CONDENSATION OF ARYL BROMIDES WITH STYRENES, CATALYZED BY NICKEL COMPLEXES IN THE PRESENCE OF ZINC

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Alkyl bromides react with styrene in MeCN in the presence of pyridine and a $(Ph_3P)_2NiCl_2$ (I)/Zn catalyst system to give E-1-phenylalk-1-enes, namely products resulting from substitution of a vinyl hydrogen atom in styrene by the alkyl residue of the alkyl bromide [1, 2].

In the present paper we have expanded this reaction to include aryl bromides. The main reaction products formed using the previously developed conditions (RBr/styrene/Zn/pyridine/complex (I) = 1/2 = 4/1/4/0.05; 65°C) were E-stilbenes, which were obtained in 70-100% yields (Table 1).

$$XC_6H_4Br + CH_2{=}CHC_6H_4Y \xrightarrow[\text{Py, MeCN}]{\text{(I) 5 mole \%, Zn}} \underset{\text{(II)}}{XC_6H_4CH{=}CHC_6H_4Y} \tag{1}$$

It was found that a mixture of $NiCl_2 \cdot 6H_2O$ with Ph_3P could be used in place of preformed complex (I) as the catalyst in these reactions (cf. No. 3).

Oligomerization of styrene to give 1,3-diphenylbut-1-ene (III) and higher oligomers occurs as a side reaction, in parallel with reaction (1).

$$CH_2 = CHC_6H_5 \xrightarrow{\text{«HNi»}} \underset{\text{(III)}}{CH_3CH(C_6H_5)CH{=}CHC_6H_5} . \tag{2}$$

In addition, when using 1,4-chlorobromobenzene, 4-bromoacetophenone, and methyl-4-bromobenzoate as the aryl bromides in the reaction mixtures, the corresponding hydrodebromination products were also found in the reaction mixtures, namely, chlorobenzene, acetophenone, and methyl benzoate (up to 7% of each) (cf. No. 8, 12, 13); in the case of bromobenzene, benzene was not detected in the product mixture.

The data in Table 1 indicate that reaction (1) is an effective method for the preparation of monosubstituted stilbenes by condensation of substituted phenyl bromides with styrene (Nos. 1-13), as well as of bromobenzene with substituted styrenes (Nos. 14 and 15). Substituents X and Y can include halogens, hydrocarbon groups, and oxygen-containing functional groups, among them carbonyl groups, which do not suppress the reaction; nitrogen-containing groups, such as nitro and amino groups, on the other hand, inhibit the reaction.

Aryl bromides are significantly more reactive than aryl chlorides in reaction (1). For instance, in the reaction of chlorobenzene with styrene the main reaction product is the dimer (III) (58%), with stilbene formed in negligible amounts (<5%). In the case of 1,4-chlorobromobenzene, 4-chlorostilbene was obtained in high yield, while 4-bromostilbene was not detected (No. 8).

The feasibility of preparing disubstituted stilbenes in this manner was demonstrated using the reaction of 4-bromoacetophenone with 4-methoxystyrene as the example (No. 16).

Reaction (1) is both regio- and stereoselective and leads exclusively to the product resulting from substitution of the β-hydrogen, in the form of the E-configurational isomer; this was established by comparison of the physical constants for compounds (IIa-j) with the literature data for the E-isomers. Furthermore, high resolution PMR spectral analysis of compounds (IIh, j) revealed that the vinyl proton signals corresponded to an AX spin system

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TABLE 1. Reaction of Aryl Bromides with Styrene[a]

No. II/II	X	Y	Product	Yield, % [b]			mp(II), °C	Lit. ref.
				(II)		(III)		
				GLC	isolated[c]	GLC		
1	H	H	(IIa)	100	86	17	124	[9]
2	H	H	(IIa)	67[d]		21		
3	H	H	(IIa)	75[e]		26		
4	4-Me	H	(IIb)	83	77	22	119	[12]
5	4-Me	H	(IIb)	72[d]		55		
6	3-Me	H	(IIc)	100		30		
7	2-Me	H	(IId)	32		30		
8	4-Cl	H	(IIe)	87[f]	75	28	128	[9]
9	4-Cl	H	(IIe)	62[d]		74		
10	4-F	H	(IIf)	88	70		124	[9]
11	4-MeO	H	(IIg)	75	67	29	136	[9]
12	4-MeCO	H	(IIh)	71[f]	60	14	141	[13]
13	4-MeOCO	H	(IIi)	87[f]	51	12	157	[13]
14	H	4-Cl[g]	(IIe)	65				
15	H	4-MeO[g]	(IIg)	64				
16	4-MeCO	4-MeO[g]	(IIj)		48		174	[14]

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[a] Using 1 mmole aryl bromide, 4 mmoles styrene, 1 mmole Zn, 4 mmoles Py, 0.05 mmole complex (I), 3 ml MeCN, 65°C, 4 h.

