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DIACETAMIDES—I

SYNTHESES OF N,N-DIACETYL-β-AMINOESTERS[1]

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Abstract—The action of boiling acetic anhydride on β-ureidoesters, β-N-carbonyl esters and β-aminoesters was studied. It was shown that no cyclization of β-ureidoesters occurred and that N,N-diacetyl and N-acetyl-β-aminoesters were the reaction products in all three cases. A satisfactory separation of these compounds by chromatography was achieved and their physical properties determined. The mechanism of the reactions is discussed briefly.

DURING an investigation concerning the retention of optical activity by the cyclization of β-ureido-esters to 5,6-dihydrouracils[3], it was of interest to determine the nature of products resulting from the reaction of β-ureidoesters with acetic anhydride.

The literature reveals that this reaction has not been investigated with α- or β-ureidoesters. The reaction of boiling acetic anhydride on unsubstituted and substituted ureas[4] results in the fission of these compounds with evolution of CO_2 and formation of diacetamides. Diacetamide derivatives have also been prepared by the action of acetic anhydride on amines,[5] monoacetylated amines,[5] isocyanates[6] and azides.[7] The syntheses of a few N,N-diacetyl-α-aminoesters[8] have also been reported, the corresponding acetylamino[9,10] and haloesters[11] being used as starting materials. However, no reaction of acetic anhydride on β-N-carbonyl esters has been investigated.

Since ureas may be considered as precursors of isocyanates, acetic anhydride should yield the same final products with β-N-carbonyl esters and β-ureidoesters. Consequently, the reaction of β-ureidoesters, β-N-carbonyl esters and β-aminoesters with acetic anhydride was investigated. It has been shown that N,N-diacetyl- and N-acetyl-β-aminoesters are the products in all three cases.

Preparation from β-ureidoesters. The properties of β-ureidoesters are summarized in Table 1. When these compounds are refluxed in excess acetic anhydride, carbon

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[1] Partially reported at the 1-st Yugoslav Congress of Pure and Applied Chemistry, Zagreb, June 1960.

[2] This paper is to be submitted by A. Kornhauser in partial fulfilment of the Ph.D. degree.

[3] D. Keglević and A. Kornhauser, *Croat. Chem. Acta* **31**, 47 (1959).

[4] A. W. Hofmann, *Ber. Dtsch. Chem. Ges.* **14**, 2733 (1881); E. A. Werner, *J. Chem. Soc.* **109**, 1120 (1916); J. N. Baxter, J. Cymerman-Craig, M. Moyle and R. A. White, *Ibid.* 659 (1956).

[5] For leading references see C. D. Hurd and A. G. Prapas, *J. Org. Chem.* **24**, 388 (1959).

[6] A. Wurtz, *Ann. Chim. Phys.* [3] **42**, 54 (1854); C. Naegeli and A. Tyabji, *Helv. Chim. Acta* **16**, 349 (1933).

[7] H. Goldstein and K. Stern, *Helv. Chim. Acta* **23**, 809 (1940); J. H. Weisburger, *J. Org. Chem.* **18**, 864 (1953).

[8] This type of compound is more correctly referred to as diacetamido esters. However, the name N,N-diacetylamino- indicates the relation between the amino acid and amine and has, therefore, been used in this paper.

[9] R. H. Wiley and O. H. Borum, *J. Amer. Chem. Soc.* **72**, 1626 (1950).

[10] J. C. Sheehan and E. J. Corey, *J. Amer. Chem. Soc.* **74**, 4555 (1952).

[11] E. Taschner and H. Szewczuk, *Roczniki Chem.* **25**, 426 (1951); S. Mejer and E. Taschner, *Ibid.* **28**, 669 (1954).

