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RING OPENING AND RING-CHAIN TAUTOMERISM IN 2-CARBALKOXY- AND 2-ACYL-2,3-DIHYDRO-1,4-BENZODIOXINS.

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Abstract - The behaviour of benzodioxin esters 1a-c and ketones 2a-c under the action of K_2CO_3 in acetone and of NaH in DMSO has been studied; the experiments were also carried out in the presence of scavengers of phenolic intermediates or products. Under the action of potassium acetonate the esters did not undergo ring opening and ring-chain tautomerism was absent; however, in the presence of 1-chloro-2-(diethylamino)ethane partial ring cleavage occurred, while the tautomerism was evidenced. The esters were easily converted into mixtures of the corresponding lactones 6a-c and acids 7a-c by the action of NaH in DMSO. Ketones 2a and 2b were stable in the K_2CO_3/acetone system, but ring-chain tautomerism was shown to be at work in the case of 2b and 2c, while the latter also underwent ring cleavage. In the same system, but in the presence of an alkylating agent, the three ketones easily underwent ring opening.

It is known that the reaction of catechol with α-halo Michael acceptors, or their precursors, in the K_2CO_3/acetone system affords 2,3-dihydro-1,4-benzodioxin derivatives; however, if β-substituted Michael acceptors are employed, the heterocyclic compounds are generally obtained in poor yield,[1-3] the main products being open chain catechol enol ethers.[4,5] The addition of catechol to an α,β-unsaturated system has been recognized as the preliminary step of two alternative pathways, nucleophilic substitution of the halogen at the newly generated sp^3-carbon (derived from the α-halogeno-Michael acceptor) occurring subsequently either intramolecularly[3] or through the attack by a second molecule of catechol anion, followed by a retro-Michael reaction leading to the catechol enol ethers.[6,7] However, the latter compounds might also originate from opening of the heterocycle, through a base catalyzed retro-Michael reaction; in this case the equilibrium between ring and chain tautomers might reasonably be shifted towards the ring tautomers when starting from α-halo-β-unsubstituted Michael acceptors. To our knowledge, the above equilibrium has not yet been systematically investigated; we have therefore decided to study the behaviour of esters 1a-c and ketones 2a-c under the action of K_2CO_3 in dry acetone (*i.e.* in the conditions usually employed for their preparation) and in a much more basic system (NaH/DMSO). The reactions were also performed in the presence of scavengers of phenolic intermediates or products.

RESULTS

The main results are summarized in the Table. Benzodioxin esters 1a-c were shown to be stable in the K_2CO_3/acetone system even in the presence of a phenol scavenger such as CH_3I (reactions 1,5,9 - see Table); in particular, stereoisomeric mixtures of both 1b and 1c were recovered unreacted.

However, esters 1a-c underwent ring cleavage in the K_2CO_3/acetone system when 1-chloro-2-(diethylamino)ethane was used as scavenger; in fact, while the α,β-unsaturated esters 3a-c and 4a-c were obtained in low yield after prolonged reation times (reactions 2,6,10), benzodioxins 1b,c were recovered as mixtures stereoisomerically different from those of the starting materials. In addition, benzodioxin esters 5a,b, lactones 6a-c and acid 7c were found among the products of the corresponding reactions.

Treatment of esters 1a-c with NaH in DMSO resulted in complete ring cleavage within very short reaction times affording mixtures of the corresponding lactones 6a-c and acids 7a-c (reactions 3,7,11). Remarkably, when the above reactions were run in the presence of CH_3I (reactions 4,8) or C_2H_5I (reaction 12) mixtures of the corresponding methyl and ethyl esters 8a,b, 8c,d and 8e,f were obtained.

