Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE DIELS–ALDER REACTION IN ORGANOMETALLIC CHEMISTRY

VI. DIELS–ALDER REACTIONS OF α-PYRONE WITH GROUP IV ELEMENT-SUBSTITUTED ACETYLENES*

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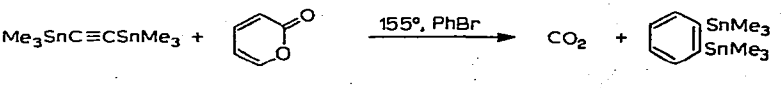
(Received July 2nd, 1971)

SUMMARY

The Diels–Alder reactions of α-pyrone with $Me_3SiC{\equiv}CSiMe_3$, $Me_3SiC{\equiv}CSiMe_2H$, $Me_2HSiC{\equiv}CSiMe_2H$, $Me_3GeC{\equiv}CGeMe_3$, $Me_3SiC{\equiv}CGeMe_3$, $Me_3SiC{\equiv}CSnMe_3$ and $EtC{\equiv}CEt$ were examined. All except the first two acetylenes gave the expected 1,2-disubstituted benzene product, in line with results obtained previously with $Me_3SnC{\equiv}CSnMe_3$. The first two acetylenes, $Me_3SiC{\equiv}CSiMe_3$ and $Me_3SiC{\equiv}CSiMe_2H$, also yielded benzene products containing substantial amounts of the 1,3-disubstituted benzenes, as well as minor amounts of the 1,4-isomers. This formation of unexpected isomers during these reactions was shown to result from acid-catalyzed rearrangement of the initially formed 1,2-disubstituted products, 1,2-$(Me_3Si)_2C_6H_4$ and 1-Me_3Si-2-$Me_2HSiC_6H_4$. The acidic impurities arose from pyrolysis of the bromobenzene solvent used or were introduced as contaminants of the α-pyrone. Such isomerizations were inhibited by addition of small amounts of triethylamine. The fact that no rearrangement took place with the other acetylenes is due to the scavenging of acidic impurities which might cause isomerization by the starting acetylene and the benzene product via metal–carbon bond cleavage processes.

INTRODUCTION

In earlier work, we had studied the reaction of α-pyrone with bis(trimethyltin)-acetylene and had found it to give 1,2-bis(trimethyltin)benzene in 50% yield (eqn. 1)[2]. Extension of this reaction to bis(trimethylsilyl)acetylene gave a rather surprising



result. Instead of the expected 1,2-bis(trimethylsilyl)benzene, the major (53% yield) product was 1,3-bis(trimethylsilyl)benzene[3]. Minor amounts of the 1,2- and 1,4-isomers were present as well. A rationalization of this finding was presented, but a more detailed study was required in order to understand these reactions.

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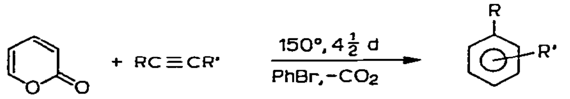
* For Part V see ref. 1.

RESULTS AND DISCUSSION

The most obvious differences between the trimethylsilyl and the trimethyltin groups are those of size and electron-releasing power. In the present case, the size difference was considered of greater importance. With two *cis* vicinal Me_3Si groups [as in 1,2-bis(trimethylsilyl)benzene], the nonbonded interactions are expected to be much more severe than in the case of two *cis* vicinal Me_3Sn groups[4]. Accordingly, in order to explore this idea relating to steric effects, a number of acetylenes bearing two Group IV element substituents was prepared[5], and these were allowed to react with α-pyrone under standard reaction conditions (150°, in bromobenzene solution, 4.5 day reaction time). The results of these experiments are shown in Table 1, and they are seen to correlate with the anticipated steric effects. The most sterically hindered acetylenes, those containing one or two tert-butyl substituents, did not react with α-pyrone at all. Those for which nonbonded interactions in the product 1,2-disubstituted benzene would be expected to be severe gave appreciable amounts of the 1,3-disubstituted benzene ($Me_3SiC{\equiv}CSiMe_3$ and $Me_3SiC{\equiv}CSiMe_2H$). Those for which steric interactions in the 1,2-disubstituted benzene product would be expected to be less severe gave only the 1,2-isomer. An explanation such as that given previously[3] thus seemed tenable. The differing reaction behavior between $Me_3SiC{\equiv}CSiMe_3$, $Me_3SiC{\equiv}CSiMe_2H$ and $Me_2HSiC{\equiv}CSiMe_2H$ seemed to speak against the operation of a major electronic effect.

