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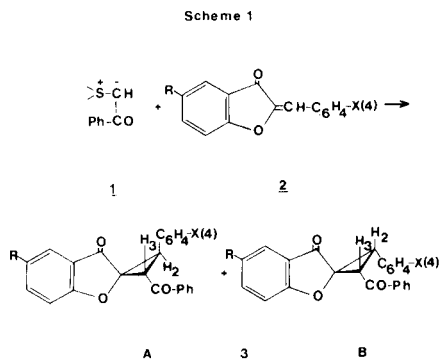
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2-Arylmethylenebenzofuran-3-ones react with carbonyl stabilized sulphur ylides yielding spiro[cyclopropane-1,2'-benzofuran-3'-ones], whose structure and stereochemistry were assigned on the basis of spectroscopic data and chemical behaviour.

*J. Heterocyclic Chem.*, 17, 777 (1980).

In continuation of our studies (1,2) devoted to the general use of sulphur ylides in heterocyclic chemistry, we wish to report the reaction between carbonyl stabilized sulphur ylides and 2-arylmethylenebenzofuran-3-ones. Treatment of dimethylsulphonium phenacylide (**1**) with several (*E*)- and (*Z*)-2-arylmethylenebenzofuran-3-ones (**2**) in boiling ethanol for 12 hours gave, in all cases investigated, a mixture of two products. The components, which were isolated in a pure state by column chromatography, were the isomers spiro[cyclopropane-1,2'-benzofuran-3'-ones] (**3a-d**), formed by 1,4-conjugate addition followed by 1,3-elimination of dimethyl sulphide



The main characteristics of compounds **3a-d** are summarized in Tables 1 and 2.

The structures of products **3a-d** were confirmed on the basis of spectroscopic data. The ir spectra show two carbonyl absorptions (benzofuranone and benzoyl groups); the <sup>1</sup>H nmr spectra exhibit an AB splitting pattern for the cyclopropane hydrogens. It is not possible to deduce the configuration of these products based only on the nmr data, because the coupling constants for the cyclopropane hydrogen atoms in each pair of isomers are almost equal.

Considerations concerning the mechanism of the cyclopropanation reaction of ylides and the steric interactions in the intermediate zwitterion (**3**) predict the preferential formation of two products: *trans*-benzoyl *cis*-phenyl and *trans*-benzoyl *trans*-phenyl (**4**). Experimental results, starting from either (*E*)- or (*Z*)-arylmethylenebenzofuranones, agree with this prediction, and confirm what we have already verified in the reaction between the ylide (**1**) and the 3-arylmethyleneindolin-2-ones (**1**).

The *trans-cis* configuration was assigned to the products that have lower chemical shifts for the cyclopropane hydrogen atoms, owing to the deshielding effect of the benzoyl and phenyl groups. The *trans-cis* configuration is more stable than the *trans-trans*, as demonstrated by the

Table 1

Physical Data for Compounds **3a-d**

Compound No.	R	X	Overall Yield (%)	Isomer	M.p. (°C)	Crystallization Solvent	Nmr			Ir (Cm <sup>-1</sup> ) ν CO	Ratio (a) A:B
							H-2	H-3	J <sub>2,3</sub> (Hz)		
<b>3a</b>	H	H	49	<b>A</b>	151-153	ethanol	4.05	4.50	8.5	1700,1680	2:1
				<b>B</b>	170-171	ethanol	3.60	4.00	9.0	1705,1675	
<b>3b</b>	H	OCH <sub>3</sub>	52	<b>A</b>	115-116	ethanol	4.15	4.58	8.5	1700,1665	2.5:1
				<b>B</b>	125-126	ethanol	3.75	4.12	9.0	1700,1670	
<b>3c</b>	H	NO <sub>2</sub>	56	<b>A</b>	162-163	<i>n</i> -butanol	3.95	4.35	8.5	1710,1680	2.5:1
				<b>B</b>	179-180	<i>n</i> -butanol	3.50	3.90	9.0	1700,1665	
<b>3d</b>	CH <sub>3</sub>	H	66	<b>A</b>	175-176	ethanol	4.12	4.58	8.5	1710,1670	3:1
				<b>B</b>	130-131	ethanol	3.73	4.15	9.0	1700,1665	

(a) Calculated from the integration of the cyclopropane proton signals in the crude reaction mixture.

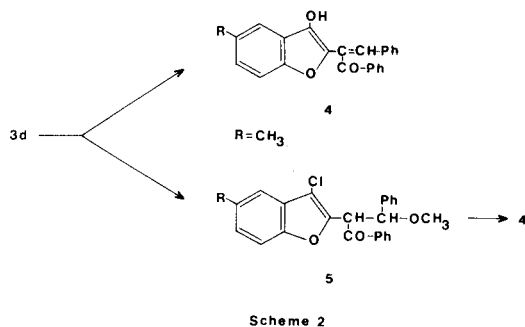
Table 2

Analytical Values for Compounds **3a-d**

Compound No.	Molecular Formula	Isomer	C	Calcd.			Analysis		
				H	N		C	H	N
<b>3a</b>	C <sub>23</sub> H <sub>16</sub> O <sub>3</sub>	<b>A</b>	81.16	4.74	—	80.91	4.41	—	
		<b>B</b>				81.12	4.62	—	
<b>3b</b>	C <sub>24</sub> H <sub>18</sub> O <sub>4</sub>	<b>A</b>	77.82	4.90	—	78.05	4.92	—	
		<b>B</b>				78.02	4.82	—	
<b>3c</b>	C <sub>23</sub> H <sub>15</sub> NO <sub>3</sub>	<b>A</b>	71.68	3.92	3.64	71.48	3.64	3.48	
		<b>B</b>				71.54	3.84	3.35	
<b>3d</b>	C <sub>24</sub> H <sub>18</sub> O <sub>3</sub>	<b>A</b>	81.34	5.12	—	81.36	5.09	—	
		<b>B</b>				80.98	5.14	—	

irradiation of isomers (**3B**) which were quantitatively transformed into the corresponding isomers (**3A**). The same treatment left the isomers (**3A**) unchanged. This type of isomerisation was also confirmed by the recent work of Decker (5) on the photoisomerisation of spiro[*cis*- and *trans*-2,3-dicarbomethoxycyclopropane-1,9-fluorene].