Ketones 2a-c, as expected, were more reactive than the corresponding esters 1a-c. Ketone 2a, apparently stable in the simple K_2CO_3/acetone system, underwent partial ring opening in the presence of CH_3I, affording α,β-unsaturated ketone 9a in low yield (reactions 13,14). When 1-chloro-2-(dietylamino)ethane was employed as the alkylating agent, however, ring cleavage occurred almost completely, and α,β-unsaturated ketone 10a was the only product (reaction 15). Analogously, both *cis* and *trans* 2b did not react in the K_2CO_3 system in the absence of scavengers, but stereoisomeric equilibration was observed (reactions 16,17). In the presence of CH_3I *trans* 2b gave a poor yield of guaiacol derivative 9b along with the same stereoisomeric equilibration of the substrate observed

Table. Reactions of esters 1a-c and ketones 2a-c

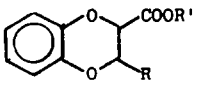
Reaction	Substrate (configuration)	Reaction system[a]	Reaction time	Conversion[b]	Products (yields)[c]			
1	1a	A,B	48 h	0%	---			
2	1a	C	48 h	60%	3a(38%)	4a(14%)	5a (6%)	6a (2%)
3	1a	D	15'	100%	6a(20%)	7a(80%)		
4	1a	E	1 h	100%	8a(80%)	8b(20%)		
5	1b (*trans* or *cis*)	A,B	48 h	0%	---			
6	1b (*trans*)	C	48 h	52%(7:4)	3b(13%)	4b(13%)	5b(16%)	6b (2%)
7	1b (*trans*)	D	15'	100%	6b(15%)	7b(85%)		
8	1b (*trans*)	E	1 h	100%	8c(33%)	8d(67%)		
9	1c (*trans* or *cis*)	A,B	48 h	0%	---			
10	1c (d)	C	48 H	57%(3:7)	3c(20%)	4c(12%)	6c(10%)	7c(15%)
11	1c (*trans* or *cis*)	D	15'	100%	6c(10%)	7c(90%)		
12	1c (*trans* or *cis*)	F	1 h	100%	8e(80%)	8f(20%)		
13	2a	A	48 h	0%	---			
14	2a	B	48 h	12%	9a			
15	2a	C	48 h	85%	10a			
16	2b (d)	A	48 h	0%(1:2)	---			
17	2b (*trans*)	A	48 h	0%(1:2)	---			
18	2b (*trans*)	B	48 h	18%(1:2)	9b(Z)			
19	2b (*trans*)	C	12 h	95%	10b(Z)			
20	2c (*trans*)	A	3 h	65%(1:3)	11c(Z)			
21	2c (*trans*)	B	48 h	85%(1:4)	9c(Z/E = 8:1)			
22	2c (*trans*)	C	12 h	95%	10c(Z)			
23	2c (*cis*)	B	48 h	85%(1:4)	9c(Z/E = 8:1)			
24	2c (*cis*)	C	8 h	95%	10c(Z)			

(a) A = K_2CO_3/acetone; B = K_2CO_3/acetone + CH_3I; C = K_2CO_3/acetone + $(C_2H_5)_2NCH_2CH_2Cl$; D = NaH/DMSO; E = NaH/DMSO + CH_3I; F = NaH/DMSO + C_2H_5I.

(b) The *cis-trans* ratio in the recovered starting material, when observed, is reported in parenthesis.

(c) Calculated by glc analysis of the crude reaction mixture.

(d) A roughly 1:1 mixture of the *cis-trans* isomers was employed in the reaction.

