Tetrahedron Vol 49, No 11, pp 2275-2286, 1993
Printed in Great Britain

0040-4020/93 $6 00+ 00

Cyclopropanation Reaction of 3-Acyl-2*H*-1-Benzopyran-2-ones with Phenacylbromide in Phase Transfer Systems

Anka Bojilova, Antoaneta Trendafilova, and Christo Ivanov

Department of Organic Chemistry, University of Sofia, Anton Ivanov 1, 1126 Sofia, Bulgaria

Nestor A. Rodios*

Laboratory of Organic Chemistry, University of Thessaloniki, GR-54006 Thessaloniki, Greece

(*Received in UK* 31 *December* 1992)

Abstract: 3-Acyl-2*H*-1-benzopyran-2-ones 1 reacted with phenacylbromide in the presence of a base to give the cyclopropane derivatives 2 and 3 in moderate yields The yields of the reaction products were substantially improved by using a catalyst (Aliquat 336 or TPBP) under phase-transfer conditions A mechanistic explanation is given for the stereoselectivity of these reactions Spectroscopic data for compounds 2 and 3 are also given

Long ago Widman found[1] that the reaction of 3-acylcoumarins 1 with phenacylchloride or phenacylbromide in the presence of sodium ethoxide resulted in the formation of 3,4-phenacylidenecoumarins 2 in low to moderate yields. In that first study Widman[1] also gave a mechanistic explanation of the above transformation, but without any examination of the stereochemistry of the cyclopropane derivatives formed.

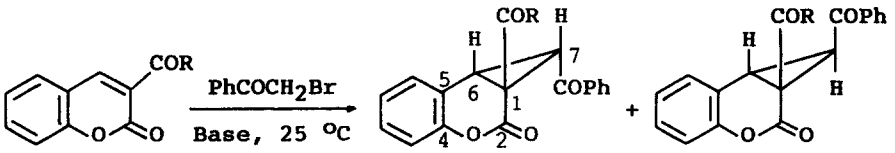
Two other papers appeared[2,3] concerning the mechanism of the above reaction, but with controversial aspects.

The formation of cyclopropane derivatives in the reaction of activated alkenes with α-haloesters or analogous compounds in the presence of a base, as well as the mechanism and the stereoselectivity of these reactions have been well studied[4-9]. It has been found that the yields and the stereoselectivity of these reactions are strongly affected by various factors related to the substituents on the double bond and the α-halo carbonyl compounds, as well as to the reaction conditions. Although there is a general agreement for the mechanism, different explanations have been given[10-12] for the stereoselectivity of these cyclopropanation reactions.

In the context of our previous work[13-15] on the reactions of 3-acylcoumarins with carbanions generated under Perkin reaction conditions and considering the above observations we decided to explore more systematically the cyclopropanation of the benzopyran-3,4-double bond in compounds of the type 1. For this study we performed the Widman reaction, modifying the reaction conditions, in order to optimize the yields of the reaction products and to examine its stereoselectivity.

RESULTS AND DISCUSSION

The 3-acylcoumarins 1 were reacted with phenacylbromide in the presence of a base giving the cyclopropane derivatives 2 and 3.



1 2 3

	R
a	OCH_3
b	OCH_2CH_3
c	$OC(CH_3)_3$
d	CH_3
e	CH_2CH_3
f	$CH(CH_3)_2$

	R
g	$C(CH_3)_3$
h	$CH(CH_2)_2$
i	C_6H_5
j	

The reaction of 3-acetylcoumarin (1d) and phenacylbromide under Widman[1] conditions gave the expected cyclopropane derivative 2d in relatively low yield (13%) and unchanged starting compound 1d (44%).

In order to improve the yields of the cyclopropane derivatives and to optimize the reaction conditions, different bases and solvents were checked as well as two-phase systems in the presence or absence of a transfer agent, acting as catalyst. Two-phase systems have been previously used[8-10,16] in cyclopropanation reactions.

Sodium hydride (NaH), 4% NaOH and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in different solvents were used as bases, but only 4% NaOH was used in phase-transfer conditions. The catalysts used in the latter cases were benzyltriethylammonium chloride (TEBA), tricaprylmethylammonium chloride (Aliquat 336), tetraphenylphosphonium bromide, benzyltriphenylphosphonium chloride (TPBP) and some other phosphorus containing compounds.

Table 1 shows the total yields and the *cis:trans* (2:3) ratio obtained from the reaction of 3-ethoxycarbonyl (1b) and of 3-acetyl (1d) coumarins with phenacylbromide under different experimental conditions. It is clearly seen that the best results are obtained under phase-transfer conditions, with TPBP or aliquat 336 as catalysts. The results of the reactions of other 3-acylderivatives 1a-j with phenacylbromide under phase-transfer conditions are summarized in Table 2.

From Tables 1 and 2 it is seen that the total yields of cyclopropane derivatives, 2+3, and the stereoselectivity of the reaction (*cis:trans* ratio) depend on the solvent, the catalyst and the amount of the base used (Table 1), as well as on the nature of the substituent of the benzopyran ring (Table 2).

Unexpectedly, the cyclopropanation of these benzopyrans is favoured by bulky substituents, and this is shown by the high yields (95%) obtained from the reaction of 3-pivaloylcoumarin (1g) with phenacylbromide, while the lowest yields (about 30%) were obtained from the benzopyrans with a less bulky substituent i.e. 1d, 1e (Table 2)

An explanation of the above observation might be the difference in

Table 1 Variations of Total Yields (%) of Cyclopropane Derivatives (**2b,d + 3b,d**) and *cis trans* (**2:3**) Ratios obtained from the Reaction of **1b,d** with Phenacylbromide under Different Experimental Conditions

Method	Reaction conditions Base[a]	Solvent	Catalyst[b]	Time (h)	Yield, % Unreacd **1b**	Total **2b+3b**	**2b·3b**	Yield, % Unreacd **1d**	Total **2d+3d**	**2d:3d**
Widman	EtONa	EtOH	-	-				44	13	100.-
A	DBU (1 1 1)	THF		48	23	57	63 36			
B1	NaH (1 1 1)	CH_2Cl_2	-	1	14	48	50 50			
B2	NaH (1 1 1)	CH_3CN	-	1	5	39	62 38	-	36	100 -
H1	4% NaOH (1 1·4)	C_6H_6	-	1	45	30	70·30			
H2	4% NaOH (1 1 4)	DMSO	-	0 5	-	54	61 39	-	40	100 -
C1	4% NaOH (1 1 4)	DMSO	TEBA	0 5	45	30	80 20			
C2	4% NaOH (1 1 4)	CH_2Cl_2	TEBA	0 5	55	36	67 33			
D1	4% NaOH (1 1 1)	CCl_4	Aliquat 336	1	11	55	93 7	37	43	100.-
D2	4% NaOH (1 1 1)	CH_2Cl_2	Aliquat 336	1				-	33	100·-
E1	4% NaOH (1.1 1)	C_6H_6	Aliquat 336	1 5	18	59	95 5	-	43	100·-
E2	4% NaOH (1 1 2)	C_6H_6	Aliquat 336	1				-	26	100 -
E3	4% NaOH (1 1 4)	C_6H_6	Aliquat 336	0 5	-	65	89 11			
F1	4% NaOH (1 1 4)	C_6H_6	TPBP	0 5	-	92	80 20			
F2	4% NaOH (1 1 2)	C_6H_6	TPBP	0 5				21	74	78 22
G1	4% NaOH (1 1 4)	C_6H_6	$Ph_4P^+Br^-$	0 5	18	48	81 19			
G2	4% NaOH (1 1 4)	C_6H_6	$Ph_3P{=}CHPh$	0 5	50	33	91 9			
G3	4% NaOH	C_6H_6	$Ph_2P(O)Et$	0 5	59	27	78 22			