TABLE 1. SUBSTITUTED β-UREIDOESTERS $R—CH(NHCONHR')—CH_2—CO_2C_2H_5$

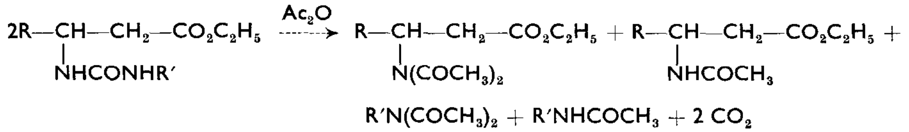
No.	R	R′	Molecular formula	M.p.° or B.p.°/mm	% Yield (crude)	Calc.			Found		
						C%	H%	N%	C%	H%	N%
III	H	1-$C_{10}H_7$	$C_{16}H_{18}N_2O_3$	4–125·5	94·0	67·11	6·34	9·78	67·17	6·39	9·77
IV	H	n-C_6H_{13}	$C_{12}H_{24}N_2O_3$	69·5–70·5	96·0	58·99	9·90	11·67	58·96	9·67	11·62
V	CH_3	1-$C_{10}H_7$	$C_{17}H_{20}N_2O_3$	134–135	80·5	67·98	6·71	9·33	68·05	6·74	9·41
VI	CH_3	H	$C_7H_{14}N_2O_3$	46–48	86·0	48·26	8·10	16·08	48·17	8·35	16·07
VII	C_6H_5	1-$C_{10}H_7$	$C_{22}H_{22}N_2O_3$	80–82	87·0	72·90	6·12	7·73	73·15	6·42	7·95
VIII	C_6H_5	n-C_4H_9	$C_{16}H_{24}N_2O_3$	161–5/0·015	85·0	65·73	8·28	9·58	65·59	8·36	9·34

TABLE 2. SUBSTITUTED N,N-DIACETYL-β-AMINOESTERS $R—CH(N(COCH_3)_2)—CH_2—CO_2C_2H_5$

No.	R	Molecular formula	B.p. °C/mm	n_D^{20}	Calc.				Found			
					C%	H%	N%	acetyl %	C%	H%	N%	acetyl %
IX	H	$C_9H_{15}NO_4$	80–83/0·018	1·4593	53·72	7·51	6·96	42·60	53·77	7·52	7·02	43·64
X	CH_3	$C_{10}H_{17}NO_4^{a,b}$	84–86/0·020	1·4530	55·80	7·96	6·51	40·00	55·77	8·13	6·75	40·40
XI	$(CH_3)_2CHCH_2$	$C_{13}H_{23}NO_4^{c}$	115–118/0·020	1·4550	60·68	9·01	5·44	33,40	60·94	8·93	5·70	33·00
XII	C_6H_5	$C_{15}H_1$-$NO_4^{b,d}$	122–125/0·015	1·5078	64·96	6·91	5·05	30·95	64·73	6·95	5·27	30·28

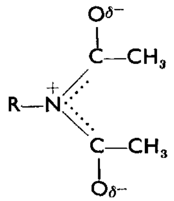
[a] M 215; found 218. [b] Freezing point in benzene. [c] $[\alpha]_D^{20}$ + 55·1 ± 2 (c 1·2, benzene). [d] M. W. calc. 277; found 276.

dioxide is evolved, its amount being nearly equimolar to the β-ureidoester used. Accordingly, four final products are anticipated.



$$2R\text{—}\underset{NHCONHR'}{CH}\text{—}CH_2\text{—}CO_2C_2H_5 \xrightarrow{Ac_2O} R\text{—}\underset{N(COCH_3)_2}{CH}\text{—}CH_2\text{—}CO_2C_2H_5 + R\text{—}\underset{NHCOCH_3}{CH}\text{—}CH_2\text{—}CO_2C_2H_5 + R'N(COCH_3)_2 + R'NHCOCH_3 + 2\,CO_2$$

The separation of the products is a tedious process as fractional distillation failed and chromatography on alumina and florisil led to partial decomposition of diacetamides. The latter may be ascribed to the effect of polarity and catalytic activity of chromatographic adsorbents on diacetamides:



Finally a deactivated charcoal[12]–Celite (2:1) column proved inert toward diacetamides, and effective in separating the mixture of diacetamide- and acetamide- compounds.

