HETEROATOM DERIVATIVES OF AZIRIDINE

V. Cleaving of Ethylenimine by Anhydrides of Monocarboxylic Acids. New Method of Synthesizing β-Acylaminoethyl Esters of Organic Acids*

M. G. Voronkov and L. A. Fedotova

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 2, pp. 302–304, 1967

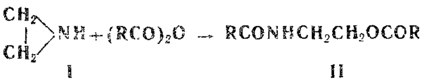
UDC 547.717+547.435

The reaction of ethylenimine with anhydrides of monocarboxylic acids $(RCO)_2O$ gives the β-acylaminoethyl esters of the acids $RCONHCH_2CH_2OCOR$, hitherto unknown (only an ester with R = Me known). When $R = C_6H_5$ dibenzoylaminoethyl benzoate $(C_6H_5CO)_2 \cdot NCH_2CH_2OCOC_6H_5$ is also formed. The IR spectra of the compounds prepared are studied.

Even at low temperatures ethylenimine (I) reacts with monocarboxylic acids, to give unstable ethylenammonium salts, readily changing into N-(β-hydroxyethyl)amides of the corresponding acids [1–3].

With chlorides of carboxylic acids, I gives N-(β-chloroethyl)amides, while in the presence of hydrogen chloride acceptors it forms the N-ethylenimides of the corresponding acids [4,5].

We show that the hitherto uninvestigated reaction of I with anhydrides of monocarboxylic acids takes place with opening of the ethylenimine ring, the equation being



I II

$R =$ a) CH_3, b) $n\text{-}C_3H_7$, c) C_6H_7

R = alkyl or aryl

The β-acylaminoethyl esters of monocarboxylic acids (II) are formed in 70–85% yields. Previously only one compound of type II with R = Me, viz. β-acetylaminoethyl acetate (IIa), made by two stage acetylation of β-ethanolamine (III) according to the equations

$$\underset{III}{HOCH_2CH_2NH_2} + (RCO)_2O \rightarrow HOCH_2CH_2NHCOR \rightarrow$$

$$\xrightarrow{-(RCO)_2O} \underset{II}{RCOOCH_2CH_2NHCOR} \xrightarrow{+(RCO)_2O} \underset{IV}{RCOOCH_2CH_2N(COR)_2}$$

$R = CH_3$

has been known.

However, the IIa obtained in this way contains an impurity of N,N,O-triacetate (IV), which cannot be removed by distillation (yield of IV with R = Me can reach 50%).

Pure IIa can be obtained by acetylating III with acetyl chloride in tetrahydrofuran solution, using ammonia gas as the hydrogen chloride acceptor [8].

Our method of preparing IIa from I and acetic anhydride allows it to be obtained in high yield and in one stage.

I reacts with butyric anhydride and benzoic anhydride similarly to acetic anhydride.

In the latter case, under the particular conditions used, it is possible to obtain, along with IIa, β-(N-dibenzoylamino)ethyl benzoate (V, $R = C_6H_5$) as well.

The IR spectra of the compounds obtained (see figure*) well confirm the structures. They all have two strong absorption bands at 1630–1687 and 1693–1742 cm^{-1} corresponding to the valence vibrations of C=O in amides and in esters of carboxylic acids, respectively.

In all the spectra the valence vibrations of the C—O ester bond correspond to a strong and constant absorption band at 1285 cm^{-1}, and a second band, not so constant in its position (1245–1291 cm^{-1}) corresponds to these vibrations too. With IIc and V, with $R = C_6H_5$, a characteristic double bond ~ 1100, 1130 cm^{-1} also belongs to these vibrations. The spectra of II also have very strong absorption at 3290–3330 cm^{-1}, inherent in the valence vibrations of the N–H group in primary amides. The lack of this band in the spectrum of V is conclusive proof that it is a N-dibenzoyl derivative.

EXPERIMENTAL

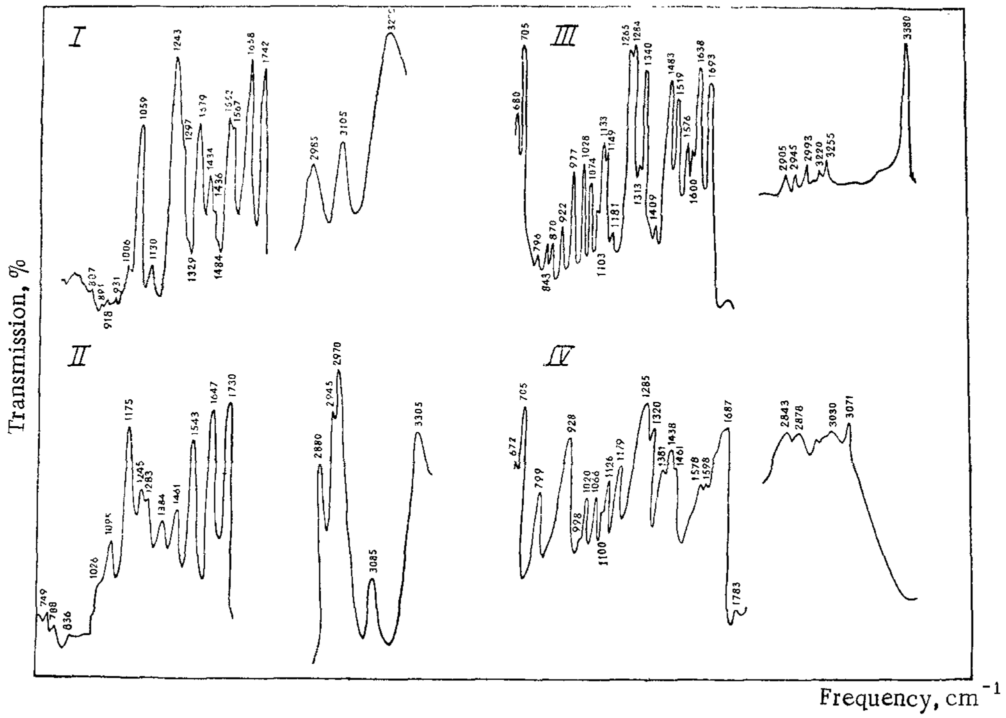
Starting materials. The 98% ethylenimine on sale was dried over Na and distilled, 56–57°, n_D^{20} 1.4123. Commercial acetic and benzoic anhydrides were used. Butyric anhydride 192–194°, n_D^{20} 1.4140 was prepared by reacting butyric acid with $SiCl_4$, then thermally decomposing the resultant tetrabutyroxysilane [9].