[a] Values in parentheses represent the molar ratio of 1 $PhCOCH_2Br$.Base [b] TEBA= benzyltriethylammonium chloride, Aliquat 336=Tricaprylmethylammonium chloride, TPBP=Benzyltriphenylphosphonium chloride

sensitivity of the starting benzopyrans 1 and/or of the reaction products 2 and 3 to the base used. Indeed, although there is a tendency for the starting benzopy-ran to be consumed by increasing the amount of the base, this is not accompanied by an analogous increase of the yields of the isolated cyclopropane derivatives (see reactions of **1a, 1d and 1g**, Table 2). Blank experiments performed under phase transfer conditions (Method E2) with compounds **1b** and **1d**, resulted in recovery of the starting compounds in 90% and 66% yields respectively, in agreement with the above assumptions.

The stereoselectivity of the reaction is influenced by the reaction conditions (see Tables 1 and 2). This has been also observed[4,5b,10] in

Table 2 Variation of Yields (%) of Cyclopropane Derivatives (2+3) and *cis·trans* (2:3) Ratios obtained from the Reaction of 1a-j with Phenacylbromide under Phase-Transfer Conditions

Start comp	Method [a]	Yield, % Unreacd 1	Total 2+3	2:3	Start comp	Method [a]	Yield, % Unreacd 1	Total 2+3	2:3
1a	D1	-	57	100 -	1e	E3	-	28	100:-
	E1	10	59	100 -					
	E2	-	63	66 34	1f	D1	36	62	29·72
	E3	-	29	100 -		E3	14	68	32 68
	F1	-	67	100 -					
					1g	D1	-	95	15.85
1b	D1	11	55	93 7		E2	-	97	23 77
	E1	18	59	95 5		E3	-	87	33.67
	E3	-	65	89 11					
	F1	-	92	80 20	1h	E1	21	59	64·36
						E3	12	60	85 15
1c	D1	22	52	90 10					
	E1	30	60	85 15	1i	D1	16	57	33·67
	E3	30	66	88 12		E2	-	55	47 53
	F1	16	81	57 43		E3	-	56	48 52
						B2		49	61 39
1d	D1	37	43	100 -					
	E1	-	43	100 -	1j	E1	8	27	100 -
	E2	-	26	100 -		E3	-	19	100 -
	F2	21	74	78 22		F1	-	30	100 -
						F2	-	49	100 -

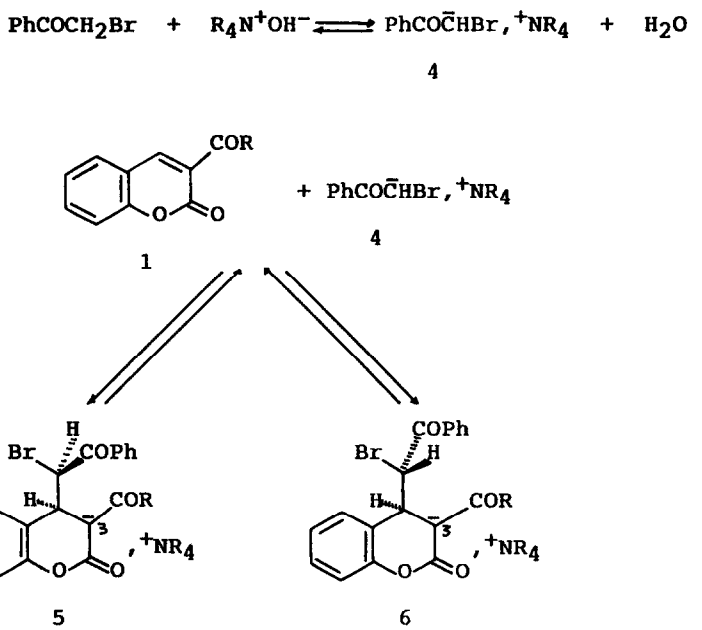
[a] For methods used see experimental

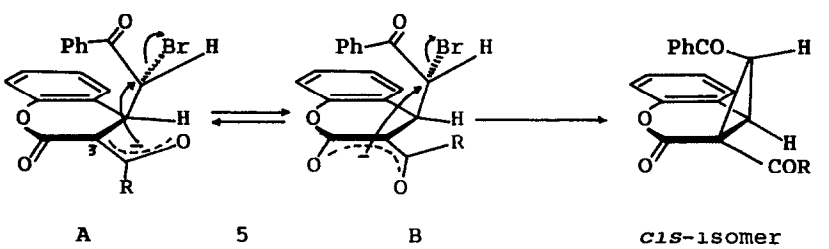
other analogous cyclopropanation reactions.

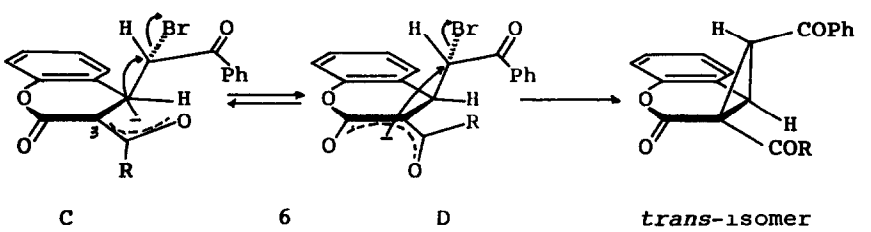
The stereoselectivity of the above reactions is also affected by steric factors,as it seen in the reactions of the 3-acylcoumarins **1a-e,h,j**, where the *cis* isomers **2a-e,h,j** are predominantly formed, whereas in the reactions of 3-isobutyryl and 3-pivaloylcoumarins (**1f,g**) the stereoselectivity is reversed, the *trans* isomers, **3f,g**, predominating substantially over the *cis*, **2f,g** (Table 2)

An explanation for the above findings could be given by considering the conformations that can be adopted by the intermediates, generated by a Michael addition of the anion **4** to the benzopyran-3,4-double bond (Scheme 1)