The physical and analytical data of isolated N,N-diacetyl-β-aminoesters are summarized in Table 2. Protected from moisture, these compounds are stable even after long standing. Compound XI represents the first optically active N,N-diacetylaminoester prepared. Hydrolysis of XI with hydrochloric acid gives optically pure L-β-amino-δ-methyl-hexanoic acid (β-homoleucine)[13], indicating that no racemization occurs. It is interesting that the optical rotation of ethyl L-N-acetyl-β-homoleucinate (XIV)[14] and XI are similar in value but opposite in direction, the absolute difference in rotation being about 100°.

From Table 3 it can be seen that the yields of N,N-diacetyl- and N-acetyl-β-aminoesters depend on the nature of both substituents in the β-ureidoester. No attempt was made to determine the exact amount of the products formed from the 3-nitrogen atom of the β-ureido-ester molecule. It was found, however, that in all cases the yields of N,N-diacetylamines are very high.

Preparation from β-N-carbonyl esters. This proved to be the best method for the synthesis of N,N-diacetyl-β-aminoesters. The yields (Table 3) are high and the separation of the reaction mixture by chromatography easy as only two components are produced.

Preparation from β-aminoesters. The total yields of acetylated β-aminoesters are relatively high (Table 3) but even after prolonged refluxing in acetic anhydride, the yields of isolated N,N-diacetyl-β-aminoesters are relatively small.

The infra-red absorption maxima of isolated products show that N,N-diacetyl- and N-acetyl-β-aminoesters absorb strongly in the 5·7 μ (C=O) region. N-acetyl-β-aminoesters and N-acetylamines show the usual amide (C=O) band at 6·06 μ and N—H deformation vibration at 6·45 μ. With N,N-diacetylamines the

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[12] G. Schramm and J. Primosigh, *Ber. Dtsch. Chem. Ges.* **76**, 373 (1943).

[13] K. Balenović and D. Brovet-Keglevic, *Arh. kem.* **23**, 1 (1951).

[14] D. Keglević, *Arh. kem.* **26**, 83 (1954).

absorption of the two diamido carbonyls is shifted toward a shorter wavelength, and the 6·45 μ peak disappears.[10,15,16] However, with N,N-diacetyl-β-aminoesters the diamide doublet and ester carbonyl band appear as two narrow maxima.[17] All these compounds show a medium absorption in 9·7 μ (indicative of C—N) region. An additional absorption in 10 μ region was observed with all N,N-diacetylamine compounds; this band is absent in the N-acetylamino analogues.

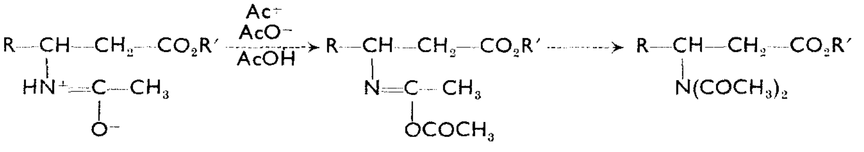
The fact that XI and XIV were optically pure regardless whether they are obtained from the corresponding β-ureidoester, β-N-carbonyl ester or β-aminoester, indicates that resonance between optically active carbon and nitrogen does not take place in these reactions. Further conclusions may be drawn from the experimental data:

