REACTION OF TETRAHYDROFUROISOXAZOLES WITH MOLYBDENUM HEXACARBONYL. A NEW ROUTE TO PREPARATION OF 3-SUBSTITUTED TETRAHYDRO- AND DIHYDROFURAN DERIVATIVES

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3-(4-X-Phenyl)-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazoles *Ia*—*If* (X = H, CH_3, CH_3O, Cl, F, C_6H_5) react with molybdenum hexacarbonyl to give not only the expected *cis*-3-aroyl-4-hydroxytetrahydrofuran *III*, but also its *trans* isomer *IV* and 3-aroyl-2,5-dihydrofuran *II*. This paper concerns a new preparation of 3-aroyl-2,5-dihydrofuran derivatives starting from 2,5-dihydrofuran via 1,3-dipolar cycloaddition of nitrile oxides, cleavage with molybdenum hexacarbonyl and dehydratation with *p*-toluenesulfonic acid. The structure of *cis*-(*III*) and *trans*-(*IV*) derivatives was deduced from both the γ-effect in the ^{13}C NMR and the DQ COSY experiment in the ^1H NMR spectra.

Recently, 4,5-dihydroisoxazoles (isoxazolines) have become important in organic synthesis as valuable precursors[1]. Their main value lies in their reductive cleavage, the so-called isoxazoline method (cycloaddition followed by a reductive ring opening) well utilized especially for preparation of γ-aminoalcohols[2-4] and β-hydroxycarbonyl compounds[5-7]. The generally employed reduction agents as lithium tetrahydroaluminate[2-4] or W-2 Raney nickel[5-7] could not be used with compounds containing another grouping undergoing reduction. Recently, the ability of transition metals to cleave the N—O bond in isoxazolines has been observed. Pentacarbonyl iron[8,9] and hexacarbonyl molybdenum[10] were shown to work in photochemical and thermal reactions, respectively. This paper is aimed to utilize products of 1,3-dipolar cycloadditions of nitrile oxides to 2,5-dihydrofuran for preparation of β-substituted tetrahydrofuran derivatives via cleavage with molybdenum hexacarbonyl.

Experimental conditions for the reaction of 3-(4-X-phenyl)-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazoles *Ia*—*If* with molybdenum hexacarbonyl were taken from the already reported paper[10] for preparation of other isoxazolines; the molar ratio of *Ia*—*If* to molybdenum hexacarbonyl was 2 : 1 and the acetonitrile contained a little

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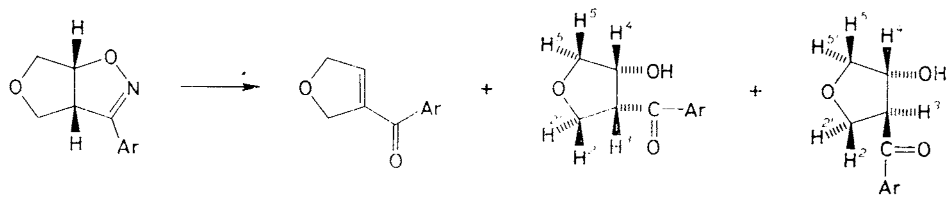
amount of water. The reaction proceeded till all the starting isoxazoline was consumed (checked by thin-layer chromatography, the reaction time is specified in the experimental section). The reaction had, contrary to our expectations, a more complicated course leading to several reaction products, although so far only one product should be formed, according to literature[8,10], namely *cis*-3-aroyl-4-hydroxytetrahydrofuran *III*. The reaction mixture was chromatographed and afforded three products, which were identified. In all experiments the first oily fraction showed a complex ^{1}H NMR spectrum with a various ratios of single groups. It was, therefore, considered that this fraction had to contain at least two compounds, one of them being isolated in a pure form (*II*).

Interpretation of spectral data indicated that this compound is not the anticipated β-hydroxyketone *III*. One series of signals in the ^{1}H NMR spectrum suggested the presence of 3-aroyl-2,5-dihydrofuran *II*, resulting from dehydratation of intermediate β-hydroxyketones.

