, and 25 ml of the solution was again distilled off. This operation was repeated once more and the residue was steam-distilled. The distillate was extracted with ether, dried over Na_2SO_4, the ether was removed, and the residue was distilled at 96–101° (2 mm). Yield 81%, n_D^{20} 1.4778. Found: C 70.40; H 9.50%. $C_9H_{14}O_2$. Calculated: C 70.20; H 9.19%.

CONCLUSIONS

The behavior of 3-substituted cyclohexanones in enamination and alkylation reactions was studied; the reaction of morpholinocyclohexen-3-one with acryloyl chloride gives 1-(cyclohexa-1',3'-dion-2'-yl)-3-propanoic acid.

LITERATURE CITED

1. E. N. Aredova, V. V. Sevost'yanova, M. M. Krayushkin, S. S. Novikov, and N. F. Karpenko, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 1489.
2. E. R. Jones and F. Sondheimer, J. Chem. Soc., 1949, 616.
3. H. Brown and C. Gara, J. Am. Chem. Soc., 83, 2952 (1961).
4. G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Tarrell, J. Am. Chem. Soc., 85, 207 (1963).
5. G. V. Kondrat'eva, V. I. Gunar, L. F. Ovechkina, S. I. Zav'yalov, and A. I. Krotova, Izv. Akad. Nauk SSSR, Ser. Khim., 1967, 636.
6. P. W. Hickmott and J. R. Hargreaves, Tetrahedron, 23, 3151 (1967).
7. I. I. Nazarov and S. I. Zav'yalov, Zh. Obshch. Khim., 25, 515 (1955).
8. M. Neeman and Y. Hashimoto, J. Am. Chem. Soc., 84, 2972 (1962).

EFFECT OF POLYSTYRENE ANIONITE ON EQUILIBRIUM RATIO BETWEEN DIASTEREOMERIC COPPER COMPLEXES OF ALANINE DIPEPTIDES

L. V. Vinogradova, V. A. Tsyryapkin,
Yu. N. Belokon', and V. M. Belikov

UDC 541.12.038:541.127.4:541.632:547.466

Diastereomers, whose ratio is not equal to one, are formed in the epimerization of the metal complexes of dipeptides that have more than one asymmetric C atom [1]. In the present paper it was shown that the position of the equilibrium between the diastereomeric complexes of dipeptides can be changed by adding anionite CG-400, which has the ability to sorb these complexes by electrostatic and hydrophobic forces, to the solution.

EXPERIMENTAL

As the starting reagents we used the dipeptides L-Ala-L-Ala and (DL)-Ala-(DL)-Ala, which were obtained from Reanal, and the strongly basic ion-exchange resin CG-400 II, which was obtained from Serva.

The chromatographic analysis of the diastereomers was run on a KLA-3B amino acid analyzer under the following conditions: a temperature of 55°C, a 14× 0.9 cm column packed with sulfo cationite Aminex Q-15 and buffered to pH 4.25, and an elution rate of 90 ml/h. Under these conditions the (DL)-Ala-(DL)-Ala is separated on the column into two peaks: D-Ala-L-Ala and L-Ala-D-Ala are eluted from the first peak (retention time 20 min), while L-Ala-L-Ala and D-Ala-D-Ala are eluted from the second peak (retention time 23 min). The dipeptide (DL)-Ala-(DL)-Ala, which contains four diastereomers, can be used instead of a mixture of the two diastereomers L-Ala-L-Ala and D-Ala-L-Ala, since the reaction of enantiomeric dipeptides and optically pure diastereomers with achiral resins and achiral reagents is completely identical.

For the epimerization to $1.25 \cdot 10^{-4}$ mole of alanylalanine (both L-Ala-L-Ala and (DL)-Ala-(DL)-Ala were taken as the starting materials) were added equimolar amounts of $Cu(OH)_2CO_3 \cdot 2H_2O$ and salicylaldehyde (SA) in 4.3 ml of 0.025 M borate buffer solution with pH 12.7. The amount of anionite CG-400 II was varied from 0 to 5 equivalents. The mixture was thermostatted at 50°. The resin precipitate was separated from the solution and analyzed separately. For the chromatographic analysis 1 ml of the solution was treated with 0.06 mole of conc. HCl. The precipitate was washed with water, 1 ml of distilled water was added, and the mixture was treated with 0.06 ml of conc. HCl. The obtained solutions were transferred to the chromatographic column of the analyzer.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 929-931, April, 1978. Original article submitted May 6, 1977.