TABLE 3. YIELDS OF N,N-DIACETYL-β-AMINOESTERS = A AND N-ACETYL-β-AMINOESTERS = B

Starting compound	R	R′	A%	B%
$R-CH-CH_2CO_2C_2H_5$	H	$1\text{-}C_{10}H_7$	53·0	8·4
$NHCONHR'$	H	$n\text{-}C_6H_{13}$	39·6	14·3
	CH_3	$1\text{-}C_{10}H_7$	69·5	25·0
	CH_3	H	22·1	40·7
	$(CH_3)_2CHCH_2$	$1\text{-}C_{10}H_7$	32·0	28·2[a]
	C_6H_5	$1\text{-}C_{10}H_7$	24·0	31·2
	C_6H_5	$n\text{-}C_4H_9$	20·5	10·0
$R-CH-CH_2CO_2C_2H_5$	H		67·0	10·6
$N{=}C{=}O$	CH_3		47·0	14·8
	$(CH_3)_2CHCH_2$		46·0	24·2[a]
	C_6H_5		51·3	12·5
$R-CH-CH_2CO_2C_2H_5$	H		44·0	45·0
NH_2	CH_3		26·2	48·3
	$(CH_3)_2CHCH_2$		32·4	47·8[a]
	C_6H_5		15·3	23·2

[a] Ref. 14 reports [α]D −30·3° (*c*, 2·30 abs. EtOH). Found: [α]D −29·5° ± 2 (*c*, 2·10, abs.EtOH), [α]D −45·0° ± 2 (*c*, 2·10 benzene).

1. *From β-aminoesters.* N-acetyl-β-aminoesters are considered the primary products. By refluxing ethyl β-aminobutyrate in acetic anhydride for one hour, only ethyl N-acetyl-β-aminobutyrate (XIII) is formed; on the other hand, pure XIII refluxed in acetic anhydride for seven hours, gives a mixture of N,N-diacetyl-β-aminoester (X) and unchanged XIII. Thus, the action of the anhydride on N-acetyl-β-aminoesters is explained by the formation of an intermediate isoimide[18] which rearranges by intramolecular acylation to N,N-diacetyl-β-aminoester:



$$R-CH(HN^{+}{=}C(O^{-})-CH_3)-CH_2-CO_2R' \xrightarrow[AcOH]{Ac^{+}\ AcO^{-}} R-CH(N{=}C(OCOCH_3)-CH_3)-CH_2-CO_2R' \longrightarrow R-CH(N(COCH_3)_2)-CH_2-CO_2R'$$

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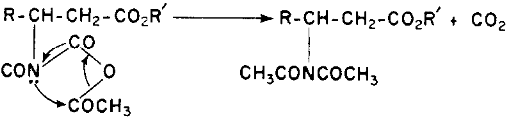
[15] J. C. Sheehan and E. J. Corey, *J. Amer. Chem. Soc.* **74**, 360 (1952).

[16] B. Witkop and J. B. Patrick, *J. Amer. Chem. Soc.* **74**, 3861 (1956).

[17] R. A. Abramovitch, *J. Chem. Soc.* 1413 (1957).

[18] D. Davidson and H. Skovronek, *J. Amer. Chem. Soc.* **80**, 376 (1958).

2. *From β-N-carbonyl esters.* The action of acetic anhydride on isocyanates with the formation of diacetamides proceeds, according to several authors[19,20] through a mixed acid anhydride which loses CO_2 and rearranges to the corresponding diacetamide. Accordingly, from β-N-carbonyl esters the following intermediate anhydride should be formed:



However, taking into account that special precautions for the purity of acetic anhydride were taken, the yields of N-acetyl-β-aminoesters seem rather high.

3. *From β-ureidoesters.* These compounds do not react with acetic anhydride at 60° and evolution of CO_2 is not observed below 100°. Concerning the rate and total yield of CO_2 evolved, β-ureidoesters and β-N-carbonyl esters behave similarly under identical experimental conditions. The action of acetic anhydride on V, when followed by I.R. spectra of the reaction mixture, reveal that only very small amounts of isocyanate are present. After fifteen minutes a very weak band at 4·4 μ (N=C=O) appears, its intensity increasing to a medium value after thirty minutes and then decreasing rapidly to only slight intensity.