The structure of spiro[cyclopropanebenzofuranone] was supported by the following chemical transformations. The reaction of compound **3d** with potassium *t*-butoxide in dimethylsulfoxide gave 2-( $\alpha$ -benzylidene)phenacyl-3-hydroxy-5-methylbenzofuran (**4**), whereas the action of methanol in the presence of hydrogen chloride (6) afforded 2-(1'-benzoyl-2'-methoxy-2'-phenyl)ethyl-3-chloro-5-methylbenzofuran (**5**).



The first reaction can be explained as an abstraction, in basic medium, of the 3-proton followed by cleavage of the cyclopropane 1,2-bond. The second reaction involves an attack of methanol on the 2-carbon atom, prompted by the protonation of the heterocyclic oxygen atom.

The correlation between **4** and **5** was achieved by the treatment of **5** with potassium hydroxide in methanol, which initiates the elimination of the methoxy group and the hydrolysis of the 3-chloro atom. Such behaviour agrees with the typical reactivity of 3-chlorobenzofuran (**7**) and the tendency of substituted dihydrochalcones to change into chalcones.

## EXPERIMENTAL

Melting points are uncorrected. Nmr spectra were recorded with a Varian A-60 spectrometer (TMS as internal standard). Ir spectra were recorded on a Perkin-Elmer 377 spectrophotometer in *ca.* 2% chloroform solution.

(*E*- and (*Z*)-2-Arylmethylenebenzofuran-3-ones (**2**).

These compounds were prepared by reported methods (8,9) from benzofuran-3-ones and the appropriate aldehyde.

Preparation of Spiro[cyclopropanebenzofuranones] (**3a-d**). General Procedure.

A solution of dimethylsulphonium phenacylide (**1**) (0.01 mole) in ethanol (26 ml.) was added to a solution of the 2-arylmethylenebenzofuran-3-ones (**2**) (0.01 mole) in the same solvent. The mixture was refluxed for 12 hours and the solvent was evaporated. The residue, which consisted of a mixture of the two isomeric spiro[cyclopropane-1,2'-benzofuran-3'-ones], was chromatographed (Kieselgel 60; benzene; flow rate 2 ml./minute) to give the pure components, the physical properties of which are summarized in Table 1.

Photoisomerisation of **3dB**.

A solution of **3dB** (0.2 g.) in benzene (50 ml.) was thoroughly purged with nitrogen and irradiated with a Phillips HPX 125-w medium pressure lamp for 2 hours. Removal of the solvent left a pale yellow residue which was crystallized from ethanol. The product (yield, 85% m.p. 175°) showed no m.p. depression when mixed with an authentic sample of **3dA**.

2-( $\alpha$ -Benzylidene)phenacyl-3-hydroxy-5-methylbenzofuran (**4**).

A mixture of compound **3d** (1 g.) and potassium *t*-butoxide (0.3 g.) in dimethyl sulfoxide (25 ml.) was allowed to stand overnight at room temperature. The solvent was evaporated under vacuum and the residue taken up with water (25 ml.) and ether (25 ml.). The aqueous layer was acidified with 10% aqueous acetic acid and the precipitate filtered. The product was purified from diisopropyl ether, m.p. 124-126°, 75% yield; nmr (deuteriochloroform):  $\delta$  2.4 (3H, s, CH<sub>3</sub>), 7.1-8.0 (13H, m, aromatics), 10.2 (1H, s, OH).

*Anal.* Calcd. for C<sub>24</sub>H<sub>18</sub>O<sub>3</sub>: C, 81.34; H, 5.12. Found: C, 81.28; H, 5.08. 2-(1'-Benzoyl-2'-methoxy-2'-phenyl)ethyl-3-chloro-5-methylbenzofuran (**5**).

A solution of **3d** (1 g.) in methanol saturated with hydrogen chloride (10 ml.) was stirred overnight. The precipitate was filtered and crystallized from methanol, m.p. 166-168°, 50% yield; nmr (deuteriochloroform):  $\delta$  2.3 (3H, s, OCH<sub>3</sub>), 5.5-6.0 (2H, dd, CH-CH, J = 11 cps), 7.2-7.75 (13H, m, aromatics).

*Anal.* Calcd. for C<sub>25</sub>H<sub>21</sub>ClO<sub>3</sub>: C, 74.82; H, 5.18. Found: C, 74.98; H, 5.22.

2-( $\alpha$ -Benzylidene)phenacyl-3-hydroxy-5-methylbenzofuran (4) from 5.

A mixture of 5 (0.4 g.) and potassium hydroxide (0.2 g.) in methanol (25 ml.) was boiled for 3 hours. The solvent was evaporated and the residue was taken up with water. The precipitate was purified from diisopropyl ether, m.p. 124-126°.

#### REFERENCES AND NOTES

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(4) In this paper, *cis* and *trans* prefixes refer to the relative configuration of the substituents in the cyclopropane ring and the cyclic carbonyl group.

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(6) In the absence of hydrogen chloride, the reaction did not occur.

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