From the conformations that the intermediate anions **5** and **6** can adopt in order to give the cyclopropane derivatives, i.e. C-3 trans to Br, forms **A** and **B** lead to the formation of the *cis* and **C** and **D** to the formation of the trans isomers (Scheme 1). Forms **B** and **D** are expected to be more favoured than **A** and **C**, since in the former the negative charge can be distributed over the two carbonyls along the O=C-C-C=O chain and stabilized by chelation to the M^+ or R_4N^+ cations present in the reaction mixture. On the other hand, form **D**, suffering from strong steric interactions between the RCO and PhCO groups, should be destabilized in favour of form **B**. This results in the formation predominantly of the *cis* isomer, and is actually observed with most of the reactions studied. However, when the 3-acyl and specifically R-substituent is bulky, the steric interactions destabilize both **B** and **D** in favour of **A** and **C** forms, from which **C** should be predominant, as a result of the interaction of the two carbonyls of the RCO and PhCO groups. This leads to the formation predominantly of the *trans* isomer as it is observed in the reactions of 3-isobutyryl- and


PhCOCH2Br + R4N+OH− ⇌ PhCOCHBr,+NR4 + H2O
4
COR
O
O
1
+ PhCOCHBr,+NR4
4
H
Br
COPh
H
COR
3
O
O
,+NR4
5
COPh
Br
H
H
COR
3
O
O
,+NR4
6


Ph
O
Br
H
H
O
O
3
O
R
A
5
B
PhCO
H
H
COR
cis-isomer


H
Br
O
Ph
H
O
O
3
O
R
C
6
D
H
COPh
H
COR
trans-isomer

Scheme 1

3-pivaloyl-coumarins (**1f,g**). Similar interactions between carbonyl groups have been accepted[4c,10,11] to take place in analogous conformations of intermediates in other cyclopropanation reactions.

It should be noted however that the presence of the base in the reaction mixture affects the *cis:trans* ratio due to isomerization of the products **2** and **3**. Treatment of compound **2b** under the conditions of method E2 for 0.5 h and in the absence of phenacylbromide, gave **2b** (82%) and **3b** (12%), whereas the *trans* isomer **3g** under the same reaction conditions gave **2g** (6%) and **3g** (88%). The same isomerization was also observed when the *cis* isomers **2a**, **2b** and **2d** were refluxed in acetic acid anhydride in the presence of triethylamine.

The analytical and spectroscopic data of all isolated compounds are in agreement with the proposed structures. Thus the IR spectra of compounds **2** and **3** show three absorption bands at $\tilde{\nu}$ = 1740-1780 cm^{-1} for the lactone, and at $\tilde{\nu}$ = 1670-1680 cm^{-1} for the 7-benzoyl carbonyl groups, whereas the 1-acyl carbonyl group absorbs at $\tilde{\nu}$ = 1690-1740 cm^{-1}.

In the ^{1}H-NMR spectra, the protons attached to the cyclopropane ring give signals at δ = 4.10-4.40 and at δ = 3.20-3.50 for the *cis* isomers **4** and at δ = 3.70-3.90 and at δ = 3.10-3.40 for the *trans* isomers. Similar shift values, i.e. at δ = 2.9-3.5, have been reported[17] for analogous cyclopropylbenzopyranones. Differentiation between *cis* and *trans* isomers have been made on the basis of the cyclopropane 6-H and 7-H coupling constants, where a large value, $J_{6,7}$ = 9.4-9.8 Hz, corresponds to the *cis*, and a small value, $J_{6,7}$ = 5.1-5.5 Hz, to the *trans* isomer[12,17].

The ^{13}C-NMR spectra, recorded for some of the compounds **2** and **3**, show peaks for all carbon atoms, as expected The cyclopropane ring carbons 1-C, 6-C and 7-C, appear at the aliphatic region of the spectrum at δ = 30-45 ppm. The assignments of the spectra have been made using the attached proton experiments (APT) and in some cases the fully coupled spectra, whereas the aromatic carbons of the benzopyran ring were assigned by analogy to the shifts of other benzopyran derivatives[18].

The mass spectra of compounds **2** and **3** show a fragmentation pattern which is in agreement with their structures. In addition to the molecular ion peak [M^+], which appears with rather low intensities, all compounds studied give peaks of moderate intensities at *m/z* = 263, which corresponds to the ion produced by cleavage of the 1-acyl group, [M^+-COR]. The base peak in the most of the spectra is at *m/z* = 105, corresponding to the benzoyl cation [$PhCO^+$].

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected - IR spectra were recorded with a Specord 71 IR or a Perkin-Elmer 297 spectrometer - ^{1}H-NMR spectra were obtained either with a Bruker WM 250 (250 MHz) or a Varian XL 200 (200 MHz) or a Bruker AW 80 (80 MHz) instrument - ^{13}C-NMR spectra were obtained with a Bruker WM 250 or a Varian XL 200 or a Varian CFT 20 instrument All NMR spectra were obtained by using TMS as internal standard in $CDCl_3$ solutions Attached proton experiments (APT) were performed on a Varian XL 200 spectrometer -Mass spectra were recorded at 70 eV with a Jeol JMS-D 300 or a VG TS-250 spectrometer -Column chromatography was carried out on silica gel (Merk 60, 0 063-0 2 mm), eluent *n*-hexane/EtOAc mixtures of increasing polarity

Preparation of Starting Materials The starting 3-acylcoumarins **1** were prepared according to the literature[14,15,19-20] and their spectroscopic characteristics (IR, ^{1}H-NMR and MS) were in agreement with their structures

Reaction of 3-Acyl-2H-chromen-2-ones* 1 *with Phenacylbromide General Procedure. A mixture of benzopyran **1** (1 mmol), phenacylbromide (1 mmol, 0 2 g) and base (1 mmol) in the appropriate solvent (10 ml) was stirred at 25 °C After a certain reaction time, depending on the base, the reaction mixture was poured in ice water (50 ml) containing a few drops of *concd* HCl The resulting emulsion was extracted with $CHCl_3$ (3x20 ml), the combined extracts were washed with water and dried (Na_2SO_4) After removing of the solvent the residue was chromatographed on silica gel (column, eluent *n*-hexane/EtOAc mixtures of increasing polarity) Depending on the base and solvent used the following methods are distinguished

Method A· Solvent THF, Base DBU, Reaction time 48 h
Method B1 Solvent CH_2Cl_2, Base· NaH, Reaction time 1 h
Method B2 Solvent CH_3CN, Base, NaH, Reaction time 1 h

Reaction of* 1 *with Phenacylbromide under Phase-Transfer Conditions -General Procedure: To a solution of benzopyran 1 (1 mmol), phenacylbromide (0 2 g, 1mmol) and a small amount of catalyst (0 01 g) in the appropriate solvent (4 ml) a solution of 4% NaOH (amount depending on the method) was added dropwise The mixture was stirred at 25 °C for a certain time and then it was poured into ice water (50 ml) containing a few drops of *concd* HCl The resulting emulsion was extracted with $CHCl_3$ (3x20 ml), the combined extracts were washed with water, a solution of 5% $NaHCO_3$, again with water and dried (Na_2SO_4) After removing of the solvent the solid residue was crystallized from EtOH to give one of the isomers The filtrates (after removing of the EtOH) were chromatographed as above to give the second isomer and the remainings of the first