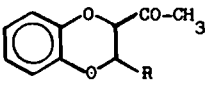


1

1a : R=H $R'=C_2H_5$

1b : $R=CH_3$ $R'=C_2H_5$

1c : $R=C_6H_5$ $R'=CH_3$

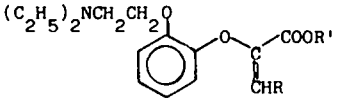


2

2a : R=H

2b : $R=CH_3$

2c : $R=C_6H_5$

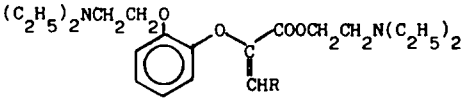


3

3a : R=H $R'=C_2H_5$

3b : $R=CH_3$ $R'=C_2H_5$

3c : $R=C_6H_5$ $R'=CH_3$

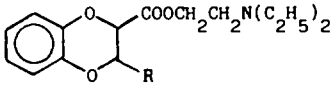


4

4a : R=H

4b : $R=CH_3$

4c : $R=C_6H_5$

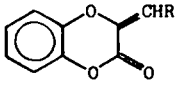


5

5a : R=H

5b : $R=CH_3$

5c : $R=C_6H_5$

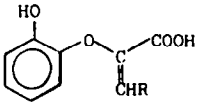


6

6a : R=H

6b : $R=CH_3$

6c : $R=C_6H_5$

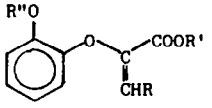


7

7a : R=H

7b : $R=CH_3$

7c : $R=C_6H_5$



8

8a : R=H $R'=R''=CH_3$

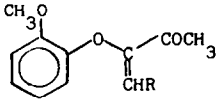
8b : R=H $R'=C_2H_5$ $R''=CH_3$

8c : $R=R'=R''=CH_3$

8d : $R=R''=CH_3$ $R'=C_2H_5$

8e : $R=C_6H_5$ $R'=CH_3$ $R''=C_2H_5$

8f : $R=C_6H_5$ $R'=R''=C_2H_5$

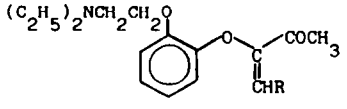


9

9a : R=H

9b : $R=CH_3$

9c : $R=C_6H_5$



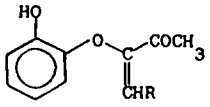
10

10a : R=H

10b : $R=CH_3$

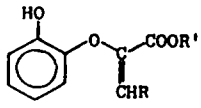
10c : $R=C_6H_5$

in the absence of scavenger. Furthermore, an almost quantitative yield of aminoether 10b was obtained when the reaction was run in the presence of 1-chloro-2-(diethylamino)ethane (reaction 19). Ring opening occurred more easily with 2c. The *trans* isomer in the simple K_2CO_3/acetone system remarkably afforded only phenol 11c, mainly as the Z isomer (reaction 20). In the presence of CH_3I the *trans* and *cis* isomers gave the same stereoisomeric mixture of 9c and of the recovered benzodioxin, in which the *trans* isomer was largely predominant (reactions 21,23). Finally, as in the case of 2a,b, in the presence of 1-chloro-2-(diethylamino)ethane, the reaction of both *cis* and *trans* 2c resulted in an almost complete ring cleavage which led to 10c as the pure Z isomer (reactions 22,24).



11

11a : R=H
11b : R=CH_3
11c : R=C_6H_5



12

12a : R=H R'=C_2H_5
12b : R=CH_3 R'=C_2H_5
12c : R=C_6H_5 R'=CH_3

DISCUSSION

From the above results the following conclusions can be drawn about ring-chain tautomerism and base catalyzed ring cleavage (two distinct, although strictly related processes) in the two series of substrates under investigation.

Potassium acetonate, the base actually present in the K_2CO_3/acetone system, is capable of inducing ring opening in 2,3-dihydro-1,4-benzodioxins provided that a sufficiently strong carbanion stabilising group is present on the heterocycle. The carbalkoxy group is unable to render the C_2-hydrogen sufficiently acidic to allow the retro-Michael reaction to occur in the presence of potassium acetonate, as shown by the stability of the esters and the absence of stereomutation in the reactions run in the presence of CH_3I; indeed ring closure of open-chain tautomers of 1b,c is not expected to be stereospecific. Thus it appears that, at least in the simple K_2CO_3/acetone system, ring-chain tautomerism does not occur with esters 1a-c. The partial ring cleavage of 1a-c in the reactions run in the presence of a basic scavenger such as 1-chloro-2-(diethylamino)ethane may well be due to the higher base concentration rather than to its strength with respect to the acetonate.(*) As for the stereochemical changes observed in the latter reactions, mechanisms involving a reversible ring opening or a ring closed enolate anion are to be considered. In view of the low carbanion stabilising power of the carbalkoxy group, as well as of the fact that stereomutation of esters 1b,c has been observed only under experimental conditions which led to open chain products (cfr. reactions 5 and 6, 9 and 10), the hypothesis can be made that ring-chain tautomerism is really operating in the reactions of 1b,c in the presence of 1-chloro-2-(diethylamino)ethane.