Therefore, an independent experiment was carried out, namely a dehydratation of β-hydroxyketones isolated from further fractions in boiling benzene under catalysis of *p*-toluenesulfonic acid and silica gel (Scheme 1). The 3-aroyl-2,5-dihydrofurans



I *II* *III* *IV*

In formulae *I*–*IV*: Ar = $-C_6H_4-X$ *a*, X = H *b*, X = OCH_3 *c*, X = CH_3 *d*, X = Cl *e*, X = F *f*, X = C_6H_5

SCHEME 1

IIa–*IIf* obtained in this way had identical R_F values and spectral data with those of the above-mentioned fraction. The dehydratation proceeds very smoothly in excellent yields even in the absence of silica gel, but more slowly. 3-(4-X-Benzoyl)-2,5-dihydrofurans *IIa*–*IIf*, isolated in pure state, have surprisingly not been reported as yet. Their structure was evidenced by following spectral data. 3-(4-Fluorobenzoyl)-2,5-dihydrofuran (*IIe*) e.g. had a prominent signal in the ^{1}H NMR spectrum at δ 4·96 due to four protons of two methylene groups at C-2 and C-5 of the tetrahydrofuran ring, another one at δ 6·58 associated with the H-4 of a vinylic grouping and further protons of an aromatic ring. The ^{13}C NMR spectrum revealed triplets

at δ 76·47 and 74·36, a singlet and a doublet at 138·07 and 141·06, respectively, proving the 2,5-dihydrofuran skeleton. The α,β-unsaturated system of *IIe* was evidenced by both the absence of an absorption band for an OH group in the IR spectrum and a ν(C=O) shift towards lower values a (C=C—C=O grouping). It was shown that 3-aroyl-2,5-dihydrofurans *IIa*–*IIf* were not formed by dehydratation during chromatography on a silica gel column, but directly in the reaction of *I* with molybdenum hexacarbonyl, as was backed by the NMR data of the crude product. Formation of dehydratation products of β-hydroxycarbonyl compounds in reactions with transition metals[8,10] has not been reported as yet. A reaction sequence: 1,3-dipolar cycloaddition of benzenenitrile oxides to 2,5-dihydrofuran, action of molybdenum hexacarbonyl and dehydratation of 3-aroyl-4-hydroxytetrahydrofurans *III*, *IV* with *p*-toluenesulfonic acid represents a new method for preparation of 3-aroyl-2,5-dihydrofurans *II* and demonstrates a further usefulness of isoxazolines as synthetic equivalents.

Further fractions contained *cis*- and *trans*-3-aroyl-4-hydroxytetrahydrofurans; those, where X = H, OCH_3, Cl could not be separated. Products were assigned the *cis* or *trans* configuration according to spectral data. Fraction 2, having higher R_F values and, due to an effect also higher chemical shifts δ for C-3 and C-4 atoms in the ^{13}C NMR spectra contain β-hydroxyketones. As reported[11] the values for C-3 and C-4 atoms of *cis*-3,4-disubstituted tetrahydofuran derivatives appear at lower δ than those of *trans* epimers. Thus, e.g. signals for C-3 and C-4 equivalent nuclei were seen at δ 36·5 and 41·7 ppm for *cis*- and *trans*-3,4-dimethyltetrahydrofuran[11], respectively. Therefore, the higher R_F values having derivatives were assigned the *trans* configuration *IV*. The corresponding signals for e.g. *trans*-3-(4-methoxybenzoyl)-4-hydroxytetrahydrofuran (*IVb*) emerged at δ 74·13 (C-4) and 55·58 (C-3) and at δ 72·90 (C-4) and 52·01 (C-3) for the *cis* isomer *IIIb*. Recently[12], the shift effect was applied to configurational and conformational stereochemical analysis. According to this paper, the spatial disposition of two vicinal hydrogen atoms in an *anti*-arrangement is associated with an upfield shift of δ values for such a carbon atom. Correlation of several derivatives showed that every *anti* hydrogen interaction increases the δ value by ~3 ppm in six-membered rings[12]. Our compounds reveal one *anti*-H interaction for each carbon of the *cis* derivative *IV*, two interactions each for C-3 and C-4 of *trans*-*V* and one interaction each for C-2 and C-5. This theory holds exactly even for derivatives *III* and *IV*; atoms C-3 and C-4 of *trans* derivatives *IV* are by one *anti*-vicinal interaction richer and disclose really higher δ values (Table I). All *trans*-derivatives *IV* have higher δ values for C-2, but lower ones for C-5. This fact could be explained by relation of chemical shifts in the ^{13}C NMR spectra upon the spatial arrangement of the γ-substituent (γ-effect, refs[13–15]), i.e. the hydroxyl and benzoyl groups.