In some cases or when DMSO was used as solvent after pouring of the reaction mixture in ice water a solid mass was precipitated, which was filtered and recrystallized from EtOH to give one of the isomers whereas the filtrates were treated as above to give the second isomer and the remainings of the first

Depending on the reaction conditions, the solvent and the catalyst used the following methods are distinguished

Method C1 Solvent DMSO, 4% NaOH 4 ml, 4 mmol (1 $PhCOCH_2Br$ NaOH = 1 1 4), Catalyst TEBA, Reaction time 0 5 h
Method C2 Solvent CH_2Cl_2 and the rest as in method B1
Method D1 Solvent CCl_4, 4% NaOH 1 ml, 1 mmol (1 $PhCOCH_2Br$ NaOH = 1 1 1), Catalyst Aliquat 336, Reaction time 1 h
Method D2 Solvent CH_2Cl_2 and the rest as in method D1
Method E1 Solvent benzene, 4% NaOH 1 ml, 1 mmol (1 $PhCOCH_2Br$ NaOH = 1 1 1), Catalyst Aliquat 336, Reaction time 1 5 h
Method E2· 4% NaOH 2 ml, 2 mmol (1 $PhCOCH_2Br$ NaOH = 1 1 2), Reaction time: 1 h and the rest as in method E1
Method E3 4% NaOH. 4 ml, 4 mmol (1 $PhCOCH_2Br$ NaOH = 1 1 4), Reaction time: 0 5 h and the rest as in method E1
Method F1 Solvent benzene, 4% NaOH 4 ml, 4 mmol (1 $PhCOCH_2Br$ NaOH = 1·1 4); Catalyst TPBP, Reaction time 15 min
Method F2 4% NaOH 2 ml, 2 mmol (1 $PhCOCH_2Br$ NaOH = 1 1 2), Reaction time· 20 min and the rest as in method F1
Method G1 Solvent benzene, 4% NaOH 4 ml, 4 mmol (1 $PhCOCH_2Br$ NaOH = 1 1 4), Catalyst $Ph_4P^+Br^-$, Reaction time 0 5 h
Method G2 Catalyst $Ph_3P{=}CHPh$ and the rest as in method G1
Method G3 Catalyst $Ph_2P(O)Et$ and the rest as in method G1
Method H1 Without catalyst, Solvent benzene, 4% NaOH 4 ml, 4 mmol (1 $PhCOCH_2Br$ NaOH = 1 1 4), Reaction time· 1 h
Method H2 Solvent DMSO, Reaction time 0 5 h and the rest as in method H1.

Methyl 4,5-Benzo-endo-7-benzoyl-3-oxa-2-oxo-cis-bicyclo[4.1 0]hept-4-en-1-carboxylate (2a) From **1a** and phenacylbromide (yield and methods prepared as in Tale 2), m.p

184-185 °C (EtOH) (ref [1] 183 °C) - IR (nujol) ν = 1765, 1740, 1670 cm^{-1}. - ^{1}H-NMR (250 MHz) δ = 3 45 (d, *J* = 9 8 Hz, 1H, 6-H), 3 83 (s, 3H), 4 18 (d, *J* = 9 8 Hz; 1H, 7-H), 6 95-7 03 (m as td, *J* = 1 4, 7 4 Hz, 1H), 7 05-7 09 (m, 1H), 7 18-7 29 (m; 2H), 7 36-7 45 (m, 2H), 7 50-7 59 (m, 1H), 7 86-7 92 (m, 2H) - ^{13}C-NMR δ = 33.71 (C-6), 33 89 (C-1), 34 85 (C-7), 53 74 (OCH_3), 113 75 (C-5), 116 71, 124 42, 128.14, 128 22, 128 73, 128 77, 129 65, 133 96 (C-4′), 136 12 (C-1′), 151 45 (C-4), 161 05 (CO-2), 167.85 (COOMe), 191 27 (COPh) - MS· *m/z* (%) = 323 (4), 322 (8) [M^+], 294 (17) 263 (24) 262 (33), 235 (8), 191 (12), 189 (25), 178 (8), 105 (100), 102 (13), 77 (65).

Methyl 4,5-Benzo-exo-7-benzoyl-3-oxa-2-oxo-cis-bicyclo[4.1.0]hept-4-en-1-carboxylate (**3a**): From **1a** and phenacylbromide (yield and methods prepared as in Table 2), m.p. 129-131 °C (*n*-hexane/ Ether) - IR (nujol) ν = 1805, 1735, 1680 cm^{-1} - ^{1}H-NMR (200 MHz)· δ = 3.24 (d, *J* = 5 3 Hz, 1H, 6-H), 3 76 (s, 3H, CH_3), 3 77 (d, *J* = 5 3 Hz, 1H, 7-H), 7.09-7.13 (m as d, 1H), 7 15-7 22 (m as td, *J* = 1 0, 7 4 Hz; 1H), 7 29-7.36 (m as td, *J* = 1.6, 7.9 Hz, 1H), 7.44-7 53 (m, 3H), 7 59-7 66 (m, 1H), 7.94-7.98 (m, 2H). -MS: *m/z* (%) = 324 (9), 323 (35) [M^+], 295 (36), 263 (62), 262 (81), 247 (19), 235 (20), 191 (19), 189 (29), 178 (16), 105 (95), 102 (15), 77 (100)

$C_{19}H_{14}O_5$ (322 30) Calcd. C 70.80 H 4 38
Found C 71 02 H 4,21

Ethyl 4,5-Benzo-endo-7-benzoyl-3-oxa-2-oxo-cis-bicyclo[4.1 0]hept-4-en-1-carboxylate (**2b**)· From **1b** and phenacylbromide (yield and methods prepared as in Table 1), m p 176-177 °C (EtOH) (ref [1] 175-176 °C) - IR (nujol) ν = 1765, 1730, 1680 cm^{-1} -^{1}H-NMR (200 MHz)· δ = 1.32 (t, *J* = 7 1 Hz, 3H, CH_2CH_3), 3 42 (d, *J* = 9 7 Hz; 1H, 6-H), 4 17 (d, *J* = 9 7 Hz, 1H, 7-H), 4 19-4 41 (m, ABX_3 spin system, 2H, CH_2CH_3), 6 96-7 12 (m, 2H), 7.20-7 29 (m; 2H), 7 38-7 47 (m; 2H), 7 51-7 60, (m; 1H), 7 87-7 92 (m, 2H) -^{13}C-NMR. δ = 13 99 (CH_3), 33 61 (C-6), 34 11 (C-1), 34 62 (C-7), 63.10 (CH_2O), 113 82 (C-5), 116 76, 124.35, 128 33, 128 69, 128 75, 129 63, 133.90 (C-4′), 136 23 (C-1′), 151 55 (C-4), 161 02 (CO-2), 167.34 (COOEt), 191 33 (COPh) -MS *m/z* (%) = 337 (4), 336 (15) [M^+], 308 (16), 264 (14), 263 (58), 262 (37), 235 (17), 203 (21), 191 (14), 178 (6), 105 (100), 77 (71)

