PHOTOCHEMICAL REACTIONS OF 2-SUBSTITUTED FURANS WITH SOME CARBONYL COMPOUNDS

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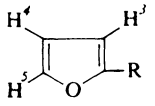
Photochemical reactions of 2-substituted furans *I*, *IV* and *V* with benzaldehyde, benzophenone and 4-methylbenzophenone gave substituted 2,7-dioxabicyclo[3,2,0]-3-heptenes, which can be used for syntheses of 2,3- or 2,4-disubstituted furans. Regioisomeric (2 : 1)-cycloadducts *XV* and *XVI* were distinguished on the basis of their ^{1}H and ^{13}C NMR spectra.

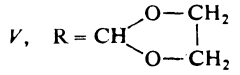
The photocycloaddition reactions of furans with carbonyl compounds are well known[1,2] and are imported mainly for the synthesis of 3-substituted furans[3,4]. In an attempt to prepare starting compounds for the syntheses of 2,3- and 2,4-disubstituted furans we studied the photoreactions of the furans *I* – *V* with chloral, benzaldehyde, benzophenone and 4-methylbenzophenone. It has been found that compound *III* is not reactive under these conditions, *IV* and *V* exhibit moderate reactivities, *I* and *II* are very reactive. The ^{1}H NMR spectra of 2-furonitrile and 2-furfuraldehyde (see[5]) suggest that the two functional groups have approximately equal electron-withdrawing effects, so that 2-furfuraldehyde cannot be expected to form oxetanes with carbonyl compounds. Besides, in photoreactions 2-furfuraldehyde behaves as a carbonyl compound[6]. The reaction mechanism is an electrophilic radical attack of the carbonyl oxygen atom[7] on the site having the highest free-valence index, as was observed with furans[8] and imidazoles[9]. Therefore, the electron-withdrawing effect of the formyl group was reduced by masking this group in the form of diacetate (compound *IV*) and ethylene acetal (compound *V*). The change was visible in the ^{1}H NMR spectra (Table I), although the calculated electron densities on the individual carbon atoms of furan are known not to correlate well with the chemical shifts of the corresponding protons[10].

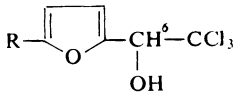
Chloral in the presence of oxygen photochemically decomposes to HCl, CO, CO_2 and $COCl_2$ (ref.[11]). Its photoreaction with furan and/or 2-methylfuran gave compounds *VI* and *VII*, in about 30% yields. However, these products can be obtained by pyroreaction in the presence of $ZnCl_2$ as catalyst[12,13]. No oxetane was detected inthe reaction mixture by ^{1}H NMR spectroscopy and gas chromatography. The photoreaction of chloral with *III* and with *IV* afforded no addition product.

The photoreaction of furan with 4-methylbenzophenone produced a mixture of compounds *VIII* and *IX* (82%), in which, judging by ^{1}H NMR spectroscopy, the compound *VIII* predominated (4 : 1). In the chromatographic separation we fur-

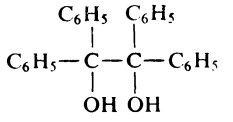


I, R = H
II, R = CH_3
III, R = CN
IV, R = $CH(OCOCH_3)_2$

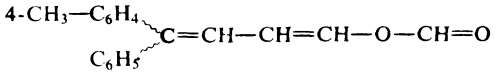




VI, R = H
VII, R = CH_3



XVII

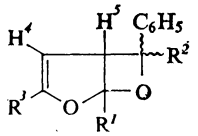


X

ther obtained compound *X* in a yield of 15%. Its formation can be interpreted as due to a rearrangement of *VIII* by the action of the adsorbent. This rearrangement was already observed with another system[3]. We did not detect the other regioisomeric (2 : 1)-cycloadduct in the reaction mixture, although the reaction of benzophenone with furan gives rise to it[14]. The ^{1}H NMR spectra of compounds *VIII* and *IX* were in agreement with those published for similar structures[14], although the assignment of correct structures to the (2 : 1)-cycloadducts of benzophenone and furan was rather a problem[14–17]. The structure of compound *IX* was corroborated by its fragmentation in mass spectrometry, the main fragment being an ion of m/z = 386, which corresponds to the tetrasubstituted 1,3-butadiene. The other isomer, whose formation is explained by inverse regioselectivity of cycloaddition of the carbonyl compound to 2,3-dihydrofuran[18], would have has a mass spectrum of different fragmentation.

