REACTION OF AMIDES OF 28-LUPANOIC ACID WITH LEAD TETRAACETATE AND IODINE MASS SPECTRA OF 12-LUPENE DERIVATIVES*

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The main products of the reaction of amides *VIII* and *X* with lead tetraacetate and iodine are corresponding isocyanates *XII* and *XIV*. 12-Lupene derivatives *XXII* and *XXIV* were also obtained in a low yield and their mass spectra are discussed. The photolysis of azide *XV* gives the isocyanate *XII* only. A number of the amides prepared, *I*, *VII*, *VIII*, *XVII* and carbamate *IX*, have antibacterial properties.

In connection with our preceding work[1,2] dealing with the functionalization of ring C of the lupane skeleton we also investigated the possibility of the introduction of a substituent into ring C or D of this skeleton *via* the amide group in the position 17β, using lead tetraacetate and iodine. This reaction was used first by Barton and Beckwith[3] with steroid derivatives. In our case we assumed that a restriction of free rotation of the amide group, caused by a suitable substitution on the nitrogen atom, would lead to a higher selectivity during the attack of the non-activated centre. Therefore the series of amides, *I*, *IV*, *VII*, *VIII* and *X*, was prepared. Amides *VIII* and *X* have been described earlier[4,5]. However, it was found that N-tert-butylamides *I* and *IV* and N-methylamide *VII* did not react with lead tetraacetate and iodine under the conditions given below (evidently for steric reasons).

An analogous reaction carried out with amide *VIII* gave a mixture of two compounds. The mixture was submitted to alkaline hydrolysis and then reacetylated. After chromatographic separation carbamate *IX* was obtained as the main product (80%), and 3β-acetoxy-28-nor-17β-carbamoyl-12-lupene (*XXIII*) as a minor product. The structure of carbamate *IX* was proved by conversion of amide *VIII* with lead tetraacetate to isocyanate *XII* which was then converted to carbamate *IX*. In contrast to this, a similar reaction carried out with amide *X* gave carbamate *XI* and lactam *XX*. The structures of *XXIII* and *XX* were proposed on the basis of the following arguments: a comparison of the IR spectrum of derivative *XXIII* and amide *VIII* indicates that the acetoxy group and the amide group remained unchanged. Ac-

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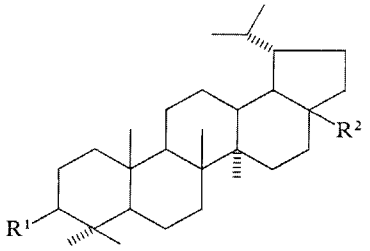
cording to the ^{1}H-NMR spectrum amide *XXIII* contains a trisubstituted double bond (δ = 5·44 p.p.m.; 1 H, bs) located in such a manner that the signals of the 8β and 14α methyls are shifted mutually in opposite directions under its effect, quite analogously as in the case of 3β,28-diacetoxy-12-lupene[1] (*XXVI*). Alkaline hydrolysis of amide *XXIII* gave 3β-hydroxyamide *XXIV*. Its mass spectrum is characteristic of 12-lupene derivative (see below). In the IR spectrum of derivative *XX* only a single amide band is present (1 682 cm^{-1}) as well as a band due to the NH



I, R^1 = $OCOCH_3$, R^2 = $CONHC(CH_3)_3$
II, R^1 = $OCOCH_3$, R^2 = $COOH$
III, R^1 = $OCOCH_3$, R^2 = $COCl$
IV, R^1 = H, R^2 = $CONHC(CH_3)_3$
V, R^1 = H, R^2 = $COOH$
VI, R^1 = H, R^2 = $COCl$
VII, R^1 = $OCOCH_3$, R^2 = $CONHCH_3$
VIII, R^1 = $OCOCH_3$, R^2 = $CONH_2$
IX, R^1 = $OCOCH_3$, R^2 = $NHCOOC_2H_5$
X, R^1 = H, R^2 = $CONH_2$
XI, R^1 = H, R^2 = $NHCOOC_2H_5$
XII, R^1 = $OCOCH_3$, R^2 = $N{=}C{=}O$
XIII, R^1 = OH, R^2 = $NHCOOC_2H_5$
XIV, R^1 = H, R^2 = $N{=}C{=}O$
XV, R^1 = $OCOCH_3$, R^2 = CON_3
XVI, R^1 = $OCOCH_3$, R^2 = $CONHNH_2$

bond (3 500 cm^{-1}). No proton on a double bond is visible in its ^{1}H-NMR spectrum, but it contains one proton on nitrogen (δ = 5·13 p.p.m., 1 H, bs). The effect of the heterocyclic ring bound with the position 13β on the shifts of the skeletal methyl groups is identical as in lupan-28→13β-olide[1] (*XXVII*), see Table I. Therefore

TABLE 1
Comparison of the ^{1}H-NMR Spectra of Lactone *XXVII* and Lactam *XX* (δ, p.p.m.)