Ethyl 4,5-Benzo-exo-7-benzoyl-3-oxa-2-oxo-cis-bicylclo[4 1.0]hept-4-en-1-carboxylate (**3b**) From **1b** and phenacylbromide (yield and method prepared as in Table 1), m p 114-116 °C (*n*-hexane/ether) - IR (nujol) ν = 1775, 1745, 1670 cm^{-1} - ^{1}H-NMR (200 MHz) δ = 1 15 (t, *J* = 7 1 Hz; 3H, CH_2CH_3), 3 20 (d, *J* = 5 3 Hz, 1H, 6-H), 3 77 (d, *J* = 5.3 Hz, 1H, 7-H), 4.08-4 31 (m, ABX_3 spin system, 2H, CH_2CH_3), 7 06-7 11 (m as dd, *J* = 1.4, 8 0 Hz; 1H), 7.13-7.21 (m as td, *J* = 1 4, 7.4 Hz, 1H), 7.27-7 36 (m as td, *J* = 1 8, 8.0 Hz; 1H), 7 43-7.53 (m; 3H), 7 57-7.66 (m, 1H), 7.94-8.00 (m, 2H). -^{13}C-NMR· δ = 13.69 (CH_3), 30.87 (C-6), 35.13 (C-7), 40 24 (C-1), 62 61 (CH_2O), 117 13, 118 95 (C-5), 125 10, 128.23, 128 47, 128.55, 129 0, 133 97 (C-4′), 136 61 (C-1′), 149 95 (C-4), 163 59, 192.37 (COPh) - MS *m/z* (%) = 337 (21), 336 (22) [M^+], 303 (27), 264 (20), 263 (63), 262 (50), 247 (33), 235 (29), 191 (25), 178 (17), 105 (100), 102 (16), 77 (73)

$C_{20}H_{16}O_5$ (336 13) Calcd C 71 40 H 4 81
Found C 71 55 H 4 91

tert-Butyl 4,5-Benzo-endo-7-benzoyl-3-oxa-2-oxo-cis-bicyclo[4.1.0]hept-4-en-1-carboxylate (**2c**): From **1c** and phenacylbromide (yield and methods prepared as in Table 2), m.p 201-203 °C (EtOH) - IR (nujol) ν = 1765, 1745, 1685 cm^{-1} - ^{1}H-NMR (250 MHz) δ = 1 51 [s; 9H, $C(CH_3)_3$], 3 37 (d, *J* = 9 6 Hz, 1H, 6-H), 4 11 (d, *J* = 9 6 Hz, 1H, 7-H), 6.97-7 03 (m as t, *J* = 7 Hz, 1H), 7 06-7.10 (m as d, *J* = 8 Hz, 1H), 7 20-7 29 (m, 2H), 7 38-7 44 (m as t, 2H), 7.51-7.57 (m as t, 1H), 7 87-7 96 (m, 2H) -^{13}C-NMR. δ = 27 85 (CH_3), 33.15 (C-6), 34 08 (C-7), 35 30 (C-1), 83 95 (CMe_3), 114.22 (C-5), 116 70, 124.34, 128 23, 128.65, 129 37, 133 63 (C-4′), 136 57 (C-1′), 151.78 (C-4), 160 96 (CO-2), 166.01 ($COOCMe_3$), 191 41 (COPh) - MS *m/z* (%) = 364 (1 5) [M^+], 291 (1), 264

(53), 263 (22), 235 (6), 191 (3), 175 (6), 105 (74), 77 (33), 57 (100)

$C_{22}H_{20}O_5$ (364 38) Calcd. C 72 51 H 5 53
Found C 72 31 H 5 65

tert-Butyl 4,5-Benzo-exo-7-benzoyl-3-oxa-2-oxo-cis-bicyclo[4 1.0]hept-4-en-1-carboxylate (3c) From 1c and phenacylbromide (yield and methods prepared as in Table 2), m p. 177-179 °C (*n*-hexane/ether) - IR (nujol) ν = 1770, 1740, 1675 cm^{-1} - ^{1}H-NMR (250 MHz) δ = 1 32 [s; 9H, $C(CH_3)_3$], 3 13 (d, *J* = 5 3 Hz, 1H, 6-H), 3 78 (d, *J* = 5 3 Hz, 1H, 7-H), 7 06-7 10 (m as d, 1H), 7.14-7 21 (m as td, 1H), 7 26-7 34 (m, 1H), 7 44-7.53 (m, 3H), 7 58-7.64 (m, 1H), 7 97-8 0 (m, 2H) - MS *m/z* (%) = 364 (0 5) [M^+], 264 (42), 263 (13), 247 (10), 235 (4), 191 (3), 105 (45), 77 (34), 57 (100), 41 (17)
$C_{22}H_{20}O_5$ (364 38) Calcd C 72 51 H 5 53
Found C 72 30 H 5 68

1-Acetyl-4,5-benzo-endo-7-benzoyl-3-oxa-cis-bicyclo[4 1 0]hept-4-en-2-one (2d) From 1d and phenacybromide· (yield and methods prepared as in Table 2), m p 185-186 °C (EtOH) (ref [1] 184 °C) - IR (nujol) ν = 1740, 1720, 1680 cm^{-1} - ^{1}H-NMR (250 MHz) δ = 2 61 (s, 3H, CH_3), 3 43 (d, *J* = 9 7 Hz, 1H, 6-H), 4 15 (d, *J* = 9.7 Hz, 1H, 7-H), 6 99-7 06 (m as td, *J* = 1 1, 7 4 Hz, 1H), 7 10 (m as d, 1H), 7 22-7 30 (m, 2H), 7 39-7 46 (m, 2H), 7 53-7 59 (m, 1H), 7 87-7 91 (m, 2H) - ^{13}C-NMR· δ = 29 58 (CH_3), 35 40 (C-6), 37 07 (C-7), 40 08 (C-1), 114 10 (C-5), 116 74, 124 50, 128 37, 128 67, 128 76, 133 92 (C-4′), 136 56 (C-1′), 151 26 (C-4), 160 80 (CO-2), 191 97 (COPh), 202.0 (COMe) - MS· *m/z* (%) = 307 (1), 306 (4) [M^+], 264 (62), 263 (48), 235 (13), 191 (8), 187 (9), 105 (100), 77 (72), 43 (34)