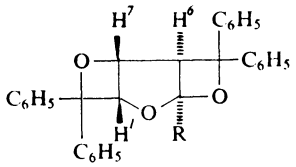
Photoreaction of compound *IV* with benzaldehyde gave a mixture of (1 : 1)-cycloadducts *XI* and *XII* in a ratio of 1 : 3 (analysis by ^{1}H NMR spectra). In chromatographic separation of the two we further obtained compound *XIII* (6%), produced by partial hydrolysis of *XII*. The *exo*- and *endo*-isomers *XIa* and *XIb* were distinguished by their ^{1}H NMR spectra. The protons H^5 (3·68δ), H^7 (7·08δ) and of the methyl group (1·74 and 1·90δ) are more shielded in the *exo*-derivative than in the *endo*-derivative: H^5 (4·30δ), H^7 (7·13δ), methyl group protons (2·00 and 2·03δ).

Photoreactions of compounds *IV* and *V* with benzophenone led to analogous mixtures of products: *XIV*–*XVII*–*XX*, respectively. The structures of compounds *XV* and *XVI* were determined on the basis of their ^{1}H NMR and ^{13}C NMR spectra, and by comparing the former with the ^{1}H NMR data of similar structures[14,15,17].

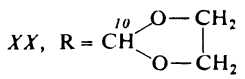


VIII, $R^1 = R^3 = H$, $R^2 = 4\text{-}CH_3—C_6H_4$
XIa,b, $R^1 = CH^8(OCOCH_3)_2$, $R^3 = H$, $R^3 = H^6$
XII, $R^1 = H^1$, $R^3 = CH^8(OCOCH_3)$, $R^2 = H^6$
XIII, $R^1 = H^1$, $R^3 = CH^8 = O$, $R^8 = H^6$
XIV, $R^1 = CH^8(OCOCH_3$. $R^3 = H$, $R^2 = C_6H_5$
XVIII, $R^1 = CH^8$  , $R^3 = H$, $R^2 = C_6H_5$

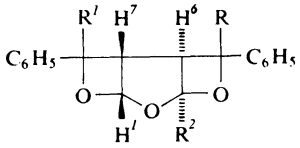
The different chemical shifts of methyl groups in the individual cycloadducts suggest that the steric hindrance of free rotation is considerable. The methyl groups are most shielded in compound *XV* (1·28 and 1·65δ), least shielded in *XIV* (1·59 and 1·89δ). In the ^{13}C NMR spectra of the cycloadducts it was possible to assign the signals of the methyl group and the carbonyl groups (~20·0δ and ~168δ). In the derivative *XIV* the doublets of the olefinic carbon atoms occurred at 102·8δ ($C_{(3)}$) and 148·7δ ($C_{(4)}$), in agreement with the reported data[19]. The difference between the (1 : 1-cycloadduct *XIV* and the (2 : 1)-cycloadducts *XV* and *XVI* is also apparent from the fact that the ^{13}C NMR spectra of compounds *XV* and *XVI* contained



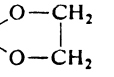
XV, R = $CH^{10}(OCOCH_3)_2$



XX, R = CH^{10}



IX, $R^1 = 4\text{-}CH_3—C_6H_4$, $R^2 = H$
XVI, $R^1 = C_6H_5$, $R^2 = CH^{10}(OCOCH_3)_2$

XIX, $R^1 = C_6H_5$, $R^2 = CH^{10}$ 

signals of four quaternary benzene-ring carbon atoms, whereas the spectrum of compound *XIV* contained only two such signals. The difference between *XV* and *XVI* is apparent from the chemical shifts of the tertiary carbon atoms at ~50δ. In *XV* it is one carbon atom $C_{(6)}$ at 55·2δ, whereas two carbon atoms are shifted in *XVI*: $C_{(6)}$ at 52·9δ and $C_{(7)}$ at 50·8δ. The fragmentation of *XV* in mass spectrometry was started by the splitting-off of benzophenone and the consecutive fragmentation was the same as with *XIV*. Compound *XVI* gave a fragment of $m/z = 358$, corresponding to 1,1,4,4-tetraphenyl-1,3-butadiene, as was the case with compound *IX*.