Proton	4α	4β	10β	8β	14α	$CH(CH_3)_2$
XXVII	0·86	0·805	0·88	1·18	1·155	0·82 d + 0·86 d J = 6·5 Hz
XX	0·86	0·81	0·89	1·18	1·12	0·81 d + 0·85 d J = 6·4 Hz

we propose the structure *XX* for this derivative. As we have supposed in the case of amide *XXIII* the lactam *XXI* as the primary structure, which in the course of the working up of the reaction mixture (hydrolysis, acetylation) was split to amide *XXIII*, we tried to cleave the lactam ring in derivative *XX* as well. This ring is more stable in this case because the alkaline hydrolysis takes place very slowly here. Therefore the reaction with lithium aluminum hydride under mild conditions was applied, during which a reduction of the amide bond does not take place. Amide *XXII* was thus obtained in the IR spectrum of which two amide bands (1588 and 1658 cm^{-1}) are present, and two sharp bands in the NH region (3360 and 3470 cm^{-1}). In its ^{1}H-NMR spectrum a signal of one proton on a double bond is present (δ = 5·44 p.p.m., 1 H, bs) together with two signals of protons on nitrogen (δ = 5·66 p.p.m., 1 H, bs, and 6·32 p.p.m., 1 H, bs). A comparison of the mass spectra of amides *XXII*, *XXIV* and 28-acetoxy-12-lupene[1] (*XXV*) proved that all three substances have the double bond in the same position. The fragmentation of 12-oleanene and 12-ursene derivatives has already been described[6,7]. 12-Lupene derivatives have not been measured so far and therefore we studied their fragmentation more closely. This takes place analogously as in 12-oleanene and 12-ursene derivatives. The molecular ions undergo retro-Diels–Alder cleavage of ring C under formation of characteristic fragments of type *a*, which appear at *m/e* 203 after the splitting off of the 17β substituent. This type of cleavage is evidently so favourable that it is not affected irrespective of whether the rings D/E are of decaline or perhydrindane type, or whether they are *cis*- or *trans*-annelated. In addition to the characteristic fragments belonging to the rings A and B (*m/e* 207, 189, 175 in the case of 3β-hydroxy derivative *XXIV* and 191 and 177 in the case of 3-deoxy derivatives *XXII* and *XXV*) an intensive ion at *m/e* 133 (ref.[6]) occurs in all spectra, also characteristic of the double bond in the position 12.

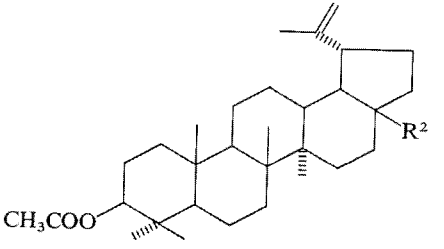
In order to confirm the reaction course amides *VIII* and *X* were submitted to the reaction with lead tetraacetate without iodine. In both cases the corresponding isocyanate *XII* or *XIV* (IR spectrum 2270 cm^{-1}) was obtained. The by-products corresponding to lactams of the type *XX*, *XXI* or unsaturated amides *XXII* and *XXIII* were not found in the reaction mixture. Both isocyanates *XII* and *XIV* were converted to corresponding carbamates *XIII* or *XI*, respectively, in ethanol.

From the facts observed it may be inferred that during the reaction of amide with lead tetraacetate and iodine mainly the ordinary thermic reaction of amide with lead tetraacetate to isocyanate (*cf*[8].) takes place in addition to the required radical functionalization catalysed with iodine. Therefore the reaction is not advantageous for the preparation of the required C- or D-substituted derivatives of lupane.