1-Acetyl-4,5-benzo-exo-7-benzoyl-3-oxa-cis-bicyclo[4 1 0]hept-4-en-2-one (3d)· From 1d and phenacylbromide (yield an methods prepared as in Table 1), oil - IR· ν = 1740, 1720, 1680 cm^{-1} - ^{1}H-NMR (250 MHz) δ = 2 45 (s, 3H, CH_3), 3 24 (d, *J* = 5 5 Hz, 1H, 6-H), 3 73 (d, *J* = 5 5 Hz, 1H, 7-H), 7.0-7 09 (m as d, 1H), 7 15-7 22 (m as td, *J* = 1 0, 7 4 Hz; 1H), 7 28-7 35 (m as td, *J* = 1 6, 7 4 Hz, 1H), 7 45-7 52 (m, 3H), 7 54-7 66 (m; 1H), 7 93-7 97 (m, 2H) - ^{13}C-NMR δ = 30 21 (CH_3), 30 88 (C-6), 37 23 (C-7), 44 64 (C-1), 116 96, 119 10 (C-5), 125 08, 128 37, 128 88, 134 02 (C-4′), 136 08 (C-1′), 149 66 (C-4), 162 42 (CO-2), 192 09 (COPh), 197 05 (COMe)
$C_{19}H_{14}O_4$ (306 30) Calcd C 74 45 H 4 60
Found C 75 00 H 4 80

4,5-Benzo-endo-7-benzoyl-3-oxa-1-propionyl-cis-bicyclo[4.1.0]hept-4-en-2-one (2e) From 1e and phenacylbromide (yield and methods prepared as in Table 2), m p 157-159 °C (EtOH) (ref [1] 157-158 °C) - IR (nujol) 1750, 1730, 1675 cm^{-1} - ^{1}H-NMR (250 MHz)· δ = 1 11 (t, *J* = 7 1 Hz, 3H, CH_2CH_3), 2 79 (dq, *J* = 7 1, 18 8 Hz, 1H, $CH_AH_BCH_3$), 3 29 (dq, *J* = 7 1, 18 8 Hz, $CH_AH_BCH_3$), 3 39 (d, *J* = 9 6 Hz; 1H, 6-H), 4 16 (d, *J* = 9 6 Hz, 1H, 7-H), 6 99-7 05 (m as td, *J* = 1 3, 7 4 Hz, 1H), 7 09-7 13 (m as dd, *J* = 1 0, 7 4 Hz, 1H), 7 22-7 30 (m, 2H), 7 39-7 45 (m, 2H), 7 52-7 59 (m as t, 1H), 7 87-7 91 (m, 2H) - MS *m/z* = 321 (1), 320 (4) [M^+], 291 (1), 264 (84), 263 (17), 235 (7), 191 (7), 187 (4), 186 (8), 105 (100), 77 (74), 57 (49)

4,5-Benzo-endo-7-benzoyl-1-isobutyryl-3-oxa-cis-bicyclo[4.1.0]hept-4-en-2-one (2f) From 1f and phenacylbromide. (yield and methods prepared as in Table 2), m p 122-124 °C (EtOH) - IR (nujol). 1755, 1720, 1680 cm^{-1} - ^{1}H-NMR (250 MHz) δ = 1 10 and 1.18 [two d, *J* = 6 9 Hz, $CH(CH_3)_2$], 3 27 (d, *J* = 9 6 Hz, 1H, 6-H), 3 60 [sept, *J* = 6 9 Hz, 1H, $CH(CH_3)_2$], 4 22 (d, *J* = 9.6 Hz, 1H, 7-H), 7 00-7.07 (m as td, *J* = 1 2, 7.4, 1H), 7 11-7.20 (m, 1H), 7 24-7 34 (m, 2H), 7 40-7 48 (m, 2H), 7 51-7 59 (m; 1H), 7 89-7 98 (m, 2H) - MS *m/z* (%) = 335 (1), 334 (1 5) [M^+], 264 (48), 235 (4), 191 (4), 105 (79), 77 (49), 71 (35), 43 (100)

$C_{21}H_{18}O_4$ (334 35) Calcd C 75 43 H 5 43
Found C 75 54 H 5 36

4,5-Benzo-exo-7-benzoyl-1-isobutyryl-3-oxa-cis-bicyclo[4.1.0]hept-4-en-2-one **(3f).** From **1f** and phenacylbromide. (yield and methods prepared as in Table 2), m.p. 141-143 °C (EtOH) - IR (nujol) ν = 1740, 1720, 1690 cm^{-1} - ^{1}H-NMR (250 MHz). δ = 1 08 and 1 14 [two d, J = 6 9 Hz; 6H, $CH(CH_3)_2$], 3 10 (d, J = 5 5 Hz, 1H, 6-H), 3 12 [sept, J = 6.9 Hz; $CH(CH_3)_2$], 3 73 (d, J = 5 5 Hz, 1H, 7-H), 7 09-7 13 (m as dd, J = 0 8, 8 2 Hz; 1H), 7.16-7.23 (m as td, J = 1 2, 7.5 Hz, 1H), 7 29-7 36 (m as td, J = 1 7, 7 5 Hz; 1H), 7 44-7 51 (m; 3H), 7 54-7 66 (m, 1H), 7 94-7 97 (m, 2H) -MS *m/z* (%) = 335 (4) [M+1], 264 (92), 247 (8), 235 (4), 191 (6), 105 (83), 102 (4), 77 (41), 71 (58), 43 (100)
$C_{21}H_{18}O_4$ (334 35) Calcd C 75 43 H 5 43
Found C 75 73 H 5 56

4,5-Benzo-endo-7-benzoyl-3-oxa-1-pivaloyl-cis-bicyclo[4.1.0]hept-4-en-2-one **(2g).** From **1g** and phenacylbromide· (yield and methods prepared as in Table 2), m p. 208-210 °C (*n*-hexane/ether). - IR (nujol) ν = 1740, 1700, 1675 cm^{-1} - ^{1}H-NMR (250 MHz)· δ = 1 29 [s, 9H, $C(CH_3)_3$], 3 17 (d, J = 9 4 Hz, 1H, 6-H), 4 12 (d, J = 9.4 Hz, 1H, 7-H), 7 03-7 09 (m as td, J = 1 3, 7 4 Hz, 1H), 7 14 (d, J = 7 8 Hz, 1H), 7 28-7 32 (m, 2H), 7 39-7 45 (m; 2H), 7 52-7 58 (m, 1H), 7 89-7 92 (m, 2H) - ^{13}C-NMR· δ = 28 14 (CH_3), 32 23 (C-6), 32 92 (C-7), 40 91 (C-1), 45 37 (CMe_3), 113 87 (C-5), 116 97, 124 59, 128.35, 128 69, 128 85, 129 63, 133 76 (C-4'), 136 48 (C-1'), 151 33 (C-4), 162 80 (CO-2), 191.97 (COPh), 206 04 ($COCMe_3$) - MS *m/z* = 349 (3), 348 (11) [M^+], 264 (50), 263 (13), 235 (4), 191 (2), 188 (4), 105 (69), 85 (13), 77 (35), 57 (100), 41 (17)
$C_{22}H_{20}O_4$ (348 32) Calcd C 75 84 H 5 79
Found C 76 06 H 5 72