Nearly all the cycloadducts decompose to the original components, as do the photocycloadducts of benzophenone and furan[20].

EXPERIMENTAL

The starting compounds, *I* (ref.[21]), *III* (ref.[22]), *IV* (ref.[23]) and *V* (ref.[24]) were prepared as described in the literature. The photoreactions were carried out in a 150 ml photoreactor[25] with filters Simax and Sial. Prior to a reaction, argon was bubbled through the reaction mixture for 10 min, then the mixture was irradiated with a 125 W medium-pressure mercury-discharge lamp Tesla RVK 125 at the temperature of the cooling water. The courses of the reactions were followed by TLC on Silufol Plates UF_{254} and by gas chromatography in an apparatus Hewleett Packard 7620 A. The melting points, determined on the Kofler stage, are not corrected. The IR spectra were measured in an apparatus UR 20 (Zeiss, Jena), UV spectra (the values of ε are given in $m^2\ mol^{-1}$) in an apparatus UV-VIS specord, the ^1H NMR spectra (δ, ppm, tetramethylsilane as internal standard) in an apparatus Tesla BS 487 C (80 MHz), the ^{13}C NMR spectra in an apparatus JEOL FX-100 and the mass spectra (70 eV, 100 μA) in an apparatus MS 902 S (AEI, Manchester). The yields of the product are referred to the starting compounds.

2,2,2-Trichloro-1-(2-furyl)ethanol (*VI*)

Anhydrous chloral (14·7 g, 0·1 mol) was added to furan (68 g, 1 mol) in the course of 2h, while the mixture was irradiated through a Simax filter and bubbled by passing Ar (to remove the acid gases). The reactor was cooled to −20°C. After the addition of chloral the mixture continued to be irradiated until it was black (5 h). The excess of furan was removed by distillation and the residue was distilled *in vacuo*; yield 6·5 g (30%) of *VI*, b.p. 125°C/2 kPa, m.p. 30°C (reported[12] m.p. 33–35°C). The course of the reaction was followed by gas chromatography. In the use of powdered calcium carbonate the yield was not much increased. IR spectrum in $CHCl_3$ (cm^{-1}): 3 600, 1 495, 1 375, 1 060. ^1H NMR spectrum (C^2HCl_3): 3·95 (s, 1 H, H^7), 5·25 (s, 1 H, H^6), 6·39 (dd, 1 H, H^4), 6·49 (dd, 1 H, H^3), 7·45 (dd, 1 H, H^5), $J_{3,4} = 3{\cdot}2$ Hz, $J_{3,5} = 0{\cdot}5$ Hz, $J_{4,5} = 2$ Hz. For $C_6H_5Cl_3O_2$ (215·5) calculated: 49·37% Cl; found 49·42% Cl.

2,2,2-Trichloro-1-(5-methyl-2-furyl)ethanol (*VII*)

A mixture of 2-methylfuran (3 g, 0·05 mol) and chloral (7·4 g, 0·05 mol) in 100 ml of benzene, containing 2 g of powdered $CaCO_3$, was irradiated for 4 h through a Simax filter at a temperature of about 20°C. At intervals argon was bubbled through the mixture to remove the acid gases. After evaporation of the solvent the polymers were removed by filtration through a 10 cm column of silica gel and the eluate was distilled *in vacuo*; yield 3·5 g (30%) of *VII*, b.p. 140°C/2 kPa[13]. IR spectrum in $CHCl_3$ (cm^{-1}): 3 590, 1 550, 1 380, 1 070. ^1H NMR spectrum in C^2HCl_3: 2·30 (d, 3 H, CH_3), 3·77 (1 H, OH), 5·14 (s, 1 H, H^6), 6·60 (m, 1 H, H^4), 6·44 (d, 1 H, H^3), $J_{3,4} = 3$ Hz, $J_{CH_3,H^4} = 1$ Hz. For $C_7H_7Cl_3O_2$ (229·5) calculated: 46·35% Cl; found: 45·98% Cl.