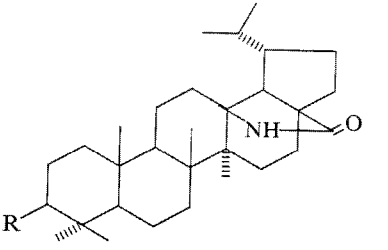
A further reaction which we carried out with the same intention as the preceding one was the photolysis of azide *XV*. Generally, this reaction can give rise to isocyanates, amides or lactams[9–12]. In our case azide *XV*, prepared by the usual sequence

from chloride *III via* hydrazide *XVI*, gave only isocyanate *XII* on photolysis under the conditions given below.

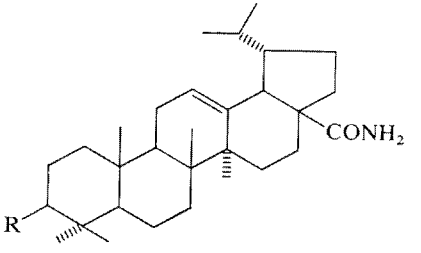
Amides *I*, *VII*, *VIII* and *XVII* and carbamate *IX* display antimicrobial activity against *Saccharomyces pasterianus*, *Trichophyton mentagrophytes*, *Candida albicans*, and *Aspergillus niger* in a 100 mcg/ml concentration.



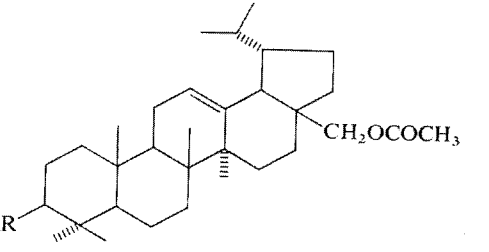
XVII, $R^2 = CONHC(CH_3)_3$
XVIII, $R^2 = COOH$
XIX, $R^2 = COCl$



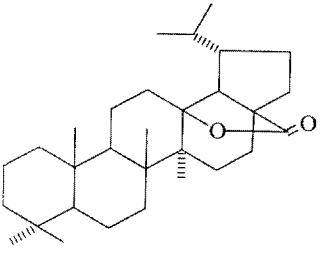
XX, R = H
XXI, $R = OCOCH_3$



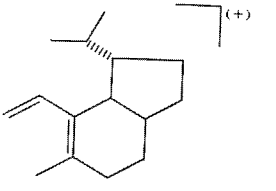
XXII, R = H
XXIII, $R = OCOCH_3$
XXIV, R = OH



XXV, R = H
XXVI, $R = OCOCH_3$



XXVII



a

EXPERIMENTAL

The melting points were measured on a Kofler block and they were not corrected. Optical rotation was measured in chloroform on the automatic ETL-NPL (Bendix-Ericsson) polarimeter with $a \pm 2°$ accuracy. The IR spectra were measured in chloroform on a UR-10, Zeiss, Jena, instrument, The ^{1}H-NMR spectra were measured in deuteriochloroform using tetramethylsilane as internal reference, on a Varian HA-100 instrument. Chemical shifts are given in p.p.m., δ-scale. The mass spectra were measured on a Varian MAT 311 apparatus, energy of ionizing electrons 70 eV, ionizing current 1 mA, ion source temperature 200°C, temperature of the direct inlet system 130–160°C. Samples for analysis were dried at 100°C and 0·1 Torr, over phosphorus pentoxide, for 8–10 hours. The reaction mixtures were extracted with ether, washed repeatedly with water, hydrochloric acid (1 : 4), sodium carbonate (5%) and water. The ethereal layer was dried over sodium sulfate, filtered and evaporated to dryness. Chromatography was carried out on neutral alumina (Reanal, act. II according to Brockmann).

Preparation of Amides

Tert-butylamide of 3-O-*acetyldihydrobetulinic acid* (I): Acid *II* (2 g) was dissolved in freshly distilled thionyl chloride (20 ml) and one drop of pyridine added. The mixture was allowed to stand at room temperature for 24 hours, then evaporated *in vacuo* and dissolved three times consecutively in benzene (50 ml) and evaporated in a vacuum. The residue was crystallized twice from benzene–light petroleum. The chloride *III* obtained (1·1 g) had m.p. 184–186°C, $[\alpha]_D$ −12° (*c* 0·65). IR spectrum: 855 (C—Cl), 1810 (COCl), 1030, 1262, 1730 ($OCOCH_3$) cm^{-1}.