Another evidence for the *cis* and *trans* configuration assignment brought foward the ^{1}H NMR spectra; assignment of the separate signal is presented in the experi-

mental section. The structure of derivatives *III* and *IV* was directly assigned from the tetrahydrofuran moiety data; this was only posible from the 300 MHz spectra (derivatives *IIIa*, *IIIb*, *IIId*, *IVa*, *IVb*, *IVd*). The *trans* derivatives *IV* are anomalous products, and therefore, further NMR technics had to be employed to ascribe undoubtedly the data obtained to individual protons. These were 2D *J*-resolved,

TABLE I
^{13}C NMR parameters of compounds *III* and *IV*

Compound	Chemical shift δ					
	C-2	C-3	C-4	C-5	C-arom	C=O
IIIa	66·87	52·37	72·84	76·12	127·95, 128·54 132·75, 137·31	196·63
IVa	69·87	56·41	75·33	75·76	128·91, 129·14 133·97, 136·36	199·02
IIIb[a]	66·99	52·01	72·90	76·06	113·68, 130·23 162·82	194·94
IVb[b]	69·04	55·38	74·13	74·83	113·97, 129·00 130·82, 163·35	197·22
IIIc[c]	66·93	52·31	72·90	76·12	128·07, 129·06 134·85, 143·05	196·11
IIId	66·87	51·47	72·78	76·06	128·65, 129·88 136·02, 137·72	195·70
IVd	69·35	55·99	75·03	75·37	128·95, 130·41 134·74, 138·48	197·40
IIIe	66·93	52·37	72·78	76·06	115·08, 115·96 131·11, 131·70 160·13, 170·19	195·09
IVe	68·80	55·58	74·01	74·83	115·37, 116·25 130·70, 131·29 160·13, 170·19	197·51
IIIf	66·93	52·48	72·84	76·12	128·42, 129·06 134·80, 139·01 144·12	196·22
IVf	68·86	55·64	74·01	74·83	126·96, 128·71 136·14, 138·77 144·74	198·39

[a] 55·47 (q, OCH_3); [b] 55·23 (q, OCH_3); [c] 21·07 (q, CH_3).

COSY, and ^1H–^{13}C heterocorrelated spectra. The 2D COSY spectra of *IIIb* and *IVb* enabled to find the interaction network between the individual protons. The 2D *J*-resolved spectrum made it possible to unequivocally determine the chemical shifts of protons, and the ^1H and ^{13}C heterocorrelated spectrum brought evidence for the mutual assignment of ^1H and ^{13}C chemical shifts. Structures of *IIIa*, *IIId* and *IVa*, *IVd* were ascribed according to analogy with *IIIb* and *IVb*, respectively.

It has been found that reaction of tetrahydrofuro[3,4-*d*]isoxazole derivatives *I* with molybdenum hexacarbonyl had an unexpected course: of three products isolated two compounds have not been observed with isoxazolines. Firstly, it is the formation of a dehydrated product *II* (12–31%), and secondly, production of *trans* derivatives *IV* (29–46%). Isolation of the unexpected *trans* deriative stimulates to complement the mechanism proposed[8,10] for formation of β-hydroxyketones from isoxazolines. According to literature[8,10], the nitrene complex generated by cleavage of the N—O bond in the isoxazoline–transition metal complex was protonated in the presence of water and transformed into an imino alcohol. The latter underwent hydrolysis to give β-hydroxyketone. With respect to this mechanism only *cis* derivatives *III* have to be produced from isoxazoline *I* with *cis* arranged hydrogen atoms. As found, a mixture of *trans-IV* in slight excess and *cis-III* was isolated with the exception of methyl derivative *Ic* affording only the *cis* derivative *IIIa*. Formation of the *trans* isomer *IV* could be rationalized either by dehydration and a re-addition of water (this being backed by the presence of the unsaturated derivative *II*), or by a direct epimerization at C-3 due to the reaction medium.