6-Phenyl-6-(*p*-tolyl)-2,7-dioxabicyclo[3,2,0]-3-heptene (*VIII*), 5,8-Diphenyl-5,8-di(*p*-tolyl)-2,4,9-trioxatricyclo[5,2,0,$0^{3,6}$] nonane (*IX*), and 4-Phenyl-4-(*p*-tolyl)-1,3-butadienylformate (*X*)

A mixture of 4-methylbenzophenone (1 g, 5 mmol) and furan (3·5 g, 0·05 mol) in 100 ml of benzene was irradiated through a Sial filter for 18 h. The remaining furan and benzene were distilled off and the polymers were precipitated by an addition of diethyl ether (20 ml). The filtrate con-

tained a mixture of *VIII* and *IX* (1·1 g, 82%) in a ratio of 4 : 1. Chromatography (Al_2O_3, C_6H_6) and fractional crystallization (C_6H_{12}, diethyl ether) gave 0·3 g (22%) of *VIII*, m.p. 110—112°C, 0·2 g (15%) of *IX*, m.p. 247—248°C (diethyl ether) and 0·2 g (15%) of *X* as an oil.

VIII: IR spectrum in $CHCl_3$ (cm^{-1}): 3 000, 1 600, 1 450, 1 140, 970. ^1H NMR spectrum in C^2HCl_3: 2·26 (s, 3 H, CH_3), 4·38 (m, 1 H, H^5), 4·95 (dd, 1 H, H^4), 6·30 (dd, 1 H, H^1), 6·42 (m, 1 H, H^3), 7·00—7·50 (m, 9 H, arom.), $J_{1,3} = 0·8$, $J_{1,5} = 3$ Hz, $J_{3,4} = 3$ Hz, $J_{3,5} = 1·2$ Hz. For $C_{18}H_{16}O_2$ (264·3) calculated: 81·79% C, 6·10% H; found: 82·30%C, 5·92% H.

IX: IR spectrum in KBr (cm^{-1}): 2 990, 1 450, 1 070, 820, ^1H NMR spectrum in C^2HCl_3: 2·31 (s, 6 H, 2 × CH_3), 3·68 (m, 2 H, H^6, H^7), 5·95 (d, 2 H, H^1, H^3), 7·15—7·30 (m, 18 H, arom.) $J_{3,6} = 4$ Hz, $J_{1,7} = 4$ Hz. Mass spectrum, *m/z* (relative intensity): 414 (1), 387 (10), 386 (25), 222 (47), 207 (11), 198 (21, 182 (10), 181 (21), 155 (36), 138 (13), 131(10), 115 (19), 105 (36), 97 (15), 96 (21), 95 (42), 91 (13), 82 (11), 77 (15), 44 (17), 43 (100), 28 (32). For $C_{32}H_{28}O_3$ (460·5) calculated: 83·45% C, 6·13% H; found: 82·98% C, 6·03% H.

X: ^1H NMR spectrum in C^2HCl_3: 2·38 and 2·40 (s, CH_3), 5·75 (m, CH), 6·9—73 (m, arom.), 8·13 (s, 1 H, O—CH=O).

endo- and *exo*-6-Phenyl-2,7-dioxabicyclo[3,2,0]-3-heptene-1-al Diacetates (*XIa* and *XIb*, respectively), 6-Phenyl-2,7-dioxabicyclo[3,2,0]-3-heptene-3-al Diacetate (*XII*) and 6-Phenyl-2,7-dioxabicyclo[3,2,0]-3-heptene-3-al (*XIII*)

A mixture of 2-furfural diacetate (2 g, 0·01 mol) and benzaldehyde (1·1 g, 0·01 mol) in 100 ml of benzene was irradiated through a Sial filter for 28 h. The solvent was distilled off and the polymers were precipitated by an addition of diethyl ether (30 ml). The filtrate contained the unreacted *IV* and the oxetanes *XI* and *XII* in a ratio of 1 : 3. Chormatography (Al_2O_3, C_6H_6) gave 0·2 g (6%) of 2-furfural diacetate, 1·5 g (50%) of an oily mixture of *XI* and *XII* and 0·2 g (6%) of *XIII* (an oil).