When V is refluxed for thirty minutes in acetic anhydride neither the starting material, nor the isocyanate can be isolated. Taking into account that more N-acetyl- and N,N-diacetyl-amino compounds are formed than CO_2 evolved, the formation of an unstable mixed anhydride which decomposes during the treatment of the reaction mixture may be assumed. Thus, the action of acetic anhydride on β-ureidoesters may proceed by the elimination of one of the amine groups from the ureido molecule and the simultaneous formation of a mixed carbaminic–carboxylic anhydride from the remaining part of the molecule. The presumption that the relative basicity of the nitrogen atoms in the β-ureidoester molecule determines which of the two amine groups will be eliminated is attractive. However, too little is known about the relative basicity of β-aminoesters compared with the amines concerned to form a conclusion at present.

EXPERIMENTAL[21]

Materials and methods

(a) *Acetic anhydride* (BDH, *analar*) was purified from traces of acetic acid by fractionation through a Siegwarth column (20 theoretical plates). The remaining light yellow liquid was distilled over fused sodium acetate through a 30 cm column, the middle fraction with a b.p. range of 1° being collected. This acetic anhydride was used throughout the work.

(b) *Carbon-celite powder.* Charcoal (BDH, activated) was treated according to Schramm and Primosigh.[12] After careful drying over P_2O_5, an intimate 2:1 mixture of carbon and celite (BDH) was prepared.

(c) *Determination of* CO_2. The reflux condenser of the apparatus was connected with two traps cooled by dry ice–aceton bath, followed by an anhydrone and two alternatively connected ascarite tubes. Dry nitrogen was passed through the system during the reaction.

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[19] W. Dieckmann and F. Brest, *Ber. Dtsch. Chem. Ges.* **39,** 3052 (1906); C. Naegeli and A. Tyabji, *Helv Chim. Acta* **17,** 931 (1934); **18,** 142 (1935).

[20] L. Ötvös, J. Marton and J. Meisel-Agoston, *Tetrahedron Letters* No. 2, 15 (1960).

[21] All m.ps and b.ps are uncorrected. Alumina used for chromatography (acid and neutral) was Merck's (Darmstadt) reagent grade and florisil (60–100 mesh silica magnesia) was from Floridin Co. Infra-red spectra were determined as liquid films with a Perkin-Elmer 137 spectrophotometer. Microacetyl determinations were carried out by alkaline saponification according to Kuhn-Roth.

Preparation of β-ureidoesters

Ethyl β-[-3-(phenyl)-ureido] butyrate[22] (I) and ethyl L-β-[-3-(1-naphtyl)-ureido]-δ-methyl hexanoate[3] (II), $[\alpha]_D$ −20·6° (ethanol) have been described in the literature. Other β-ureidoesters were obtained according to the general method given by Morsch.[22] For III, V and VII the starting material was the corresponding β-aminoester (15 mmoles) dissolved in absolute ether (50 ml) to which 1-naphthyl isocyanate (15 mmoles) in absolute ether (50 ml) was slowly added. After standing overnight at 0°, white crystals separated, which were collected and dried. For IV and VIII the starting material was the corresponding β-N-carbonyl ester[23] (10 mmoles), which was added to the appropriate amine (10 mmoles) as described above. VI was received by introducing dry ammonia in a solution of β-N-carbonyl butyric ethyl ester[23] (20 mmoles) in dry chloroform. After removing the solvent *in vacuo*, the remaining viscous oil was dissolved in chloroform and pet ether added till turbidity. After cooling overnight, white crystals separated. For analyses all β-ureidoesters were recrystallized from chloroform–pet ether.

