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Stereochemistry of Ionic Thiol Addition to Acetylenic Ketones

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Synopsis. Piperidine-catalysed addition of thiols to benzoyl- and *p*-chlorobenzoyl-phenylacetylenes in benzene gave a mixture of (*E*)- and (*Z*)-1-aryl-3-arylthio-3-phenyl-2-propen-1-ones. However, in methanol or aqueous 1,4-dioxane only the (*Z*)-isomers were obtained. Configurational assignments to the isomers were based on NMR, UV, and IR spectroscopy.

Although the nucleophilic thiol addition to acetylenes[1-3] has been studied no reports seem to deal with such addition to acetylenic ketones. The present publication describes the nucleophilic addition of thiols to benzoyl- and *p*-chlorobenzoyl-phenylacetylenes. The work was undertaken primarily to elucidate the stereochemistry of the mono-adducts for such addition, and also to study the effect of solvents on these additions.

Piperidine-catalysed addition of *p*-bromophenyl thiol to benzoyl-Ia and *p*-chlorobenzoyl-Ib-phenylacetylenes in benzene gave a mixture of (*E*)*-1-aryl-3-*p*-bromophenylthio-3-phenyl-2-propen-1-ones IIa and IIb, and their (*Z*)*-isomers IIIa and IIIb, respectively. The ratio of the (*E*)- to the (*Z*)-isomers in both cases was about 1 : 3.

The structures of IIa and IIb and IIIa and IIIb were confirmed by analytical data, electronic and infrared spectra. Their configurational assignments were based primarily on electronic spectroscopy since the absorption maxima of III are shifted slightly towards the red with intensification when compared with the corresponding II isomers. This indicates that IIa and IIb have the (*E*)-configuration, whereas IIIa and IIIb have the (*Z*)-configuration. This is consistent with the *cis-trans* relationship[4] on the one hand and *cis-* and *trans-*chalcones[5] on the other. Further confirmation for these configurational assignments was gained from infrared spectroscopy. $\nu_{C=O}$ of the (*E*)-isomers II are at a relatively higher value than those of the corresponding (*Z*)-isomers III. The configurational assignments to IIa and IIIa were confirmed by studying their NMR spectra. This was based on the deshielding effect caused by a phenyl group on a *β-cis* olefinic proton relative to a *trans* proton,[6] a feature characteristic of a number of styrene derivatives.[7,8] According to our data (Table 1), no vinyl proton signal for IIIa can be observed; apparently, it is hidden in the multiplet of aromatic protons, and must acquire the (*Z*)-configuration.

Isomer IIIa was identical with the product obtained by treating *cis*-(H/Ph)-*β*-bromochalcone[9] with *p*-bromophenylthiolate at 0 °C. The authentic sample is the (*Z*)-isomer since similar reactions are known to proceed with retention of configuration.[10]

When the addition of *p*-bromophenyl thiol to Ia or Ib was conducted in methanol or aqueous 1,4-dioxan, only the (*Z*)-isomers III were obtained in a nearly quantitative yield.

The investigation was extended to include the addition of other thiols such as benzyl-, *p*-tolyl-, and phenylthiols to Ia and Ib. In the case of the two latter thiols, when the addition was conducted in benzene a mix-

TABLE 1. ACTION OF THIOLS ON Ia AND Ib

Thiol	Product	Melting point	Yield %	Formula	Found (%) C	H	S	Calcd (%) C	H	S
A	IIa	95—97	20	$C_{21}H_{15}BrSO$	63.9	3.9	8.2	63.8	3.8	8.1
	IIIa	167—169 Yellow	70 (90)	$C_{21}H_{15}BrSO$	64.0	3.8	8.0	63.8	3.8	8.1
	IIb	85—86	30	$C_{21}H_{14}BrClSO$	58.7	3.4	7.5	58.7	3.3	7.45
	IIIb	153—155 Yellow	65 (98)	$C_{21}H_{14}BrClSO$	58.8	3.3	7.5	58.7	3.3	7.45
B	IIc	70—72	20	$C_{21}H_{16}SO$	79.8	5.1	10.2	79.7	5.1	10.1
	IIIc	105—107 Yellow	70 (95)	$C_{21}H_{16}SO$	79.9	5.2	10.1	79.7	5.1	10.1
	IId	97—98	25	$C_{21}H_{15}ClSO$	71.2	4.3	9.0	71.1	4.25	9.1
	IIId	121—122 Yellow	70 (98)	$C_{21}H_{15}ClSO$	71.0	4.2	9.2	71.1	4.25	9.1
C	IIe	78—90	25	$C_{22}H_{18}SO$	80.1	5.5	9.7	80.0	5.45	9.7
	IIIe	174—176 Yellow	70 (94)	$C_{22}H_{18}SO$	79.9	5.3	9.9	80.0	5.45	9.7
	IIf	89—91	20	$C_{22}H_{17}ClSO$	72.5	4.8	9.1	72.4	4.7	8.7
	IIIf	129 Yellow	75 (96)	$C_{22}H_{17}ClSO$	72.4	4.9	9.0	72.4	4.7	8.7
D	IIIg	132—134 Yellow	80 (95)	$C_{22}H_{18}SO$	80.1	5.5	9.9	80.0	5.45	9.7
	IIIh	110 Yellow	85 (95)	$C_{22}H_{17}ClSO$	72.5	4.8	8.8	72.4	4.7	8.7

A=*p*-Bromophenyl thiol, B=Phenyl thiol, C=*p*-Tolyl thiol, D=Benzyl thiol.
Yields in parentheses are those obtained in methanol or aqueous 1,4-dioxan.

