6. K. Venkataraman (editor), The Analytical Chemistry of Synthetic Dyes, Wiley (1977).
7. A. Zhunke, Nuclear Magnetic Resonance in Organic Chemistry [Russian translation], Mir, Moscow (1974), p. 50.
8. A. Gordon and R. Ford, The Chemist's Companion, Wiley (1973).
9. German Patent No. 593672; Frdl., 20, 1313 (1934).

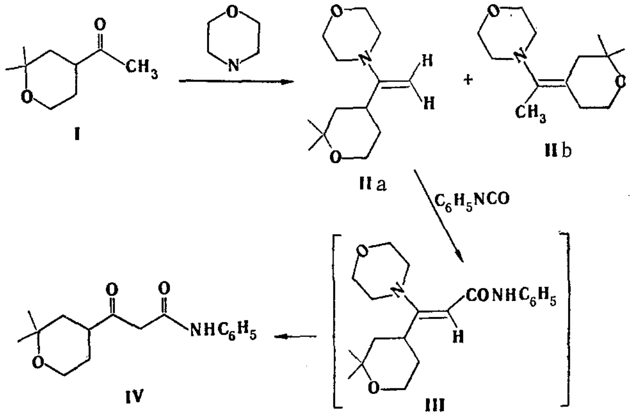
PREPARATION OF β-(2,2-DIMETHYLTETRAHYDRO-4-PYRANYL)-β-OXOPROPIONIC ACID ANILIDE

R. S. Vartanyan and Zh. V. Kazaryan

UDC 547.811+547.483.3

A method for the synthesis of β-(2,2-dimethyltetrahydro-4-pyranyl)-β-oxopropionic acid anilide by the successive conversion of methyl 2,2-dimethyltetrahydro-4-pyranyl ketone to an enamine and reaction of the latter with phenyl isocyanate with subsequent hydrolysis in an acidic medium is proposed.

In a continuation of our research on the synthesis of β-dicarbonyl compounds, viz., derivatives of saturated six-membered heterocycles [1, 2], we undertook the synthesis of β-(2,2-dimethyltetrahydro-4-pyranyl)-β-oxopropionic acid anilide starting from methyl 2,2-dimethyltetrahydro-4-pyranyl ketone (II) [3], which was converted to a morpholino enamine by the method proposed in [4] with titanium tetrachloride as the catalyst. Despite our expectations, instead of two alternative enamines IIa,b we obtained only enamine IIa. The desired β-keto anilide IV was obtained by reaction of the latter with phenyl isocyanate and subsequent hydrolysis. The indicated transformations are presented in the following scheme:



EXPERIMENTAL

Analysis by gas–liquid chromatography was carried out with a Khrom-4 chromatograph with glass packed columns with XE-60 silicone on Chromaton N-AW silanized with hexamethyldisiloxane as the liquid phase. The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard.

1-Morpholino-1-(2,2-dimethyltetrahydro-4-pyranylidene)ethane (IIa). A solution of 7.6 g (0.04 mole) of $TiCl_4$ in 30 ml of pentane was added gradually to a cooled (to 0°C) mixture of 12 g (0.077 mole) of ketone I and 21 g (0.24 mole) of morpholine in 50 ml of absolute ether in a nitrogen atmosphere, after which the reaction mixture was warmed up to room temperature and refluxed for 6 h. The resulting precipitate was removed by filtration and washed with absolute ether, the filtrate was distilled to remove the solvent, and the residue was vacuum

---

A. L. Mndzhoyan Institute of Fine Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan 375014. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1189-1190, September, 1981. Original article submitted December 10, 1980.

0009-3122/81/1709-0882$07.50

distilled to give 10.4 g (60.0%) of enamine IIa with bp 122-128°C (4 mm), n_D^{20} 1.4912, and d_4^{20} 1.0041. IR spectrum: 1650 cm^{-1} (C=C). PMR spectrum (CCl_4): 1.06 and 1.12 (6H, s, CH_3), 1.60 (4H, m, 3- and 5-CH_2), 2.50 (5H, m, 4-CH and CH_2OCH_2), 3.52 (6H, m, 6-CH_2 and CH_2NCH_2), and 2.00 ppm (3H, s, CH_3C=). Found: C 69.4; H 10.1; N 6.0%. $C_{13}H_{23}NO_2$. Calculated: C 69.3; H 10.3; N 6.2%.