[b] Yield of stilbenes (II) are presented based on aryl bromide; yields of styrene dimer (III) are calculated based on styrene.

[c] Isolated from reactions using four-fold increased reagent charge.

[d] Reaction carried out without pyridine.

[e] Catalyst: mixture of 0.05 mmole $NiCl_2$ $6H_2O$ with 0.1 mmole Ph_3P.

[f] The hydrodebromination product (7%) was also detected in the reaction mixture.

[g] With 2 mmoles of the corresponding styrene.

with a spin–spin coupling constant of ca. 16 Hz, which is evidence of their E-configurations. The PMR spectra of several of the compounds in this series (II) are summarized in Table 2.

Reaction (1) is sensitive to steric factors: in the case of 2-bromotoluene as the reagent the yield of 2-methylstilbene was 32% (No. 7), whereas α-methylstyrene did not react with bromobenzene.

The mechanism of reaction (1) is probably similar to that of the analogous reaction carried out in the presence of Pd complexes [3], and thus would involve the following stages: oxidative addition of ArX to Ni^0, addition of the resulting $ArNi^{II}X$ species to the double bond of styrene $Ar'CH{=}CH_2$, β-elimination of $HNi^{II}X$ from the intermediate $Ar'CH(NiX)CH_2Ar$ to give stilbene, and regeneration of Ni^0 from $HNi^{II}X$ by reaction with Zn, pyridine, and solvent. The appearance of hydrodebromination products can be attributed to a reaction leading to the formation of an $Ar^{\cdot}$ radical and $Ni^{I}X$, which takes place simultaneously with oxidative addition of ArX to Ni^0 [4].

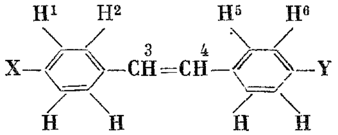
The hydride complex $HNi^{II}X$ can catalyze the formation of styrene dimer (III) [5]. Pyridine apparently promotes the conversion of $HNi^{II}X$ to Ni^0, since in the absence of pyridine the yield of stilbene is diminished and the amount of dimer (III) formed increases (cf. Nos. 5 and 9). A stoichiometric amount of Zn is necessary for regeneration of the catalyst in each catalytic cycle [2, 6].

The following individual experiments also demonstrate that reaction (1) can be used for the synthesis of distyrylbenzenes and dienes:

$$1,4\text{-}C_6H_4Br_2 + CH_2{=}CHC_6H_5 \rightarrow \underset{(IV)}{1,4\text{-}(C_6H_5CH{=}CH)_2\cdot C_6H_4}\ , \qquad (3)$$

$$(CH_3)_2C{=}CHBr + CH_2 = CHC_6H_5 \rightarrow \underset{(V)}{(CH_3)_2C = CHCH{=}CHC_6H_5}\ . \qquad (4)$$

TABLE 2. Proton Chemical Shifts (δ,ppm) of Substituted Stilbenes*



Compound	H_X	H^1	H^2	H^3	H^4	H^5	H^6	H_Y
(IIj)	2,52	7,89 (8,4) †	7,60 (8,4)	7,29 (16,2)	7,15 (16,2)	7.53 (8,7)	7,07 (8,7)	3,82
(IIh)	2,73	8,36 (8,4)	7,90 (8,4)	7,55 (16,5)	7,45 (16,5)	7,58–7,87		
(IIi)	3,92	8,04	7,56	7,14–7,50				
(IIg)	3,75	6,77 (8,0)	7,34 (8,0)	7,06	6,98	7,10–7,40		
(IIb)	2,33			6,92–7,52				

*CCl_4 solutions versus TMS as internal standard.

†Values of $J_{1,2}$, $J_{3,4}$, and $J_{5,6}$ in Hz are given in parentheses.

Thus, E,E-1,4-distyrylbenzene (IV) was obtained in 71% yield from 1,4-dibromobenzene and styrene, while E-1-phenyl-4-methylpenta-1,3-diene (V) was obtained in 62% yield from 1-bromo-2-methylpropene and styrene.

EXPERIMENTAL

Commercial grade aryl bromides were used without further purification. Pyridine and MeCN were dried over KOH and $CaCl_2$, respectively, and distilled from CaH_2 under Ar. Zn dust was activated with dilute HCl, washed with water and alcohol, and dried under vacuum. 1-Bromo-2-methylpropene [3] and complex (I) [7] were prepared via known methods. 4-Methoxy- and 4-chlorostyrene were prepared by cross-coupling vinyl bromide with 4-methoxy- or 4-chlorophenylmagnesium bromide in THF [8]. All reactions were carried out under Ar.