4,5-Benzo-exo-7-benzoyl-1-pivaloyl-3-oxa-cis-bicyclo[4.1.0]hept-4-en-2-one **(3g).** From **1g** and phenacylbromide (yield and methods prepared as in Table 2), m p 166-168 °C (EtOH) - IR (nujol) ν = 1735, 1705, 1680 cm^{-1} - ^{1}H-NMR (250 MHz) δ = 1 23 [s, 9H, $C(CH_3)_3$], 3 07 (d, J = 4 9 Hz, 1H, 6-H), 3 87 (d, J = 4 9 Hz, 1H, 7-H), 7.11-7 14 (m as dd, J = 0 8, 8 1 Hz, 1H), 7 17-7 24 (m as td, J = 1 2, 7 4 Hz, 1H), 7 31-7 37 (m as td, J = 1 6, 7 7 Hz, 1H), 7 44-7 50 (m, 3H), 7 54-7 62 (m, 1H), 7 94-7 98 (m, 2H) - ^{13}C-NMR δ = 27 55 (CH_3), 30 81 (C-6), 33 99 (C-7), 44 92 (C-1), 45 95 (CMe_3), 117 33, 118 39 (C-5), 125 27, 128.41, 128 44, 128 71, 129 12, 133 60 (C-4'), 137 41 (C-1'), 150 01 (C-4), 162 39 (CO-2), 193 73 (COPh), 203 44 ($COCMe_3$) -MS *m/z* (%) = 349 (1), 348 (2) [M^+], 291 (12), 264 (46), 263 (4), 247 (21), 235 (2), 191 (4), 105 (48), 85 (22), 77 (31), 57 (100), 41 (17)
$C_{22}H_{20}O_4$ (348 38) Calcd C 75 84 H 5 79
Found C 76 17 H 6 04

4,5-Benzo-endo-7-benzoyl-1-cyclopropylcarbonyl-3-oxa-cis-bicyclo[4.1.0]hept-4-en-2-one **(2h)** From **1h** and phenacylbromide (yield and methods prepared as in Table 2), m.p 141-143 °C (EtOH) - IR (nujol) ν = 1740, 1700, 1675 cm^{-1} - ^{1}H-NMR (250 MHz) δ = 0.96-1 10 (m, 1H), 1 12-1 29 (m, 3H), 2 65-2 95 (m, 1H), 3 39 (d, J = 9 6 Hz; 1H, 6-H), 4 19 (d, J = 9 6 Hz, 1H, 7-H), 7 03 (m as td, J = 1 3, 7 4 Hz, 1H), 7 18 (m as d, 1H), 7 23-7 30 (m, 2H), 7 39-7 45 (m, 2H), 7 52-7 59 (m, 1H), 7 88-7 91 (m, 2H) -MS *m/z* (%) =332 (2) [M^+], 264 (6), 263 (0 3), 191 (4), 179 (2), 105 (84), 77 (46), 69 (100), 41(50)
$C_{21}H_{16}O_4$ (332 24) Calcd C 75 89 H 4 85
Found C 76 23 H 5 05

4,5-Benzo-exo-7-benzoyl-1-cyclopropylcarbonyl-3-oxa-cis-bicyclo[4.1.0]hept-4-en-2-one **(3h)** From **1h** and phenacylbromide (yield and methods prepared as in Table 2), m p 124-126 °C (EtOH) - IR (nujol) ν = 1745, 1695, 1675 cm^{-1} - ^{1}H-NMR (250 MHz). δ = 0 77-0 88 (m, 1H), 0 93-1 06 (m, 2H), 1 13-1 26 (m, 1H), 2 29-2 38 (m, 1H), 3 24 (d, J =

5.4 Hz, 1H, 6-H), 3 81 (d, J = 5 4 Hz, 1H, 7-H), 7 05 (dd, J = 0 9, 8 1 Hz, 1H), 7 18 (td, J = 1 2, 7 5 Hz, 1H), 7 31 (td, J = 1 5, 7 8 Hz, 1H), 7 46-7 52 (m, 3H), 7 57-7 64 (m, 1H), 7.96-8 01 (m, 2H). - MS *m/z* (%) = 333 (0 6), 332 (2) [M^+], 264 (9), 263 (1), 191 (2), 178 (2), 105 (51), 77 (28), 69 (100), 41 (38)

$C_{21}H_{16}O_4$ (332 24) Calcd C 75 89 H 4 85
Found C 76 20 H 5 10

4,5-Benzo-1,endo-7-dibenzoyl-3-oxa-bicyclo[4.1.0]hept-4-en-2-one (**2i**) From **1i** and phenacylbromide (yield and methods prepared as in Table 2), m p 190-192 °C (*n*-hexane/ether) (ref [1] 189-190 °C) - IR (nujol) ν = 1750, 1700, 1685 cm^{-1} - ^{1}H-NMR (200 MHz) δ =3 45 (d, J = 9 6 Hz, 1H, 6-H), 4 37 (d, J = 9 6 Hz, 1H, 7-H), 7 04-7 13 (m as td, J = 1 4, 7 4 Hz, 1H), 7 18-7 22 (dd, J = 1 0, 8 2 Hz, 1H), 7 28-7 46 (m; 6H), 7 52-7 60 (m, 1H), 7 79-7 83 (m, 2H), 7 91-7 96 (m, 2H) - ^{13}C-NMR δ = 33 13 (C-6), 33 74 (C-7), 33.88 (C-1), 113 93 (C-5), 117 16, 124 82, 128 33, 128 44, 128 62, 128 77, 128 95, 129 03, 129 79, 133 85 (C-4"), 133 93 (C-4'), 135.02 (C-1"), 136 26 (C-1'), 151 29 (C-4), 163 25 (CO-2), 191 15, 191 75 - MS *m/z* (%) = 369 (1), 368 (2) [M^+], 264 (1), 263 (5), 235 (2), 105 (100), 77 (35)

4,5-Benzo-1,exo-7-dibenzoyl-3-oxa-bicyclo[4 1 0]hept-4-en-2-one (**3i**)· From **1i** and phenacylbromide (yield and methods prepared as in Table 2), m p 159-161 °C (EtOH) (ref [1] 148-152 °C) - IR (nujol) ν = 1740, 1690, 1675 cm^{-1} - ^{1}H-NMR (200 MHz) δ = 3 39 (d, J = 5 1 Hz, 1H, 6-H), 3 88 (d, J = 5 1 Hz, 1H, 7-H), 7 14-7 26 (m, 2H), 7.32-7 41 (m, 3H), 7 44-7 63 (m, 3H), 7 83-7 88 (m, 2H), 7 92-7 97 (m, 2H) - ^{13}C-NMR δ = 31 46 (C-6), 35 33 (C-7), 43 91 (C-1), 117 42, 118 78 (C-5), 125 35, 128 49, 128 63, 128 74, 128 81, 129 10, 129 24, 133 84 (C-4"), 133 88 (C-4'), 134 92 (C-1"), 136 98 (C-1'), 150 14 (C-4), 162 52 (CO-2), 188 40, 193 05 - MS *m/z* = 369 (0 5), 368 (1) [M^+], 324 (0 1), 105 (100), 77 (31)