While the formation of open-chain esters 3a-c does not deserve any comment, that of aminoalkyl

(*) The effectiveness of 1-chloro-2-(diethylamino)ethane as alkylating agent of the open-chain tautomers 12a-c (in contrast to CH_3I or C_2H_5I) cannot be ascribed to neighbouring participation by nitrogen, since similar results were obtained when 1-chloro-3-(diethylamino)propane was employed as the scavenger for the phenolic intermediates or products.

esters 4a-c and 5a-c needs some mechanistic explanation. Probably, both basic esters are formed through the preliminary lactonization of the corresponding open-chain tautomers 12a-c; ring opening of lactones 6a-c would then give the potassium salts of acids 7a-c, which might undergo amino-alkylation of both the carboxylic and the phenolic groups, affording 4a-c. Only with the less hindered substrates 1a,b the simple aminolkylation of the more acidic function could be followed by ring closure leading to the benzodioxin esters 5a,b. Indeed, formation of 5c was never observed. Strong support to the above views, concerning the intermediate lactonization of the open-chain tautomers 12a-c, was given by the obtainment of mixtures of methyl and ethyl esters 8a,b 8c,d and 8e,f respectively, when the above reactions were run in the presence of CH_3I or C_2H_5I.

As expected, the base strength of the reaction medium was found to be a dominating factor in favouring ring cleavage of esters 1a-c; in fact, they were converted quantitatively into acids 7a-c and lactons 6a-c by the action of NaH in DMSO solution under very mild conditions and in the absence of any scavenger of free phenolic groups. Also, in the simple K_2CO_3/acetone system, when a phenolic compound is present in fair amounts in the reaction medium (as clearly is the case in the usual synthesis of 1a-c starting from catechol and the proper α,β-dibromo ester or the corresponding α-bromo Michael acceptor) the active base is no longer the acetonate, but the phenolate anion; then, ring opening of the formed esters 1a-c does occur and an equilibrium is established between ring and chain tautomers, its position being eventually influenced by substitution at C_3. This is confirmed by ring opening and equilibration of isomeric mixtures of 1b,c in the K_2CO_3/acetone system in the presence of phenol or catechol. Consequently the much better yields obtained in the preparation of 1a (74%)[3] in comparison with those of 1b (28%)[3] and 1c (16%)[2] cannot be explained solely in terms of steric hindrance and/or electronic effects exerted by the substituent on the α-bromo Michael acceptor.(*)

The behaviour of ketones 2a-c is intrinsically less complicated: the more efficient carbanion stabilization offered by the acetyl group, as well as substitution on the heterocycle appear to be important factors in determining the equilibrium position between 2a-c and 11a-c. In the case of 2a the equilibrium appears to be entirely shifted towards the heterocycle in the presence of potassium acetonate; however, the existence of ring-chain tautomerism is revealed by the esperiments run in the presence of scavengers (see reactions 14,15). As a matter of facts, with the ketones a ring-closed enolate anion may also be involved in the reactions eventually leading to ring cleavage, the phenoxide being an excellent nucleofuge in this type of process. This enolate-ring opening mechanism may also explain the stereomutation observed with ketones 2b,c in the simple K_2CO_3/acetone system (see reactions 16, 17, 20).

EXPERIMENTAL

All melting points and boiling points are uncorrected. NMR spectra were taken on a Perkin-Elmer R-24 spectrometer or on a Bruker LXP 300 instrument, with chemical shifts reported in ppm downfield from internal reference Me_4Si. Infrared spectra were taken on a Perkin-Elmer Model 257 infrared

(*) The low yields previously described for 1b are due to the concurrent formation of lacton 6b and acid 7b, the major products of the reaction; the latter separates from the reaction medium as the potassium salt together with inorganic salts, and consequently is going to be lost in the absence of an acidic treatment of the cake obtained after filtration of the final acetone solution. It is noteworthy that lactones 6a and 6c were not observed in the preparation of 1a and 1c, respectively. The thermal or acid catalyzed lactonization of acid 7b to 6b already appears in the literature;[4] however, we have established that lactone 6b is stable in boiling anhydrous acetone, but is almost completely converted into the potassium salt of 7b in the presence of K_2CO_3. Also different mixtures of 6b and 7b are obtained by treating with aqueous acids a solution of 6b in an organic solvent, depending on the experimental conditions.

spectrophotometer. Mass spectra were obtained from a RMU-7, double focusing spectrometer or from a Perkin-Elmer 270 instrument, directly connected to a gas chromatograph, operating at 80 eV; column: SE 30, 5% on Chromosorb P, 80-100 mesh (silanized); temperature: 155°. Elemental analyses (C,H and occasionally N) gave satisfactory results within ±0.4% of the calculated values. Preparative thin-layer chromatography (TLC) were carried on commercial silica gel plates (E. Merck, 2.0 mm thickness).