β-Acetylaminoethyl acetate (IIa). A solution of 57.5 g (0.56 mole) Ac_2O in 50 ml benzene was cooled to 0°, and 5.93 g (0.14 mole) I added, and the whole then heated on a water-bath for 30 min, and left overnight. Next day the solvent and excess Ac_2O were distilled off, and the residue vacuum-distilled. Repeated vacuum distillation gave 15.5 g (77.5%) IIa, 133–135° (4 mm), n_D^{20} 1.4557. The literature gives 142° (5.1 mm), n_D^{20} 1.4510. Found: C 49.43; H 7.49; N 9.53%; M 143.5. Calculated for $C_6H_{11}NO_3$: C 49.62; H 7.59; N 9.66% M 145.1. Colorless liquid, readily soluble in water (neutral reaction) and the usual organic

---

*For Part IV see [10].

*The IR spectra were determined with an IKS-14 spectrograph, in the regions 700–1800 and 2800–3500 cm^{-1}.



IR spectra: 1) Acetylaminoethyl acetate (IIa); 2) β-butyrylaminoethyl butyrate (IIb): 3) β-benzoylaminoethyl benzoate (IIc); 4) dibenzoylaminoethyl benzoate (V).

solvents. Heating with excess 0.1 N NaOH caused practically complete saponification.

Reaction of equimolecular amounts of I and Ac_2O gave a lower yield of IIa, 63.5%, along with 4% of a viscous yellow oil, 150–165° (4 mm), n_D^{20} 1.4520 not further investigated.

β-Butyrylaminoethyl butyrate (IIb). 45.0 g (0.28 mole) butyric anhydride was stirred and held at 0°, and 8.6 g (0.2 mole) I added dropwise. The reaction mixture was heated for 2 hr on a boiling water bath, then refluxed for 1 hr, after which the products were vacuum-distilled. 28.0 g (70%) IIb distilled over at 160–165° (7 mm), n_D^{20} 1.4520. Found: C 59.65; H 9.18; N 7.24%; M 197.8. Calculated for $C_{10}H_{19}NO$: C 59.72; H 9.47; N 6.90%; M 201.0. Also obtained was 2.9 g viscous yellow oil 240–243° (7 mm), n_D^{20} 1.4765, not further investigated. Reaction of I with butyric anhydride in a 1:1 ratio gives a lower yield of IIb, 56%.

β-Benzoylaminoethyl benzoate (IIc) and β-dibenzoylamino benzoate (V, R = C_6H_5). 4.3 g (0.1 mole) I in 10 ml ether was added dropwise to a solution of 22.6 g (0.1 mole) benzoic anhydride in 40 ml ether. The solid which crystallized out on evaporating off the solvent was treated with hot petrol ether. The solution was filtered, and on cooling white crystals of V came out, mp 115°. Yield 4.6 g (12%). V was readily soluble in ether, EtOH, benzene, $ChCl_3$, EtOAc, and dioxane, it had limited solubility in petrol ether and hexane, and was insoluble in water. Found: C 71.66; H 5.66; N 5.08%; M 258.5. Calculated for $C_{23}H_{19}N_2O_4$: C 71.37; H 5.57; N 5.20%; M 269.0.

That part of the reaction product which was insoluble in petrol ether was readily soluble in the usual organic solvents, (other than hexane and petrol ether), and it was twice recrystallized from aqueous EtOH. Yield of IIc 14.0 g (50%), white leaflets mp 89°. Found: C 73.41; H 5.04; N 3.55%. Calculated for $C_{16}H_{15}NO_3$: C 74.00; H 5.09; N 3.75%.

When the reaction was run with a small excess of (0.1 g), the yield of IIc, mp 86–87° was 23.0 g (85.5%). However, then it was not possible to isolate V.

REFERENCES

1. G. D. Jones, J. Zomlefler and K. Hawkins, J. Org. Chem., **9**, 500, 1944.
2. S. Gabriel, Ber., **21**, 1049, 1888.
3. D. H. Powers, V. B. Schatr and L. B. Clapp, J. Am. Chem. Soc., **77**, 907, 1955.
4. S. Fabriel and R. Steizner, Ber., **28**, 2925, 1895.
5. H. Bestian. Ann., **566**, 210, 1950.
6. K. Hens, and W. Bebenburg, Ann., **595**, 55, 1955.
7. E. T. Roe, T. D. Miles and D. Swern, J. Am. Chem. Soc., **74**, 3442, 1952.
8. I. Wadso, Acta Chem. Scand., **16**, 487, 1962.
9. K. D. Petrov and M. I. Itkina, ZhOKh, **17**, 220, 1947.
10. M. G. Voronkov and L. A. Fedotova, KhGS [Chemistry of Heterocyclic Compounds], 545, 1966.

12 October 1965

Institute of Organic Synthesis,
AS LatvSSR, Riga