* The nomenclature of *cis/trans* isomers used herein follows the IUPAC 1968 Tentative Rules, Section E, Fundamental Stereochemistry, *J. Org. Chem.*, **35**, 2849 (1970).

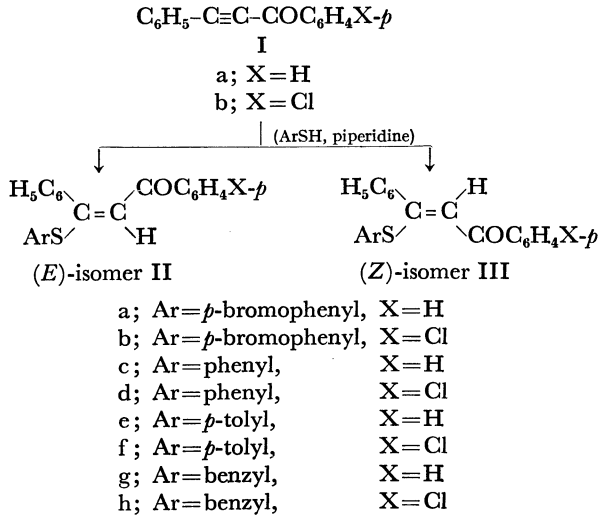
Table 2. Spectral data for compounds II and III

Compound	Electronic spectra λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}	Infrared spectra $\nu_{C=O}$ (cm^{-1})
IIa[a]	210	17925	230	16595	332	12945	1645
			264	12445			
IIb	208	16460	250	22790	332	12200	1647
IIc	212	18325	256	13845	330	13435	1645
IId	210	17720	264	24285	335	13280	1643
IIe	220	22060	257	15860	332	16620	1645
IIf	220	18955	263	10660	336	15660	1645
IIIa[b]	210	20220	224	18200	334	17860	1620
			266	14490			
IIIb	210	18800	266	14950	336	17895	1620
IIIc	212	18930	259	14185	335	19445	1620
IIId	212	18540	265	14345	338	19590	1622
IIIe	210	23880	258	17550	335	22430	1620
IIIf	210	19250	263	13755	339	18915	1620
IIIg	212	19320	258	12660	340	18015	1620
IIIh	211	17640	264	12050	336	17895	1620

a) $\tau(CDCl_3)$ 3.58 (1H, singlet), 2.2—2.8 (14H, multiplet).
b) $\tau(CDCl_3)$ 1.8—2.9 (15H, multiplet)

ture of (*E*)- and (*Z*)-isomers IIc—f and IIIc—f, respectively, was obtained; benzyl thiol, however, yielded only the (*Z*)-isomers IIIg and IIIh with either of the two ketones. In methanol or aqueous 1,4-dioxan, only the (*Z*)-isomers III were obtained in a nearly quantitative yield.

The structures of IIb—f and IIIb—h were confirmed by analytical data, electronic and infrared spectra. Their stereochemical configurations were established by analogy of their electronic spectra with those of IIa and IIIa, respectively. Furthermore, $\nu_{C=O}$ of the (*E*)-isomers are of a higher frequency than those of the (*Z*)-isomers.



a; Ar=*p*-bromophenyl, X=H
b; Ar=*p*-bromophenyl, X=Cl
c; Ar=phenyl, X=H
d; Ar=phenyl, X=Cl
e; Ar=*p*-tolyl, X=H
f; Ar=*p*-tolyl, X=Cl
g; Ar=benzyl, X=H
h; Ar=benzyl, X=Cl

Experimental

All melting points are not corrected. Infrared and electronic spectra were measured on a Unicam SP 1200 spectrophotometer (KBr discs) and Beckmann DK 1 spectrophotometer (in methanol), respectively. NMR spectra (in $CDCl_3$) were determined on a Varian T 60 instrument using TMS as an internal reference. Light petroleum refers to the fraction of bp 60—80 °C, unless otherwise stated.

(E)-*IIa—f and* (Z)-*IIIa—h 1-Aryl-3-arylthio-3-phenyl-2-propen-1-ones.* To a solution of the ketone (0.004 mol) and phenyl-, *p*-tolyl-, *p*-bromophenyl, or benzyl-thiol (0.004 mol) in benzene (5 ml) was added two drops of piperidine and the solution was allowed to stand at room temperature overnight. Crystallization of the filtered solid products from benzene-light petroleum gave the (Z)-*Title compounds.* Evaporation of the mother-liquors at room temperature gave a solid residue which was fractionally crystallized from the same solvent to give an additional amount of the (*Z*)-isomers besides the (*E*)-*Title compounds.*

When methanol was used as a solvent, a quantitative yield of the (*Z*)-isomers was obtained immediately. However, in the case of aqueous 1,4-dioxan they were obtained after being left to stand overnight. The results are shown in Table 1.

(Z)-*IIIa.* To a cold solution (0 °C) of *cis*-(H/Ph)-*β*-bromo-chalcone[9] (0.5 g) in ethanol (10 ml) was added dropwise an alcoholic solution of sodium *p*-bromophenyl thiolate (0.4 g). After 1 hr at 0 °C the precipitated product was filtered off and crystallized from benzene–light petroleum to give (Z)-*3-p-bromophenylthio-1,3-diphenyl-2-propen-1-one* IIIa in yellow needles, mp 167—169 °C. Found: C, 63.9; H, 3.6; S, 8.2%. Calcd for $C_{21}H_{15}BrSO$: C, 63.8; H, 3.8; S, 8.1%.

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