Starting materials. The following substrates were prepared according to known methods. Ethyl 2,3-dihydro-1,4-benzodioxin-2-carboxylate 1a.[8] Ethyl 2,3-dihydro-3-methyl-1,4-benzodioxin-2-carboxylate 1b (obtained as pure *cis* and *trans* isomers[14]). Methyl 2,3-dihydro-3-phenyl-1,4-benzodioxin-2-carboxylate 1c (obtained as a mixture of *cis/trans* isomers in 1:1 ratio[2] and as pure *cis* and *trans* isomers[13]). 2-Acetyl-2,3-dihydro-1,4-benzodioxin 2a.[9] 2-Acetyl-2,3-dihydro-3-methyl-1,4-benzodioxin 2b (as a mixture of *cis/trans* isomers in 1:1 ratio[5]); the pure *trans* isomer 2b (m.p. 56-8°) was obtained by repeated crystallization from hexane. 2-Acetyl-2,3-dihydro-3-phenyl-1,4-benzodioxin 2c (as the pure *trans* isomer[10]); the pure *cis* isomer was obtained as an oil from column cromatography of the mixture of isomers over silica gel 40 by elution with benzene-hexane 2:1.

General procedures. The solution of the 2,3-dihydro-1,4-benzodioxin derivative (0.02 moles) in dry acetone (100 ml) was refluxed (see reaction time in the Table) in the presence of anhydrous K_2CO_3 (0.03 moles) (procedure A). In the experiments with a scavenger of free phenolic groups 0.2 moles of CH_3I (or C_2H_5I) (procedure B) or 0.022 moles of $(C_2H_5)_2NCH_2CH_2Cl$ (procedure C) were added to the reaction mixture. The final mixture, after filtration, was evaporated to dryness. The residue underwent IR, NMR and/or GC/MS analysis. Separation and/or purification of the products were generally obtained by fractional distillation or by column or TLC chromatography. In the reactions run in the presence of NaH (procedure D) the solution of the substrate (0.01 moles) in DMSO (5-10 ml) was added to a suspension of 80% NaH in mineral oil (0.02 moles) in DMSO (20 ml) under stirring, keeping the temperature under 40°C. In the experiments with a scavenger (procedure E or F) 0.1 moles of CH_3I (or C_2H_5I) were added. At the end of the reaction, the mixture was cooled, poured over ice, carefully acidified with 1:1 HCl and extracted with CH_2Cl_2. After evaporation of the solvent, the residue underwent IR, NMR and/or GC/MS analysis. Separation and/or purification of the products were obtained by fractional distillation and/or crystallization.

Ethyl 2-[2-(diethylaminoethoxy)phenoxy]-2-propenoate 3a. Oil: b.p. 195-200°/0.6 mm; IR (thin film): 1750,1635 cm^{-1}; NMR ($CDCl_3$): δ 1.05(t,6H,CH_3), 1.08(t,6H,CH_3), 2.40-3.03(m,6H,CH_2), 3.95-4.52 (m,4H,OCH_2,$COOCH_2$), 4.60 and 5.56(d,1H,=CH_2), 6.85-7.25(m,4H,ArH); Mass spectrum: m/e 307 (M^+), 292, 279, 234, 209, 162, 147, 135, 121, 100, 86 (100).

Ethyl 2-[2-(2-diethylaminoethoxy)phenoxy]-2-butenoate 3b. The product was only obtained in mixture with 5b. The identification was based on the IR, NMR and GC/MS analyses of the mixture. Mass spectrum: m/e 321 (M^+), 306, 248, 222, 176, 147, 121, 99, 86 (100).