Preparation of N,N-*diacetyl- and* N-*acetyl-β-aminoesters*

(a) *From β-ureidoesters.* A ratio of 6–17 mmoles of β-ureidoester was suspended in 15–40 ml acetic anhydride and refluxed under anhydrous conditions for 3–4 hr. The evolution of CO_2 started within 5–15 minutes and reached its maximum after 1–2 hr of heating. When β-(1-naphtyl)-ureidoesters (II, III, V and VII) were used, the oil obtained after the removal of acetic anhydride *in vacuo* was dissolved in 5–20 ml benzene and pet ether added to turbidity. After standing at 0°, N,N-diacetyl-1-naphthylamine was collected and washed with small quantities of pet ether. Yields of 70–80% were obtained based on the β-ureidoester used. This precipitation was omitted when I, IV, VI and VIII were used, as no crystalline compounds could be obtained. In all cases the oils were distilled (0·05 mm) and the colorless distillate chromatographed on the charcoal-celite column. (See under Chromatography.)

(b) *From β-*N-*carbonyl esters.* A ratio of 2·5–22·8 mmoles of β-N-carbonyl ester was dissolved in 5–25 ml acetic anhydride and refluxed under anhydrous conditions for 3–4 hr. Acetic anhydride was removed *in vacuo* and the resulting oils distilled and chromatographed as under (a).

(c) *From β-aminoesters.* To 3–6 mmoles of β-aminoester a tenfold quantity (by weight) of acetic anhydride was gradually added with shaking. After the evolution of heat ceased, the solution was refluxed under anhydrous conditions for 10–12 hr. Acetic anhydride was removed *in vacuo* and the remaining oils distilled and chromatographed as under (a). In the case of V, the reaction was also carried out by addition of a few drops of pyridine but this had no effect on the total yield or the ratio of the reaction products X and XIII.

Chromatography

Attempted resolution of N,N-*diacetyl- and* N-*acetyl-amino derivatives on celite, alumina and florisil.* All experiments were carried out with the reaction mixture obtained by the action of acetic anhydride on ethyl β-[-3-(phenyl)-ureido] butyrate (I). The oil obtained after removal of acetic anhydride and distillation *in vacuo*, was put on the celite column. In all cases the oil came out as a single peak. On acidic and neutral alumina and florisil, eluted successively with petroleum ether–benzene, benzene and chloroform, the oil spread in a continuous series of oily fractions, in all of which white crystals identified as acetanilide, appeared. When pure diacetanilide was passed under the same conditions through acidic and neutral alumina and florisil up to 60% of the compound placed on the column was eluted as acetanilide.

Chromatography on carbon–celite column. Per 1 g of previously distilled reaction mixture 16 g of carbon–celite powder was mixed in a slurry with pet ether–chloroform (5:2), and a column (1·5 × 50 cm) packed. The chromatogram was developed successively with 100 ml pet ether–chloroform (5:2) and 75 ml chloroform, 15 ml fractions being collected. N,N-diacetylamino derivatives are eluted first, while chloroform eluates N-monoacetyl derivatives. The purity of fractions was examined by elemental anlayses, refractive indices, acetyl determinations, and I.R. spectra. Pure N,N-diacetyl-β-aminoesters absorb with the same intensity in 9·7 μ and 10 μ region, and by estimation of relative intensity of absorption in 10 μ region the purity of fractions was judged. If the mixture contained

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[22] K. Morsch, *Monatsh.* **64**, 333 (1934).

[23] K. Schlögl, *Monatsh.* **89**, 61 (1958).

two different N,N-diacetylamino compounds, as was the case with I, IV, VI and VIII, overlapping always occurred and no complete separation of the two components could be obtained even after repeated chromatography. The poorest resolution was achieved with the products obtained from I; from IV 70% N,N-diacetyl-1-hexylamine and from VIII 45% N,N-diacetyl-1-butylamine were isolated after repeated chromatography.

N,N-*Diacetyl*-1-*butylamine*. (Found: N, 9·11. $C_8H_{15}NO_2$ requires: N, 8·91%).

N,N-*Diacetyl*-1-*hexylamine*. (Found: C, 64·96; H, 10·64; N, 7·62. $C_{10}H_{19}NO_2$ requires: C, 64·83; H, 10·34; N, 7·56%).

Table 2 summarizes physical and analytical data of isolated N,N-diacetyl-β-aminoesters, and in Table 3 the yields of N,N-diacetyl- and N-acetyl-β-aminoesters based on the chromatographic data are presented.