Chloride *III* (1 g) was dissolved in benzene (70 ml) and tert-butylamine (420 mg) was added dropwise to it and the solution was refluxed for 2 hours. After another 12 hours of standing at room temperature the mixture was evaporated in a vaccum and worked up. After filtration through a small column of alumina, evaporation and crystallization (benzene–ethanol) 730 mg of tert-butylamide *I* were obtained, m.p. 221–223°C, $[\alpha]_D$ −14° (*c* 0·70). IR spectrum: 1033, 1260, 1730 ($OCOCH_3$), 1510, 1669, 3462 (CONH) cm^{-1}. For $C_{36}H_{61}NO_3$ (555·8) calculated: 77·78% C, 11·06% H, 2·52% N; found: 77·63% C, 11·19% H, 2·61% N.

Tert-butylamide of 3-O-*acetylbetulinic acid* (XVII): Acid *XVIII* (2 g) was converted to chloride in the same manner as acid *II*. The crude chloride *XIX* was crystallized from benzene–light petroleum, yield 750 mg, m.p. 232–233°C. IR spectrum: 1029, 1260, 1736 ($OCOCH_3$), 858, 1815 (COCl), 1651 (C=C) cm^{-1}. From the mother liquors 3-O-acetyloxoallobetulin[13] (250 mg) was obtained. Chloride *XIX* (750 mg) was converted similarly as *III* to tert-butylamide *XVII*. Chromatography on alumina (80 g) with benzene gave amide *XVII* (600 mg), m.p. 149–152°C, $[\alpha]_D$ +10° (*c* 0·59). For $C_{36}H_{59}NO_3$ (553·8) calculated: 78·07% C, 10·74% H, 2·53% N; found: 77·84% C, 10·49% H, 2·40% N.

Tert-butylamide of 3-*deoxydihydrobetulinic acid* (IV): Acid *V* (2 g) was converted to its chloride in the same manner as acid *II*. The crude chloride *VI* (1·7 g) was crystallized from benzene–chloroform, m.p. 225–227°C, $[\alpha]_D$ −23° (*c* 0·59). IR spectrum: 851, 1816 (COCl). Chloride *VI* (1·6 g) was converted to tert-butylamide *IV* analogously as *III*. After crystallization from chloroform–methanol 1·5 g of product were obtained, m.p. 229–231°C, $[\alpha]_D$ −22° (*c* 0·64). IR spectrum; 1510, 1669, 3460 (CONH) cm^{-1}. For $C_{34}H_{59}NO$ (397·8) calculated: 82·03% C, 11·95% H, 2·81% N; found: 82·38% C, 12·04% H, 2·65% N.

N-*Methylamide of* 3-O-*acetyldihydrobetulinic acid* (*VII*): Chloride *III* (2 g) was dissolved in benzene (150 ml) saturated with methylamine and the solution was allowed to stand at room temperature for 12 hours in a stoppered flask. The reaction mixture was then filtered through

a small column of alumina and evaporated. A double crystallization from chloroform–methanol gave amide *VII* (1·5 g), m.p. 157–159°C, $[\alpha]_D$ −14° (*c* 0·64). IR spectrum: 1034, 1260, 1726 ($OCOCH_3$), 1522, 1665, 3488 (CONH) cm^{-1}. For $C_{33}H_{55}NO_3$ (513·8) calculated: 77·14% C, 10·79% H, 2·73% N; found: 77·51% C, 10·52% H, 2·52% N.

Reaction of Amides with Lead Tetraacetate and Iodine

a) Lead tetraacetate (700 mg) and iodine (450 mg) were suspended in a solution of tert-butylamide *IV* (210 mg) and the mixture irradiated with a UV lamp Tesla THK 100 under nitrogen and cooling for 10 hours. Sial glass was used. The cooling was eliminated and irradiation continued for another 6 hours, then cooled, filtered, washed with a 5% sodium thiosulfate solution and water, dried and vacuum distilled. After crystallization of the residue from benzene–chloroform the starting amide *IV* (180 mg) was obtained.

b) Methylamide *VII* (200 mg) was submitted to the same reaction conditions as amide *IV*. After crystallization from chloroform–methanol 160 mg of the starting amide *VII* were obtained.