Methyl 2-[2-(2-diethylaminoethoxy)phenoxy]-3-phenyl-2-propenoate 3c. The product was isolated in pure state as an oil by preparative TLC (eluent: n-BuOH-CH_3COOH-H_2O 4:1:2); IR (thin film): 1735,1650 cm^{-1}; NMR ($CDCl_3$): δ 1.06(t,3H,$NCH_2\underline{CH_3}$), 2.48-3.08(m,6H,CH_2N), 3.77(s,3H,$COOCH_3$), 4.26 (t,2H,OCH_2), 6.86-8.02(m,10H,ArH,=CH); Mass spectrum: m/e 369 (M^+), 354, 310, 298, 238, 121, 86 (100).

2-Diethylaminoethyl 2-[2-(2-diethylaminoethoxy)phenoxy]-2-propenoate 4a. Oil: b.p. 225-230°/0.7 mm; IR (thin film): 1740, 1635 cm^{-1}; NMR ($CDCl_3$): δ 1.10(t,12H,$CH_2\underline{CH_3}$), 2.45-3.10(m,12H,$\underline{CH_2}CH_3$), 4.15 (t,2H,$COOCH_2$), 4.40(t,2H,OCH_2), 4.67 and 5.60(d,1H,=CH_2), 6.92-7.35(m,4H,ArH); Mass spectrum: m/e 378 (M^+), 363, 349, 279, 262, 234, 208, 171, 162, 135, 100, 86 (100).

2-Diethylaminoethyl 2-[2-(2-diethylaminoethoxy)phenoxy]-2-butenoate 4b. Oil: b.p. 255-260°/0.8 mm; IR (thin film): 1730,1665 cm^{-1}; NMR ($CDCl_3$): δ 0.97(t,6H,$CH_2\underline{CH_3}$), 1.07(t,6H,$CH_2\underline{CH_3}$), 1.78(d,3H, $CH\underline{CH_3}$), 2.48(q,4H,NCH_2), 2.63(m,6H,NCH_2), 2.93(t,2H,NCH_2), 4.16(t,2H,OCH_2), 4.17(t,2H,OCH_2), 6.67 (q,1H,=CH), 6.69-6.95(m,4H,ArH); Mass spectrum: m/e 392 (M^+), 391, 377, 363, 293, 209, 176, 147, 100, 86 (100).

2-Diethylaminoethyl 2-[2-(2-diethylaminoethoxy)phenoxy]-3-phenyl-2-propenoate 4c. The product was isolated as an oil in pure state by preparative TLC (eluent: n-BuOH-CH_3COOH-H_2O 4:1:2); IR (thin film): 1735,1650 cm^{-1}; NMR ($CDCl_3$): δ 0.99(t,3H,$NCH_2\underline{CH_3}$); 1.06(t,3H,$NCH_2\underline{CH_3}$), 2.35-3.05(m,12H,CH_2N), 4.23(t,2H,$COOCH_2$), 4.27(t,2H,OCH_2), 6.80-8.07(m,10H,ArH,=CH).

2-Diethylaminoethyl 2,3-dihydro-1,4-benzodioxin-2-carboxylate 5a. The compound was identified by comparison of its mass spectrum with that of an authentic sample.[11] Mass spectrum: m/e 279 (M^+), 264, 209, 191, 162, 135, 100, 86 (100).

2-Diethylaminoethyl 2,3-dihydro-3-methyl-1,4-benzodioxin-2-carboxylate 5b. The compound 5b was not

isolated in pure state, and identified by GC/MS. Mass spectrum: m/e 293 (M^+), 278, 221, 194, 176, 149, 121, 109, 99, 86, (100).

3-Methylene-1,4-benzodioxin-2(3H)-one 6a. IR and NMR spectra were in accordance with those of the literature:[12] m/e 162 (M^+, 100), 134, 105, 92.

3-Ethylidene-1,4-benzodioxin-2(3H)-one 6b. White crystals: m.p. 74-75° (from EtOH). M.p., IR, NMR and mass spectra were in accordance with those of an authentic sample.[3] Mass spectrum: m/e 176 (M^+), 147 (100), 135, 121, 71.