EXPERIMENTAL

The ^1H NMR spectra of deuteriochloroform solutions were measured with a Tesla BS 487 C apparatus operating at 80 MHz and a Varian VXR 300 instrument. The ^{13}C NMR spectra of deuteriated dimethyl sulfoxide solutions were recorded with a Jeol FX-100, tetramethylsilane being the internal reference; chemical shifts are given in ppm. The IR spectra of chloroform solutions were taken with a Unicam SP-100 spectrometer in 0·208 mm-cells; the wavenumbers are given in cm^{-1}. Melting points are uncorrected. The reaction course and the purity of compounds were checked by thin-layer chromatography using Silufol sheets (detection by UV_{254} light or iodine vapours, elution system hexane–ethyl acetate 2: 5. The syntheses of 3-(4-X-phenyl)--3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazoles *Ia*–*Ie* and *If* were already described in refs[16,17] and ref.[9], respectively.

Reaction of Fused Isoxazolines *I* with Molybdenum Hexacarbonyl

Molybdenum hexacarbonyl (1·3 g; 5 mmol) was added to a solution consisting of *I* (10 mmol) in acetonitrile (50 ml) containing 50 drops of water. The mixture was refluxed till the stain of the starting material disappeared (TLC). The mixture was cooled, silica gel (10 g) was added, and the solvent was removed. The residue was chromatographed on a silica gel-packed column with hexane–ethyl acetate 2 : 5.

Substance *Ia* afforded: *a*) 3-*Benzoyl*-2,5-*dihydrofuran* (IIa), m.p. 98–100°C, yield 31%. For $C_{11}H_{10}O_2$ (174·2) calculated: 75·84% C, 5·79% H; found: 76·03% C, 5·55% H. ^{1}H NMR spectrum: 5·00 d, d, 4 H (2 × H-2, 2 × H-5, $J < 1·0$ Hz); 6·63 d, d, 1 H (H-4); 7·37–8·06 m, 5 H (H-arom). *b*) cis-3-*Benzoyl*-4-*hydroxytetrahydrofuran* (IIIa), m.p. 62–65°C, yield 20%. For $C_{11}H_{12}O_3$ (192·2) calculated: 68·73% C, 6·29% H, found: 68·59% C, 6·40% H. IR spectrum: 1 602 (C=C), 1 681 (C=O), 3 475 (OH). ^{1}H NMR spectrum: 3·87 m, 1 H (H-5); 3·95 m, 1 H (H-5′); 3·98 m, 1 H (H-2′); 4·16 m, 1 H (H-3); 4·25 m, 1 H (H-2); 4·77 m, 1 H (H-4); 7·50 to 7·57 m, 3 H (H-arom); 7·95–8·07 m, 2 H (H-arom). *c*) trans-3-*Benzoyl*-4-*hydroxytetrahydrofuran* (IVa), m.p. 48–51°C, yield 29%. For $C_{11}H_{12}O_3$ (192·2) calculated: 68·73% C, 6·29% H; found: 68·81% C, 6·14% H. IR spectrum: 1 600 (C=C), 1 685 (C=O), 3 470 (OH). ^{1}H NMR spectrum: 3·84 m, 1 H (H-5); 3·91 m, 1 H (H-5′); 3·99 m, 1 H (H-2′); 4·02 m, 1 H (H-3); 4·31 m, 1 H (H-2); 4·71 m, 1 H (H-4); 7·37–7·56 m, 3 H (H-arom); 7·95–8·08 m, 2 H (H-arom).

Substance *Ib* afforded: *a*) 3-(4-*Methoxybenzoyl*)-2,5-*dihydrofuran* (IIb), m.p. 110–112°C, yield 21%. For $C_{12}H_{12}O_3$ (204·2) calculated: 70·57% C, 5·92% H; found: 70·49% C, 6·13% H. ^{1}H NMR spectrum: 3·86 s, 3 H (OCH_3); 4·95 d, d, 4 H (2 × H-2, 2 × H-5, $J < 1·0$ Hz); 6·55 d, d, 1 H (H-4); 6·93 and 7·95 d, d, 4 H (H-arom). *b*) cis-3-(4-*Methoxybenzoyl*)-4-*hydroxytetrahydrofuran* (IIIb), m.p. 75–78°C, yield 27%. For $C_{12}H_{14}O_4$ (222·2) calculated: 64·85% C, 6·35% H; found: 65·00% C, 6·27% H. IR spectrum: 1 607 (C=C), 1 675 (C=O), 3 455 (OH). ^{1}H NMR spectrum: 3·87 m, 1 H (H-5); 3·94 m, 1 H (H-5′); 3·97 m, 1 H (H-2′); 4·18 m, 1 H (H-3); 4·20 m, 1 H (H-2); 4·74 m, 1 H (H-4); 3·89 s, 3 H (OCH_3); 6·95 and 7·95 d, d, 4 H (H-arom). *c*) trans-3-(4-*Metocybenzoyl*)-4-*hydroxytetrahydrofuran* (IVb), m.p. 88–90°C, yield 36%. For $C_{12}H_{14}O_4$ (222·2) calculated: 64·85% C, 6·35% H; found 64·70% C, 6·31% H. IR spectrum: 1 603 (C=C), 1 678 (C=O), 3 450 (OH). ^{1}H NMR spectrum: 3·91 m, 1 H (H-5′); 3·82 m, 1 H (H-5); 3·96 m, 1 H (H-3); 3·98 m, 1 H (H-2′); 4·30 m, 1 H (H-2); 4·70 m, 1 H (H-4); 3·88 s, 3 H (OCH_3); 6·92 and 7·96 d, d, 4 H (H-arom).