c) Lead tetraacetate (1·65 g) and iodine (1 g) were suspended in a solution of amide *VIII* (500 mg) and the mixture was refluxed and irradiated under stirring with a 500 W lamp for one hour. The reaction mixture was cooled, filtered, washed with 5% sodium thiosulfate solution and evaporated. The residue was dissolved in benzene (25 ml), additioned with 20 ml of 10% ethanolic potassium hydroxide, and the mixture was refluxed for 2 hours. After evaporation it was worked up. The residue was dissolved in pyridine (5 ml) and acetic anhydride (2 ml) and allowed to stand at room temperature for 24 hours. The mixture was then evaporated *in vacuo* and worked up. After chromatography on alumina (80 g), elution with benzene, carbamate *IX* (400 mg) was obtained first, m.p. 278–280°C, $[\alpha]_D$ −13° (*c* 0·61). IR spectrum: 1032 1260, 1728 ($OCOCH_3$), 1508, 3460 (CONH) cm^{-1}. ^{1}H-NMR spectrum: 0·77 d + 0·86 d, J = 6·8 Hz ($CH(CH_3)_2$), 0·85 (4α-CH_3, 4β-CH_3), 0·87 (10β-CH_3), 0·94 (14α-CH_3), 1·02 (8β-CH_3), 2·03 (CH_3COO), 4·43 bs (NH), 4·50 m (3α-H), 1·23 t + 4·06 q, J = 7 Hz (CH_3CH_2O—) p.p.m. For $C_{34}H_{57}NO_4$ (543·8) calculated: 75·09% C, 10·57% H, 2·58% N; found: 75·19% C, 10·73% H, 2·42% N. Next, amide *XXIII* (25 mg) was eluted, m.p. 263–265°C, $[\alpha]_D$ +17° (*c* 0·45). IR spectrum: 1031, 1260, 1728 ($OCOCH_3$), 1590, 1666, 3380, 3500 ($CONH_2$) cm^{-1}. ^{1}H-NMR spectrum: 0·80 d + + 0·91 d, J = 6·9 Hz ($CH(CH_3)_2$), 0·88 (4α-CH_3, 4β-CH_3), 0·94 (10β-CH_3), 0·99 (8β-CH_3), 1·175 (14α-CH_3), 4·52 m (3α-H), 2·04 (CH_3COO), 5·44 bs ($C_{(12)}$-H), 6·32 bs + 5·73 bs (NH_2) p.p.m.

Amide *XXIII* (15 mg) was dissolved in benzene (3 ml), 1 ml of 10% potassium hydroxide solution in ethanol was added, and the mixture was refluxed for 2 hours. After working up an amorphous hydroxy derivative *XXIV* (9 mg) was obtained. IR spectrum: 1583, 1660, 3365, 3470 ($CONH_2$), 3435, 3600 (OH) cm^{-1}. MS *m/e*: 455 (M^+, $C_{30}H_{49}NO_2$ by HR), 440, 411, 247, 234, 229, 207, 203, 189, 175, 133 (base peak).

d) Lead tetraacetate (2·1 g) and iodine (1·2 g) were suspended in a solution of amide *X* (600 mg) in benzene (100 ml) and the mixture was further processed as under *c*). After chromatography on alumina (80 g) with benzene amorphous carbamate *XI* (490 mg) was obtained $[\alpha]_D$ −6° (*c* 0·67). IR spectrum: 1505, 3460 (NHCO) cm^{-1}. For $C_{32}H_{55}NO_2$ (485·8) calculated: 79·12% C, 11·41% H, 2·88% N; found: 78·80% C, 11·18% H, 3·08% N. Further 50 mg of lactam *XX* were eluted, m.p. 178–181°C (ether), $[\alpha]_D$ −23° (*c* 0·18); IR spectrum: 1682, 3500 (NHCO cm^{-1}). ^{1}H-NMR spectrum: 0·81 d + 0·85 d, J = 6·4 Hz ($CH(CH_3)_2$), 0·81 (4β-CH_3), 0·86 (4α-CH_3), 0·89 (10β--CH_3), 1·12 (14α-CH_3), 1·18 (8β-CH_3), 5·13 bs (NH). For $C_{30}H_{49}NO$ (439·7) calculated: 81·94% C, 11·23% H, 3·19% N; found: 81·71% C, 11·54% H, 3·12% N.

A solution of lactam *XX* (20 mg) in 10 ml of ether was additioned with 20 mg of lithium aluminum hydride and the mixture was refluxed for one hour, then decomposed with water and extracted with ether. After working up 10 mg of amorphous amide *XXII* were obtained. IR spectrum: 1588, 1658, 3360, 3470 ($CONH_2$) cm^{-1}. ^{1}H-NMR spectrum: 5·44 bs ($C_{(12)}$-H), 5·66 bs + + 6·32 bs (NH_2). MS *m/e*: 439 (M^+, $C_{30}H_{49}NO$, by high resolution), 424, 395, 247, 234, 229, 203, 191 (base peak) 177, 133.