3-Benzylidene-1,4-benzodioxin-2(3H)-one 6c. White crystals (m.p. 170-73°, from benzene); m.p., IR and NMR spectra were in accordance with those of an authentic sample.[13]

2-(2-Hydroxyphenoxy)-2-propenoic acid 7a.[12] The product could be isolated in pure state only as disodium salt; m.p. 280°(dec.); IR (nujol): 1630,1600 cm^{-1}; NMR (D_2O): δ 4.32 and 5.12(d,1H,=CH_2), 6.52-7.05 (m,4H,ArH).

2-(2-Hydroxyphenoxy)-2-butenoic acid 7b. The product was purified by crystallization: m.p. 108-110° (from benzene). M.p., IR and NMR spectra were in accordance with those of an authentic sample.[4]

2-(2-Hydroxyphenoxy)-3-phenyl-2-propenoic acid 7c. The product was purified by crystallization: m.p. 138-140° (from benzene). M.p., IR and NMR spectra were in accordance with those of an authentic sample.[12]

Methyl 2-(2-methoxyphenoxy)-2-propenoate 8a. Oil: b.p. 130-135°/0.6 mm; IR (thin film): 1740, 1630 cm^{-1}; NMR ($CDCl_3$): δ 3.79(s,3H,$COOCH_3$), 3.81(s,3H,OCH_3), 4.61 and 5.55(d,1H,=CH_2), 6.83-7.34(m,4H,ArH).

Ethyl 2-(2-methoxyphenoxy)-2-propenoate 8b. Oil: b.p. 135-140°/0.6 mm; IR (thin film): 1740, 1630 cm^{-1}; NMR ($CDCl_3$): δ 1.28(t,3H,$COOCH_2\underline{CH_3}$), 3.81(s,3H,OCH_3), 4.27(q,2H,$COOCH_2$), 4.61 and 5.55 (d,1H,=CH_2), 6.83-7.34(m,4H,ArH).

Methyl 2-(2-methoxyphenoxy)-2-butenoate 8c. Oil: b.p. 150-155°/0.8 mm; IR (thin film): 1730, 1660 cm^{-1}; NMR ($CDCl_3$): δ 1.15(t,3H,$COOCH_2\underline{CH_3}$), 2.05(d,3H,=CH-$\underline{CH_3}$), 3.85(s,3H,OCH_3), 4.18(q,2H, $COO\underline{CH_2}CH_3$), 6.75(q,1H,=$\underline{CH}$-CH_3), 6.75-7.15(m,4H,ArH).

Ethyl 2-(2-methoxyphenoxy)-2-butenoate 8d. Oil: b.p. 155-160°/0.8 mm (lit.[4] 125-128°/0.5 mm); IR (thin film): 1730,1660 cm^{-1}; NMR ($CDCl_3$): δ 1.15(t,3H,$COOCH_2\underline{CH_3}$), 1.75(d,3H,=CH-$\underline{CH_3}$), 3.90 (s,3H,OCH_3), 4.18(q,2H,$COO\underline{CH_2}CH_3$), 6.74(q,1H,=$\underline{CH}$-CH_3), 6.75-7.16(m,4H,ArH).

Methyl 2-(2-ethoxyphenoxy)-4-phenyl-2-propenoate 8e. Oil: b.p. 185-190°/0.8 mm; IR (thin film): 1725,1640 cm^{-1}; NMR ($CDCl_3$): δ 1.44(t,3H,$OCH_2\underline{CH_3}$), 3.74(s,3H,$COOCH_3$), 4.18(q,2H,$O\underline{CH_2}CH_3$), 6.80-7.73 (m,10H,ArH,=CH).

Ethyl 2-(2-ethoxyphenoxy)-4-phenyl-2-propenoate 8f. Oil: b.p. 190-195°/0.8 mm; IR thin film): 1725,1640 cm^{-1}; NMR ($CDCl_3$): δ 1.17(t,3H,$COOCH_2\underline{CH_3}$), 1.44(t,3H,$OCH_2\underline{CH_3}$), 4.18(q,4H,$O\underline{CH_2}CH_3$, $COO\underline{CH_2}CH_3$), 6.80-7.73(m,10H,ArH,=CH).