TABLE 1

DIELS-ALDER REACTIONS OF α-PYRONE WITH GROUP IV-SUBSTITUTED ACETYLENES



R	R'	GLC yield (%)	Isomer distribution		
			1,2	1,3	1,4
Me_3Ge	Me_3Ge	54[a]	100		
Me_3Si	Me_3Sn	50[a]	100		
Me_3Si	Me_3Ge	74	100		
Me_2HSi	Me_2HSi	52	100	Trace	
Me_2HSi	Me_3Si	61	79	21	Trace
Me_3Si	Me_3Si	73	41	56	3
Me_3C	Me_3Sn	no reaction			
Me_3C	Me_3Si	no reaction			
Me_3C	Me_3C	no reaction			
C_2H_5	C_2H_5	12[a]	100		

[a] Isolated yield.

Further work, however, showed that 1,3-bis(trimethylsilyl)benzene was *not* the initial product of the α-pyrone/$Me_3SiC{\equiv}CSiMe_3$ reaction, rather that it was the result of an isomerization of the initially formed 1,2-bis(trimethylsilyl)benzene. The latter was quite stable toward isomerization as the pure compound when heated at 145° for 4.5 days. However, when it was heated in bromobenzene solution in a sealed tube at 150±5° for 4.5 days, complete isomerization to a mixture of 96% 1,3-bis(trimethylsilyl)benzene and 4% of the 1,4-isomer occurred[*]. Other experiments in which 1,2-bis(trimethylsilyl)benzene was heated in bromobenzene solution (sealed tube) for 48 h showed that sample handling was of critical importance. When the filled Pyrex tubes in which these experiments were carried out were cooled to −78° and partially evacuated to 70 mm to facilitate sealing, isomerization was extensive. On the other hand, when such tubes containing 1,2-bis(trimethylsilyl)benzene in bromobenzene were cooled in liquid nitrogen and evacuated to 0.01 mm prior to sealing, only a negligible amount of isomerization occurred. These experiments implicated the bromobenzene solvent, or more likely, its thermal decomposition product(s), as the agent responsible for the observed 1,2- to 1,3-bis(trimethylsilyl)benzene isomerization. These results are shown in Table 2, together with the results of similar studies with other solvents. Isomerization also took place in iodobenzene and carbon tetrachloride, but not in benzene, chlorobenzene, cyclohexane, dioxane and di-n-butyl ether. A very minor amount of isomerization was found to occur in 1,2-dichlorobenzene. The experiments with bromobenzene solutions already mentioned and the formation of a pink coloration in

TABLE 2

INFLUENCE OF SOLVENT UPON THE REARRANGEMENT OF 1,2-BIS(TRIMETHYLSILYL)BENZENE AT 150° FOR 48 HOURS IN SEALED TUBES

Solvent	Product: normalized % $(Me_3Si)_2C_6H_4$		
	1,2	1,3	1,4
Benzene	100[a]	0	0
Chlorobenzene	100[a]	0	0
Bromobenzene	39[b]	59	2
	99[c]	1	0
	98[c]	2	0
Iodobenzene	0[b,d]	91	9
	86[c]	13	1
	98[c]	2	0
1,2-Dichlorobenzene	96[b]	4	0
Carbon tetrachloride	87[b]	13	0
	84[c]	16	0
	87[c]	13	0
Cyclohexane	100	0	0
Dioxane	100	Trace	0
Di-n-butyl ether	100	0	0
(None)	100[a]	0	0

[a] Duplicate (or greater) determinations. [b] Cooled to −78°, evacuated to 70 mm before being sealed. [c] Cooled to −198° and evacuated to 0.01 mm before being sealed. [d] Pink coloration immediately after being sealed.