3β-Acetoxy-17β-isocyanato-28-norlupane (*XII*)

Lead tetraacetate (200 mg) was suspended in a solution of amide *VIII* (100 mg) in benzene (20 ml) and the mixture was stirred and refluxed for one hour. After cooling it was filtered and worked up. The residue when crystallized from benzene–ether afforded isocyanate *XII* (70 mg), m.p. 280 to 283°C, $[\alpha]_D$ +5° (*c* 0·182). IR spectrum: 1033, 1260, 1730 ($OCOCH_3$), 2270 (NCO) cm^{-1}. ^{1}H-NMR spectrum: 0·755 d + 0·89 d, J = 6·7 Hz ($CH(CH_3)_2$, 0·85 (4α-CH_3, 4β-CH_3), 0·89 (10β-CH_3), 0·92 (14α-CH_3), 1·06 (8β-CH_3), 2·04 (CH_3CO), 4·48 m (3α-H). For $C_{32}H_{51}NO_3$ (497·7) calculated: 77·21% C, 10·33% H, 2·82% N; found: 77·22% C, 10·34% H, 2·67% N.

Carbamate *XIII*

A solution of 10% potassium hydroxide (15 ml) in ethanol was added to a solution of isocyanate *XII* (100 mg) in benzene and the mixture was refluxed for 2 hours. After evaporation and working up 90 mg of amorphous carbamate *XIII* were obtained, $[\alpha]_D$ −7° (*c* 0·62). IR spectrum: 1504, 1725, 3453 (CONH), 3622 (OH) cm^{-1}. For $C_{32}H_{55}NO_3$ (501·8) calculated: 76·59% C, 11·05% H, 2·79% N; found: 76·01% C, 10·57% H, 2·57% N.

17β-Isocyanato-28-norlupane (*XIV*)

Lead tetraacetate (400 mg) was suspended in a solution of amide *X* (100 mg) in benzene (40 ml) and the mixture was refluxed for one hour, cooled, filtered and worked up. The residue was crystallized from ether–benzene to afford isocyanate *XIV* (85 mg), m.p. 167—170°C, $[\alpha]_D$ −11° (*c* 0·64). IR spectrum: 2270 (NCO) cm^{-1}. ^{1}H-NMR spectrum: 0·75 d + 0·87 d, J = 6·8 Hz ($CH(CH_3)_2$), 0·80 (4α-CH_3), 0·85 (4β-CH_3, 10β-CH_3), 0·93 (14α-CH_3), 1·06 (8β-CH_3). For $C_{30}H_{49}NO$ (439·7) calculated: 81·94% C, 11·23% H, 3·19% N; found: 81·71% C, 11·38% H, 2·91% N.

3-O-Acetyl-dihydrobetulinic Acid Azide (*XV*)

Hydrazine hydrate (100%, 3 ml) was added dropwise to a solution of crude chloride *III* (1 g) in ether (50 ml) at 0°C under stirring. Flakes of hydrazide separated immediately. The mixture was poured into icy water (50 ml) and extracted with ether. After the conventional working up amorphous hydrazide *XVI* (500 mg) was obtained, $[\alpha]_D$ −12° (*c* 0·59). IR spectrum: 1021, 1256, 1723 ($OCOCH_3$), 1624, 1663, 3320 ($CONHNH_2$) cm^{-1}.

A solution of 250 mg of sodium nitrite in the smallest amount of water was added to a solution of hydrazide *XVI* (400 mg) in 95% acetic acid (20 ml) at 0°C, and the mixture was shaken for one minute. It was diluted with water and extracted twice with heptane. Both extracts were combined, washed with ice-cold water, 5% sodium carbonate solution and again with cold water. After drying in a current of air 310 mg of azide *XV* were obtained. IR spectrum: 1710, 2145 (CON_3), 1026, 1260, 1729 ($OCOCH_3$) cm^{-1}.

Photolysis: A solution of azide *XV* (300 mg) was irradiated at 15°C with a 100 W UV lamp THK 100 Tesla (Sial glass) for 2 hours and then evaporated in a vacuum. The residue was crystallized from benzene–ether, giving isocyanate *XII* (270 mg), m.p. 280—282°C, $[\alpha]_D$ +3° (*c* 0·62).

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