XIa: ^1H NMR spectrum in C^2HCl_3: 2·00 (s, 3 H, CH_3), 2·03 (s, 3 H, CH_3), 4·30 (dd, 1 H, H^3), 5·20 (m, 1 H, H^5), 5·58 (d, 1 H, H^6), 6·55 (d, 1 H, H^3), $J_{3,4} = 3$ Hz, $J_{4,5} = 4$ Hz, $J_{5,6} = 4$ Hz.

XIb: ^1H NMR spectrum in C^2HCl_3: 1·74 (s, 3 H, CH_3), 1·90 (s, 3 H, CH_3), 3·68 (dd, 1 H, H^5), 5·20 (m, 1 H, H^4), 5·58 (d, 1 H, H^6), 6·55 (d, 1 H, H^3), 7·08 (s, 1 H, H^7), 7·25—7·50 (m, 5 H, atom), $J_{3,4} = 3$ Hz, $J_{4,5} = 3$ Hz, $J_{5,6} = 4$ Hz.

XII: ^1H NMR spectrum in C^3HCl_3): 2·08 (s, 6 H, 2 × CH_3), 3·90 (dd, 1 H, H^5), 5·69 (dd, 1 H, H^6), 6·18 (d, 1 H, H^4), 6·68 (d, 1 H, H^1), 7·25—7·50 (m, 6 H, arom., H^7).

XIII: IR spectrum in $CHCl_3$ (cm^{-1}): 3 000, 1 700, 1 610, 1 450, 1 240; ^1H NMR spectrum in C^2HCl_3: 3·90 (dd, 1 H, H^5), 5·65 (d, 1 H, H^6), 6·45 (d, 1 H, H^4), 6·63 (d, 1 H, H^1), 7·40 (m, 5 H, arom), 9·59 (s, 1 H, H^7), $J_{1,5} = 4$ Hz, $J_{4,5} = 3$ Hz, $J_{5,6} = 3$ Hz.

6,6-Diphenyl-2,7-dioxabicyclo[3,2,0]-3-heptene-1-al Diacetate (*XIV*), 5,5,9,9-Tetraphenyl-2,4,8-trioxatricyclo[5,2,0,$0^{3,6}$]-nonane-3-al Diacetate (*XV*) and 5,5,8,8-Tetraphenyl-2,4,9-trioxatricyclo[5,2,0,$0^{3,6}$]-nonane-3-al Diacetate (*XVI*)

A mixture of 2-furfural diacetate (2·0 g, 0·01 mol) and benzophenone (1·82 g, 0·01 mol) in 150 ml of benzene was irradiated through a Sial filter for 27 h. After removal of the solvent and the polymers (separated by an addition of diethyl ether) the mixture contained compounds *IV*, *XIV*, *XV*, *XVI* and *XVII* in a ratio of 5 : 2 : 1, respectively (judging by ^1H NMR). Following chromatography (Al_2O_3, C_6H_6) and fractional crystallization (ethyl acetate, diethyl ether, cyclohexane)