3-(2-Methoxyphenoxy)-3-buten-2-one 9a. The compound was obtained impure of 2a. NMR ($CDCl_3$): δ 2.42 (s,3H,$COCH_3$), 3.83(s,3H,OCH_3), 4.48 and 5.40(d,1H,=CH_2), 6.85-7.18(m,4H,ArH). Mass spectrum: m/e 192 (M^+), 149 (M-$COCH_3$).

(Z)-3-(2-Methoxyphenoxy)-3-penten-2-one 9b. The product was obtained as a pure oil by column chromatography (silica gel 40, eluent: benzene). NMR ($CDCl_3$): δ 1.72(d,3H,CH_3), 2.18(s,3H,$COCH_3$), 3.86(s,3H,OCH_3), 6.54(q,1H,=CH), 6.58-7.04(m,4H,ArH). Mass spectrum: m/e 206 (M^+, 100), 175, 163, 148, 135, 124, 121, 109, 92.

3-(2-Methoxyphenoxy)-4-phenyl-3-buten-2-one 9c. The crude reaction product was a mixture of Z and E isomers. The pure ipomers were isolated by column chromatography (silica gel 40; eluent: benzene-hexane, benzene and $CHCl_3$). NMR of the E-isomer ($CDCl_3$): δ 2.28(s,3H,$COCH_3$), 3.86(s,3H,OCH_3), 6.25(s,1H,=CH), 6.90-7.60(m,9H,ArH). NMR of the Z-isomer ($CDCl_3$): δ 2.23 (s,3H,$COCH_3$), 3.91 (s,3H,OCH_3), 6.68-7.90(m,10H,ArH,=CH). Mass spectrum: m/e 268 (M^+), 225, 210, 197 (100), 182, 165, 124, 109, 77.

3-[2-(2-Diethylaminoethoxy)phenoxy]-3-buten-2-one 10a. Oil, which decomposes by distillation. The product was obtained in pure state by preparative TLC (eluent: n-ButOH-CH_3COOH-H_2O 4:1:2), NMR ($CDCl_3$): δ 1.02(t,3H,$NCH_2\underline{CH_3}$), 2.45(s,3H,$COCH_3$), 2.59(q,4H,$\underline{CH_2}CH_3$), 2.83(t,2H,$\underline{CH_2}N$), 4.05(t,2H,OCH_2),

4.38 and 5.33(d,1H,=CH_2), 6.70-7.20(m,4H,ArH). Mass spectrum: m/e 277 (M^+), 262, 234, 206, 178, 136, 135, 121, 109, 107, 100, 87, 86 (100).

(Z)-3-[2-(2-Diethylaminoethoxy)phenoxy]-3-penten-2-one 10b. Oil: b.p. 200-205°/0.6 mm; NMR ($CDCl_3$): δ 1.08(t,6H,CH_3), 1.74(d,3H,=CH-CH_3), 2.20(s,3H,$COCH_3$), 2.64(q,4H,N CH_2CH_3), 2.90(t,2H,OCH_2CH_2), 4.16(t,2H,OCH_2), 6.56(q,1H,=$CHCH_3$), 6.62-7.06(m,5H,ArH).

(Z)-3-[2-(2-Diethylaminoethoxy)phenoxy]-4-phenyl-3-buten-2-one 10c. Oil: b.p. 202-205°/0.8 mm; NMR ($CDCl_3$): δ 1.08(t,6H,CH_3), 2.25(s,3H,$COCH_3$), 2.42-3.05(m,6H,CH_2N), 4.18(t,2H,OCH_2), 6.62-7.80 (m,10H,ArH,=CH). Mass spectrum: m/e 353(M^+), 338, 310, 254, 211, 197, 181, 165, 145, 121, 100, 86 (100).

(Z)-3-(2-Hydroxyphenoxy)-4-phenyl-3-buten-2-one 11c. The pure product (m.p. 78-79°) was obtained by crystallization from cyclohexane. M.p., IR and NMR spectra were in accordance with those of an authentic sample.[5] Mass spectrum: m/e 254 (M^+), 211, 210, 197, 165, 145, 135, 121 (100), 103.

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