$C_{24}H_{16}O_4$ (368 37) Calcd C 78 25 H 4 38
Found C 77 89 H 4 45

4,5-Benzo-endo-7-benzoyl-1-nicotinoyl-3-oxa-cis-bicyclo[4.1.0]hept-4-en-2-one (**2j**) From **1j** and phenacylbromide (yield and methods prepared as in Table 2), m.p 174-176 °C EtOH) - IR (nujol) ν = 1740, 1680 cm^{-1} - ^{1}H-NMR (250 MHz) δ = 3 51 (d, J = 9.6 Hz, 1H, 6-H), 4 35 (d, J = 9 6 Hz, 1H, 7-H), 7 06-7 12 (m as td, J = 1 3, 7 4 Hz, 1H), 7 17-7 21 (m, 1H), 7 29-7 48 (m, 5H), 7 55-7 62 (m, 1H), 7 92-7 97 (m, 2H), 8 11 (ddd, J = 1 6, 2 2, 8 0 Hz, 1H), 8 77 (dd, J = 1 6, 4 8 Hz, 1H), 9 03 (dd, J = 1 7 Hz, 1H) - MS *m/z* (%) = 370 (5), 369 (6) [M^+], 325 (1), 263 (37), 247 (4), 235 (17), 219 (7), 191 (14), 178 (8), 130 (3), 106 (100), 105 (79), 102 (7), 78 (51), 77 (48)

$C_{23}H_{15}NO_4$ (369 36) Calcd C 74 49 H 4 09 N 3 79
Found C 75 02 H 3 80 N 3 74

Isomerization of compounds **2** *(cis isomers) to* **3** *(trans isomers)* A mixture of the *cis* isomer **2** (1 mmol) and triethylamine (1 mmol) in acetic acid anhydride (8 ml) was refluxed for 3 h and then the reaction mixture was worked up as above and after column chromatography was isolated

1 From **2a** (0 322 g, 1 mmol) Unchanged **2a** 0 17 g (53%), m p. 183-184 °C, identical with the starting compound
3a (*trans* isomer) 0 06 g (19%), m p 128-130 °C, with spectroscopic data identical to those given previously

2 From **2b** (0 336 g, 1 mmol) Unchanged **2b** 0 17 g (51%), m p 175-177 °C, identical with the starting compound
3b (*trans* isomer) 0 09 g (27%), m p 113-115 °C, with spectroscopic data identical to those given previously

3. From **2d** (0 306 g, 1 mmol) Unchanged 2d 0 215 g (70%), m p 184-186 °C, identical with the starting compound
3d (*trans* isomer) 0 05 g (16%) as an oil, with spectroscopic data identical to those given previously

Treatment of compound **2d** (0 15 g, 0 5 mmol) in benzene (2.5 ml) with 4% NaOH solution, in the presence of Aliquat 336 (phase transfer conditions, Method E2) at 25 °C for 0 5 h gave, after column chromatography, unreacted starting compound **2d** 0.12 g (80%) and the *trans* isomer **3d** 0 018 g (12%) Similarly, treatment of compound **3g** (0 17 g, 0 5 mmol) in the same way as above, gave, after column chromatography, unreacted starting compound **3g** 0 15 g (88%) and the *cis* isomer 2g 0 01 g (6%)

REFERENCES

1. Widman, O *Ber. Dtsch Chem. Ges* **1918**, *51*, 533-541, Widman, O *ibid* **1918**, *51*, 907-911
2 Wawzoñek, S ; Morreal, C E *J Am Chem Soc* 1960, *82*, 439-441
3. Risinger, G E , Timm, G E. *Chem and Ind* **1967**, 158-159
4 4a· McCoy, L L *J. Org Chem* **1960**, *25*, 2078-2082, 4b McCoy, L L *J Am Chem Soc* **1962**, *84*, 2246-2248, 4c McCoy, L L , Nachtigall, G W *J Org Chem* **1962**, *27*, 4312-4316, 4d McCoy, L L *ibid* **1964**, *29*, 240-241
5. 5a· Fraisse, R , Jacquier, R *Bull Soc Chim Fr* **1957**, 986, 5b. Fraisse, R *ibid* **1959**, 1102, 5c Fraisse, R , Guitard, M *ibid* **1960**, 418, 5d Fraisse, R , Guitard, M *ibid* **1960**, 788; 5e Fraisse, R , Guitard, M *ibid.* **1961**, 200.
6 Mousseron, M ; Fraisse, R , Bonavent, G *C R Acad Sci* **1959**, *248*, 2840.
7 Bonavent, G ; Causse, M , Guitard, M , Fraisse-Jullien, R *Bull Soc Chim Fr* **1964**, 2462-2471
8 Jończyk, A ; Makosza, M *Synthesis* **1976**, 387-388
9. Artaud, J , Seyden-Penne, J , Viout, P *Synthesis* **1980**, 34-36
10 Akabori, S., Yoshii, T *Tetrahedron Lett* 1978, 4523-4526
11 Inouye, Y , Inamasu, S , Horiike, M , Ohno, M , Walborsky, H M *Tetrahedron* **1968**, *24*, 2907-2920
12 Kyriakakou, G , Roux-Schmitt, M C , Seyden-Penne, J *Tetrahedron* **1975**, *31*, 1883-1888
13 Bojilova, A *Synth Commun.* **1990**, *20*, 1967-1976
14 Ivanov, C , Bojilova, A *Chem Ber* **1978**, *111*, 3755
15 Bojilova, A., Rodios, N., Nikolova, R , Ivanov, C *Liebigs Ann Chem* **1991**, 1279-1284; Bojilova, A.; Rodios, N A , Nikolova, R , Ivanov, C *Synth Commun* **1992**, *22*, 741-754
16 Jończyk, A , Kwast,A ; Macosza, M *Tetrahedron Lett* **1979**, 541-544, Artaud, J , Seyden-Penne, J , Viout, P *ibid* **1980**, *21*, 613-616
17 Nowick, J S , Danheiser, R L *Tetrahedron* 1988, *44*, 4113-4134, Abdallah, H ; Gree, R, Carrié, R *Bull. Soc Chim Fr* **1984**, 338-344
18 Macias, F. A , Massanet, G M , Rodriguez-Luis, J , Salva, J *Magn Reson Chem* **1989**, *27*, 892-894.
19. Deanand, F M ; Kevinpark, B *J. Chem Soc , Perkin Trans 1*, **1976**, 1260-1268
20 Pocheco, H , Gatto, R *Bull Soc Chim Fr* **1960**, 95-98