there was obtained 0·8 g (21%) of *IV*; 0·8 g (21%) of *XIV*; m.p. 153—154°C (cyclohexane, diethyl ether); 0·8 g (21%) of *XV*), m.p. 217—218°C (ethyl acetate, diethyl ether); 0·7 g (18%) of *XVI*, m.p. 140—141°C (ethyl acetate, diethyl ether) and 0·3 g (8%) of *XVII*, m.p. 183—185°C (reported[26] m.p. 185—186°C). IR spectrum in $CHCl_3$ (cm^{-1}): *IV*: 1 760, 1 500, 1 380, 1 230, 1 140; *XIV*: 1 760, 1 610, 1 450, 1 230; *XV*: 1 760, 1 450, 1 230, 1 080; *XVI*: 1 760, 1 450, 1 300, 1 010; *XVII*: 3 600, 1 490, 1 350, 1 020. ^{1}H NMR spectrum in C^2HCl_3: *XIV*: 1·59 (s, 3 H, CH_3), 1·86 (s, 3 H, CH_3), 4·60 (dd, 1 H, H^5), 4·87 (dd, 1 H, H^4), 6·41 (dd, 1 H, H^3), 7·00 (s, 1 H, H^8), 7·18—7·42 (m, 10 H, arom), $J_{3,4}$ = 3 Hz, $J_{3,5}$ = 1 Hz; *XV*: 1·28 (s, 3 H, CH_3), 1·65 (s, 3 H, CH_3), 4·28 (s, 1 H, H^6), 4·86 (d, 1 H, H^1), 5·26 (d, 1 H, H^7), 6·34 (s, 1 H, H^{10}), 7·12—7·50 (m, 20 H, arom.), $J_{1,7}$ = 4 Hz; *XVI*: 1·45 (s, 3 H, CH_3), 1·82 (s, 3 H, CH_3), 3·59 (d, 1 H, H^7), 3·99 (s, 1 H, H^6), 6·01 (d, 1 H, H^1), 6·71 (s, 1 H, H^{10}), 7·10—7·50 (m, 20 H, arom.), $J_{1,7}$ = 4 Hz. ^{13}C NMR spectrum in C^2HCl_3: *XIV*: 20·0 (q, CH_3), 20·4 (q, CH_3), 53·2 (d, $C_{(5)}$), 85·1 (d, $C_{(8)}$), 94·5 (s, $C_{(6)}$), 102·8 (d, $C_{(4)}$), 111·0 (s, $C_{(1)}$), 124·7—128·5 (m, 10 C, aro.), 142·4 (s, α-C arom.), 144·8 (s, α-C arom.), 148·7 (d, $C_{(3)}$), 168·5 (s, 2 × C=O); *XV*: 19·6 (s, CH_3), 20·0 (s, CH_3), 55·2 (d, $C_{(6)}$), 81·6 (d, $C_{(1)}$, 82·4 (s, $C_{(5)}$), 85·8 (d, $C_{(10)}$), 90·1 (d, $C_{(7)}$), 90·1 (s, $C_{(9)}$), 114·5 (s, $C_{(3)}$), 124·8—128·4 (m, 20 C, aro.), 140·7 (s), 141·0 (s), 143·3 (s), 144·2 (s) (all α-C arom.), 168·3 and 168·5 (s, 2 × C=O); *XVI*: 19·8 (s, CH_3), 20·4 (s, CH_3), 50·8 (d, $C_{(7)}$), 52·9 (d, $C_{(6)}$), 84·5 (s, ($C_{(5)}$ and $C_{(8)}$), 85·8 (d, $C_{(10)}$), 108·6 (d, $C_{(1)}$), 114·0 (s, $C_{(3)}$), 125·1—128·8 (m, 20 C, arom.), 141·5 (s), 144·5 (s), 145·7 (s) (all α-C arom.), 168·3 (s, 2 × C=O). Mass spectrum, *m/z* (relative intensity in %): *XIV*: 380 (8), 278 (10), 223 (14), 222 (58), 221 (22), 198 (10), 155(16), 131 (12), 115 (24), 105 (18), 95 (22), 77 (10), 44 (16), 43 (100, 28 (32); *XV*: 381 (4), 350 (8),278 (6), 264 (6), 250 (8), 223 (11), 222 (42), 221 (17), 198 (30), 183 (14), 166 (11, 165 (15), 155 (38), 115 (19), 105 (36), 103 (14), 97 (21), 96 (36), 95 (61), 84 (14), 83 (15), 82 (25), 77 (19), 56 (15), 55 (19), 43 (100), 28 (21); *XVI*: 359 (1), 358 (3), 265 (1), 182 (11, 106 (27), 105 (100), 99 (18), 98 (18), 97 (27), 95 (23), 91 (27), 85 (32), 83 (27), 81 (23), 77 (55), 71 (46), 70 (27), 69 (32), 59 (23), 57 (77), 56 (32), 55 (41), 43 (96), 41 (46,) 28 (50).