Substance *Ic* afforded: *a*) 3-(4-*Methylbenzoyl*)-2,5-*dihydrofuran* (IIc), m.p. 35°C, yield 25%. For $C_{12}H_{12}O_2$ (188·2) calculated: 76·57% C, 6·43% H; found: 76·77% C, 6·49% H. IR spectrum: 1 609 (C=C), 1 685 (C=O). ^{1}H NMR spectrum: 3·68 s, 3 H (CH_3); 4·96 d, d, 4 H (2 × H-2, 2 × H-5, $J < 1·0$ Hz); 6·60 d, d, 1 H (H-4); 7·27 and 7·73 d, d, 4 H (H-arom). *b*) cis-3-(4-*Methylbenzoyl*)-4-*hydroxytetrahydrofuran* (IIIc), m.p. 119–121°C, yield 46%. For $C_{12}H_{34}O_3$ (206·2) calculated: 69·88% C, 6·84% H; found: 69·92% C, 6·73% H. IR spectrum: 1 610 (C=C), 1 671 (C=O), 3 465 (OH). ^{1}H NMR spectrum: 2·40 s, 3 H (CH_3); 3·35 m, 1 H (OH); 3·82–4·43 m, 5 H (2 × H-2, 2 × H-5, H-3); 4·67 m, 1 H (H-4); 7·27 and 7·90 d, d, 4 H (H-arom).

Substance *Id* afforded: *a*) 3-(4-*Chlorobenzoyl*)-2,5-*dihydrofuran* (IId), m.p. 83–85°C, yield 22%. For $C_{11}H_9ClO_2$ (208·6) calculated: 63·32% C, 4·34% H; found: 63·51% C, 4·29% H. ^{1}H NMR spectrum: 4·93 d, d, 4 H (2 × H-2t 2 × H-5, $J < 1·0$ Hz); 6·67 d, d, 1 H (H-4); 7·28 and 7·75 d, d, 4 H (H-arom). ^{13}C NMR spectrum: 74·77 t (C-5); 76·47 t (C-2); 115·31, 116·19, 131·23, 131·64, 149·77 (C-arom); 138·25 and 141·52 (C-vinyl); 298·56 s (C=O). *b*) cis-3-(4-*Chlorobenzoyl*)-4-*hydroxytetrahydrofuran* (IIId), m.p. 68–69°C, yield 24%. For $C_{11}H_{11}ClO_3$ (226·6) calculated: 58·29% C, 4·89% H; found: 58·37% C, 5·02% H. ^{1}H NMR spectrum: 3·91 m, 1 H (H-5); 3·95 m, 1 H (H-5′); 4·00 m, 1 H (H-3); 4·09 m, 1 H (H-2′); 4·30 m, 1 H (H-2); 4·77 m, 1 H (H-4); 7·42 and 7·90 d, d, 4 H (H-arom). *c*) trans-3-(4-*Chlorobenzoyl*)-4-*hydroxytetrahydrofuran* (IVd), m.p. 72–73°C, yield 33%. For $C_{11}H_{11}ClO_3$ (226·6) calculated: 58·29% C, 4·89% H; found: 58·37% C, 5·02% H. ^{1}H NMR spectrum: 3·86 m, 1 H (H-5); 3·88 m, 1 H (H-5′); 4·00 m, 1 H (H-3); 4·12 m, 1 H (H-2′); 4·30 m, 1 H (H-2); 4·67 m, 1 H (H-4); 7·40 and 7·88 d, d, 4 H (H-arom).