Acid hydrolysis of ethyl L- N,N-*diacetyl-β-amino-δ-methyl hexanoate* (XI)

498 mg (1·94 mmoles) of XI ($[\alpha]_D$ +55·1°, in benzene) was refluxed with 5 ml HCl (1:1) for 2 hr. The mixture was evaporated *in vacuo*, the remaining oil dissolved in water, re-evaporated and taken in 50 ml H_2O. A 10% excess of freshly prepared suspension of Ag_2O was gradually added under stirring. AgCl was filtered off, H_2S introduced into the filtrate, Ag_2S removed by centrifugation and the clear supernatant evaporated to dryness. The residue was dissolved in hot absolute ethanol, treated with charcoal and precipitated with absolute ether. 51·4 mg (18·2%) of white crystals, m.p. 215–216°, $[\alpha]_D$ +25·1° ± 3, (*c*, 0·815, water) were obtained. (Reported[13]: m.p. 215–216°, $[\alpha]_D$ +28·0°, *c*, 3, water).

Ethyl β-N-*acetyl butyrate* (XIII)

1·366 g (10·4 mmoles) ethyl β-amino butyrate was refluxed in acetic anhydride (7 ml) for 1 hr. Acetic anhydride was removed *in vacuo* and the remaining oil distilled (b.p. 109–112°, 0·02 mm, reported[24]: b.p. 158°, 12 mm). Yield: 825 mg (46·0%). (Found: N, 8·07; acetyl, 25·75. Calc. for $C_8H_{15}NO_3$: N, 8·08; acetyl, 24·85%).

Conversion of XIII *to ethyl* N,N-*diacetyl-β-amino butyrate* (X)

1·802 g (10·4 mmoles) XIII was refluxed with acetic anhydride for 7 hr. After removal of acetic anhydride, the remaining oil was distilled (b.p. 80–90°, 0·015 mm) and submitted to charcoal–celite chromatography. 766 mg (34·2%) of X and 960 mg (53·5%) of unchanged XIII were obtained.

Reaction of V *and acetic anhydride at* 60°

A suspension of 1·10 g (3·66 mmoles) V in 7 ml acetic anhydride was kept at 60° for 1 hr. There was no evolution of CO_2. Acetic anhydride was removed *in vacuo* and the residue recrystallized from chloroform–pet ether. 852 mg (77·3%) of white crystals were obtained, m.p. 136–138°, which gave no depression on admixture with an authentic sample of V.

Reaction of V *and acetic anhydride at reflux temperature for* 30 *min.*

1·55 g (5·17 mmoles) V in 5 ml acetic anhydride was refluxed under anhydrous conditions for 30 min. 28·5 mg CO_2 (21%) were collected in the absorption tubes. Acetic anhydride was removed *in vacuo* the residue dissolved in chloroform (20 ml) and the remaining crystals (20 mg) filtered off. They were identified as N,N′-di-naphthylurea m.p. 273–275°. The filtrate was evaporated to dryness, the residue dissolved in 2 ml chloroform and subjected to charcoal–celite chromatography. Pet ether–chloroform eluted 450 mg (38·2%) of N,N-diacetyl-1-naphthylamine and 100 mg (9·0%) of ethyl N,N-diacetyl-β-amino butryate (X). Further elution with chloroform afforded 656 mg (73·5%) ethyl N-acetyl-β-amino butyrate (XIII) and 232 mg (24·3%) N-acetyl-1-naphthylamine.

Acknowledgments—The authors are indebted to Mrs. O. Hadžija for performance of numerous micro-analyses and microacetyl determinations. Thanks are also due to Mrs. D. Orlić for her valuable technical assistance, and to Mr. T. Magjer for carrying out the infra-red spectra.

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[24] A. Skita and C. Wulff, *Liebigs Ann.* **453**, 190 (1927).