XIV: For $C_{22}H_{20}O_6$ (380·4) calculated: 69·46% C, 5·30% H; found: 69·99% C, 5·40% H.

XV: For $C_{35}H_{30}O_7$ (562·6) calculated: 74·72% C, 5·38% H; found: 74·38% C, 5·46% H.

XVI: For $C_{35}H_{30}O_7$ (562·6) calculated 74·72% C, 5·38% H; found: 74·40% C, 5·39% H.

2-(6,6-Diphenyl-2,7-dioxabicyclo[3,2,0]-3-heptene-1-yl)-1,3-dioxolane (*XVIII*),
2-(5,5,8,8-Tetraphenyl-2,4,9-trioxatricyclo[5,2,0,$0^{3,6}$]-3-nonyl)-1,3-dioxolane (*XIX*)
and 2-(5,5,9,9-Tetraphenyl-2,4,8-trioxatricyclo[5,2,0,$0^{3,6}$]-3-nonyl)-1,3-dioxolane (*XX*)

A mixture of *V* (1·4 g, 0·01 mol) and benzophenone (1·82 g, 0·01 mol) in 100 ml of benzene was irradiated through a Sial filter for 16 h. After removal of the solvent and the polymers (separated by adding 15 ml of diethyl ether) we obtained a mixture of *V* : *XVIII* : *XIX* : *XX* : *XVII* in a ratio of 3 : 1·5 : 1·5 : 1 : 1. Chromatography (Al_2O_3, C_6H_6) afforded 0·6 g (19%) of *V*; 0·7 g (22%) of *XVIII*, m.p. 155—156°C (ethyl acetate, diethyl ether), 0·9 g (28%) of *XIX*, m.p. 201—202°C (cyclohexane); 0·5 g (15%) of *XX*, m.p. 227—228°C (cyclohexane, diethyl ether) and 0·4 g (13%) of *XVII*, m.p. 183—185°C (diethyl ether). IR spectrum in KBr (cm^{-1}): *V*: 3 020, 1 500, 1 350, 1 160; *XVIII*: 3 020, 1 600, 1 450, 1 140; *XIX*: 3 020, 1 450, 1 180; *XX*: 3 020, 1 450, 1 090. ^{1}H NMR spectrum in C^2HCl_3: *XVIII*: 3·75—4·00 (m, 4 H, 2 × CH_2), 4·48 (d, 1 H, H^5), 4·88 (dd, 1 H, H^4), 6·45 (d, 1 H, H^3), 7·00—7·50 (m, 10 H, arom), $J_{3,4}$ = $J_{4,5}$ = 3 Hz; *XIX*: 3·25 to 3·70 (m, 4 H, 2 × CH_2), 4·05 (m, 2 H, H^6, H^7), 4·75 (s, 1 H, H^{10}), 6·00 (d, 1 H, H^1), 7·13—7·48 (m, 20 H, arom.), $J_{1,7}$ = 4 Hz; *XX*: 3·22—3·68 (m, 4 H, 2 × CH_2), 4·27 (m, 2 H, H^6, H^{10}), 4·85 (d, 1 H, H^1), 5·31 (d, 1 H, H^7), 7·15—7·50 (m, 20 H, arom.), $J_{1,7}$ = 4·5 Hz. Mass spectrum, *m/z* (relative intensity in %): *XVIII*: 322 (9), 294 (12), 139 (24), 115 (12), 105 (18), 73 (100),

45)18), 44 (15), 28 (27); *XIX*: 322 (1), 294 (7), 268 (7), 207 (17), 182 (12), 167 (17), 165 (12), 105 (24), 77 (17), 73 (100), 45 (15), 44 (15), 28 (30).

XVIII: For $C_{20}H_{18}O_4$ (322·3) calculated: 74·52% C, 5·63% H; found: 74·40% C, 5·58% H.

XIX: For $C_{33}H_{28}O_5$ (504·6) calculated: 78·55% C, 5·59% H; found: 78·51% C, 5·71% H.

XX: For $C_{33}H_{28}O_5$ (504·6) calculated: 78·55% C, 5·59% H; found: 78·42% C, 5·65% H.

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