Substance *Ie* afforded: *a*) 3-(4-*Fluorobenzoyl*)-2,5-*dihydrofuran* (IIe), m.p. 93–95°C, yield 12%. For $C_{11}H_9FO_2$ (192·2) calculated: 68·74% C, 4·72% H; found: 68·84% C, 4·55% H. IR spectrum:

1 605 (C=C), 1 650 (C=O). ^{1}H NMR spectrum: 4·96 d, d, 4 H (2 × H-2, 2 × H-5, $J < 1·0$ Hz); 6·58 d, d, 1 H (H-4); 7·20 and 7·85 d, d, 4 H (H-arom). ^{13}C NMR spectrum: 74·36 t (C-5); 76·41 t (C-2); 115·31, 116·90, 131·12, 131·52, 160·01 (C-arom); 138·07 and 140·94 (C-vinyl); 198·10 s (C=O). *b*) Mixture of cis- and trans-3-(4-*fluorobenzoyl*-4-*hydroxytetrahydrofurans* (IIIe, IVe), oil, *IIIe* : *IVe* = 38 : 62 (as calculated from the integrated signal intensities of the ^{1}H NMR spectrum), yield of *IIIe* + *IVe* = 59%. IR spectrum: 1 605 (C=C), 1 685 (C=O), 3 455 (OH). ^{1}H NMR spectrum: 3·20 bs, 1 H (OH); 3·80–4·40 m, 5 H (2 × H-2, 2 × H-5, H-3); 4·67 m, 1 H (H-4); 7·00–7·25 m, 2 H (H-arom); 7·87–8·10 m, 2 H (H-arom).

Substance *If* afforded: *a*) 3-(4-*Phenylbenzoyl*)-2,5-*dihydrofuran* (IIf), m.p. 118–120°C, yield 14%. For $C_{17}H_{14}O_2$ (260·3) calculated: 81·58% C, 5·64% H; found: 81·73% C, 5·61% H. ^{1}H NMR spectrum: 5·01 d, d, 4 H (2 × H-2, 2 × H-5, $J < 1·0$ Hz); 6·70 d, d, 1 H (H-4); 7·42–8·13 m, 9 H (H-arom). ^{13}C NMR spectrum: 74·42 t (C-5); 76·47 t (C-2); 126·96, 128·36, 129·12, 129·36, 138·25, 144·16 (C-arom); 138·83 and 140·88 (C-vinyl). *b*) Mixture of cis- an trans-3-(4-*phenylbenzoyl*)-4-*hydroxytetrahydrofurans* (IIIf, IVf), oil, *IIIf* : *IVf* = 43 : 57, yield of *IIIf* + *IVf* = 84%. IR spectrum: 1 608 (C=C), 1 684 (C=O), 3 480 (OH). ^{1}H NMR spectrum: 3·72 bs, 1 H (OH); 3·87–4·35 m, 5 H (2 × H-2 2 × H-5, H-3); 4·77 m, 1 H (H-4); 7·40–8·01 m, 9 H (H-arom).

Dehydration of *cis*-3-(4-Methoxybenzoyl)-4-hydroxytetrahydrofuran (*IIIb*)

Compound *IIIb* (75 mg; 0·3 mmol), *p*-toluenesulfonic acid (10 mg; 0·06 mmol) and silica gel (1 g) in benzene (30 ml) were refluxed for 3 h. Chloroform was added to the cooled mixture, which was then filtered through a short column packed with silica gel (20 g). The concentrated filtrate afforded pure 3-(4-methoxybenzoyl)-2,5-dihydrofuran (*IIb*) (65 mg, 87%).

Dehydration of the Mixture of *cis*- and *trans*-3-(4-
-Fluorobenzoyl)-4-hydroxytetrahydrofurans (*IIIe*, *IVe*)

The approximately equimolar mixture of *IIIe* and *IVe* (0·3 g; 1·4 mmol) was treated as in the preceding experiment (reflux time 6 h), chromatographed (silica gel, hexane–ethyl acetate 3 : 5) yielding 0·2 g (74%) of 3-(4-fluorobenzoyl)tetrahydrofuran (*IIe*), m.p. 93–95°C and 75 mg of the unreacted *IVe*. The spectral data of the former were identical with those of *IIe* obtained from the reaction of molybdenum hexacarbonyl with *Ie*.

The yields of further dehydrations were as follows: *IIa* (88%), *IId* (78%), *IIf* (69%).

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