β-(2,2-Dimethyltetrahydro-4-pyranyl)-β-oxopropionic Acid Anilide (IV). A 2.4-g (0.02 mole) sample of phenyl isocyanate was added with stirring to a solution of 4.5 g (0.02 mole) of enamine IIa in 40 ml of dry chloroform, after which stirring was continued for 4-5 h, and the mixture was then refluxed for 1 h. The solvent was removed by distillation, and the residue was dissolved in carbon tetrachloride. Pentane was added to the solution, and the precipitated crystals of N-phenylcarbamoylmorpholine (mp 157-158°C) were separated. The residual 5.4 g (78%) of III was hydrolyzed without further purification by acidification with 7% hydrochloric acid solution. The mixture was allowed to stand at room temperature for 24 h, after which it was extracted with benzene. The extract was dried with magnesium sulfate, the solvent was removed by distillation, and the residue was crystallized from ether. If necessary, the product was purified through the copper chelate (mp 125-126°C). Workup gave 5.2 g (82% based on III) of amide IV with mp 71-72°C. IR spectrum: 1710 (C=O, ketone), 1675 (C=O, amide), and 3300 cm^{-1} (N—H). PMR spectrum ($CDCl_3$): 1.2 (6H, s, 2-CH_3), 1.60 (4H, m, 3- and 5-CH_2), 2.80 (1H, m, 4-CH), 3.70 (2H, m, 5-CH_2), 3.60 (2H, s, $COCH_2CO$), and 7.4 (5H, m, C_6H_5). Found: C 70.1; H 7.7; N 5.0%. $C_{16}H_{21}NO_3$. Calculated: C 69.8; H 7.7; N 5.1%.

LITERATURE CITED

1. R. S. Vartanyan, Zh. V. Kazaryan, and S. A. Vartanyan, Khim. Geterotsikl. Soedin., No. 3, 309 (1979).
2. R. S. Vartanyan, Zh. V. Kazaryan, A. P. Engoyan, and S. A. Vartanyan, Khim. Geterotsikl. Soedin., No. 4, 466 (1979).
3. R. A. Kuroyan, A. I. Markosyan, and S. A. Vartanyan, Arm. Khim. Zh., 32, 801 (1979).
4. W. A. White and H. Weingarten, J. Org. Chem., 32, 213 (1967).

MECHANISM OF THE THIO-CLAISEN REARRANGEMENT OF 3-METHYLALLYL PHENYL SULFIDE

T. A. Danilova, R. G. Aukharieva,
S. N. Petrov, S. Ya. Grobovenko,
and E. A. Viktorova

UDC 542.971.2:547.712:547.735

The thio-Claisen rearrangement of isomeric 3- and 1-methylallyl phenyl sulfides was investigated. It is demonstrated that the thio-Claisen rearrangement of the 3-methyl isomer is preceded by its thioallyl rearrangement to the 1-methyl isomer. The latter undergoes thio-Claisen rearrangement to o-(3-methylallyl)thiophenol, which is cyclized to 2-ethyl-2,3-dihydrobenzothiophene and 2-methylthiochroman under the reaction conditions.

We have previously reported [1-3] that the final product of the thio-Claisen rearrangement of 3-methylallyl phenyl sulfide (I) both in the presence of nitrogen bases [2, 3] and under heterogeneous acid-catalysis conditions [1, 3] is a mixture of two-ring compounds of the 2,3-dihydrobenzothiophene and thiochroman series. In the present research the sequence of the conversions of sulfide I to two-ring compounds was ascertained in a homogeneous medium in the presence of quinoline, since under these conditions the principal rearrangement process is not complicated by side and secondary reactions.

The realization of the rearrangement of sulfide I (Table I) showed that the composition of the resulting mixture of sulfides II-V is close to that obtained previously by Kwart and

---

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1191-1194, September, 1981. Original article submitted February 18, 1981.