GLC analyses were performed in a Tsvet-110 chromatograph using a 2000 × 3 mm column filled with 3% SE-30 on Chromatone H-super support with He carrier gas. PMR spectra of compounds (IIh, j) were recorded on a Bruker 250 MHz spectrometer; spectra of (IIb, g, i) were obtained on a Tesla 100 MHz spectrometer.

Stilbenes were prepared by a general method, which is described here using the synthesis of 4-methoxystilbene as an example.

4-Methoxystilbene (IIg). To a solution of 0.125 ml (1 mmole) 4-bromoanisole, 0.46 ml (4 mmoles) styrene, and 0.32 ml (4 mmoles) Py in 3 ml MeCN was added 0.032 g (0.05 mmole) complex (I) and 0.065 g (1 mmole) Zn dust, and the mixture was stirred for 4 h at 65°C. An internal standard (naphthalene) was added to the mixture, and the yields of products were determined by GLC. To isolate (IIg), the mixture was poured into 4% HCl, extracted with ether, washed with water, and dried over $CaCl_2$; the ether was evaporated and the residue was recrystallized from MeOH. Yield 0.5 g (67%) of 4-methoxystilbene, mp 135°C [9].

Other stilbenes were also purified by recrystallization from MeOH, while stilbene (IIj) was recrystallized from a mixture of methanol–acetone. Styrene dimer (III) was completely separated from the stilbenes at the recrystallization stage.

1,4-Distyrylbenzene (IV). A mixture of 0.236 g (1 mmole) 1,4-dibromobenzene, 0.46 ml (4 mmoles) styrene, 0.67 ml (8 mmoles) Py, 0.065 g (0.1 mmole) complex (I) and 0.32 g (5 mmoles) Zn dust in 5 ml MeCN was stirred for 4 h at 65°C; the mixture was diluted with 4% HCl, filtered, and the product recrystallized from o-xylene. Yield 0.20 g (71%) of (IV), mp 260-262°C [10].

1-Phenyl-4-methylpenta-1,3-diene (V). A mixture of 0.36 ml (4 mmoles) 1-bromo-2-methylpropene, 0.92 ml (8 mmoles) styrene, 1.34 ml (16 mmoles) Py, 0.13 g (0.2 mmole) complex (I), and 0.13 g (2 mmoles) Zn dust in 10 ml MeCN was stirred for 4 h at 50°C. After conventional workup and distillation, the yield of (V) was 0.32 g (51%), bp 85-90°C (4 mm Hg); PMR spectrum (δ, ppm, $DCCl_3$): 1.84 s (6H), 5.9 d (1H), 6.29 d (1H) and 6.75-8.60 m (6H); cf. [11].

CONCLUSIONS

Condensation of aryl bromides with styrenes in acetonitrile in the presence of nickel organometallic complex catalysts and metallic zinc occurs regio- and stereoselectively to give E-stilbenes.

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PREPARATION OF SUBSTITUTED 3-HYDROXY-3-TRIFLUOROMETHYL-2(3H)BENZOFURANONES

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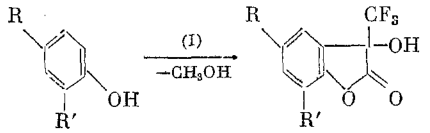
Trihydroxybenzenes, resorcinol, its simple mono- and diethers and other phenols containing electron donor substituents in meta positions undergo regioselective, uncatalyzed C-alkylation by polyfluorocarbonyl compounds in aprotic solvents. The position is governed by the ortho-para orientation of the substituents [1]. In this work we report the noncatalyzed, thermal reactions of phenols with $CF_3COCOOMe$ (I).

It has been shown that phenols in aprotic media (benzene, toluene, $MeNO_2$), not susceptible to mild C-alkylation, resemble alcohols [2] forming thermally unstable O-alkylation products with ketoester I. Conversion to C-alkylation products was quite rapid at 140-145°C and was accompanied by intramolecular condensation to give 3-hydroxy-3-trifluoromethyl-2(3H)-benzofuranones. Thus hydroquinone and catechol were heated (140-145°C, 6 h) with an equimolar amount of ketoester (I) in benzene to give 3,5-dihydroxy-3-trifluoromethyl-2(3H)benzo[b]furanone (II) and 3,7-dihydroxy-3-trifluoromethyl-2(3H)benzo[b]furanone (III) in 90 and 70% yields respectively.



R = OH, R' = H (II), R = H, R' = OH (III).

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