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[*] Similar control experiments with 1-trimethylsilyl-2-dimethylsilylbenzene (*cf.* Table 5) indicated that the formation of some 1,3- and 1,4-isomer in addition to the expected 1,2-isomer in the case of the α-pyrone/$Me_3SiC{\equiv}CSiMe_2H$ reaction was due to the same cause: isomerization of the 1,2-isomer when it was heated in bromobenzene solution.

some of the iodobenzene solutions suggested that some pyrolysis of the solvents was occurring, during the sealing of the tubes and, in the case of the reactions carried out at atmospheric pressure for 4–5 days, during the heating period. Likely decomposition products would be halogen atoms and molecular halogens. To test the effect of the latter, solutions of 1,2-bis(trimethylsilyl)benzene in cyclohexane containing 1 mole % of bromine or iodine were heated at 150° for 2 days. Isomerization occurred in both samples: the bromine-containing sample was converted to a mixture of 97% 1,3-bis(trimethylsilyl)benzene and 3% 1,4-isomer, while the sample to which iodine had been added contained a mixture of 40% 1,2- and 60% 1,3-bis(trimethylsilyl)benzene. In both reaction mixtures the color due to the free halogen had been discharged and both mixtures fumed on exposure to moist air and smelled of hydrogen halide. Presumably, halogen atoms did form and abstracted hydrogen atoms to form hydrogen halides. It thus was quite possible that in the observed isomerization we were dealing with an acid-catalyzed rearrangement of the type known to occur with 1,2-dialkylbenzenes[6].

This possibility was examined experimentally by heating benzene solutions of 1,2-bis(trimethylsilyl)benzene to which catalytic quantities of trifluoroacetic and *p*-toluenesulfonic acids had been added (sealed tube) for 48 h at 150°. In the experiment with added CF_3CO_2H, the solution after the heating period was found to contain 1.5% 1,2-, 94% 1,3- and 4.5% 1,4-bis(trimethylsilyl)benzene, in addition to a small quantity of trimethylphenylsilane. The *p*-toluenesulfonic acid catalyst yielded a mixture of 60% 1,3- and 22% 1,4-bis(trimethylsilyl)benzene and 18% trimethylphenylsilane. The latter arose from protodetrimethylsilylation of 1,2-bis(trimethylsilyl)benzene. Benzoic acid did not catalyze the isomerization of 1,2-bis(trimethylsilyl)benzene under these conditions.

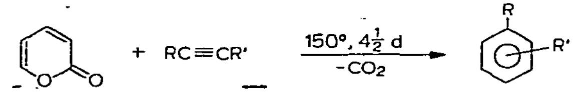
The observed strong acid-catalyzed rearrangement of 1,2-bis(trimethylsilyl)benzene to its 1,3- and 1,4-isomers was surprising in view of the facility with which protonic acids cleave the Si–C(aryl) bond[7]. However, our experiments were all carried out in organic medium, and the Si–C(aryl) cleavage rate depends on the acidity function of the medium[8]. It would seem that under our experimental conditions the acid catalyst can exist long enough to catalyze the rearrangement.

A further complication in the Diels–Alder reactions of α-pyrone with the Group IV element-substituted acetylenes is the apparent presence of acidic impurities in α-pyrone. No isomerization resulted when 1,2-bis(trimethylsilyl)benzene was heated at 150° for 4.5 days in benzene solution, but when a benzene solution containing this compound and α-pyrone was heated under the same conditons, a mixture of 89% 1,2- and 11% 1,3-bis(trimethylsilyl)benzene was formed. Furthermore, a Diels–Alder reaction between $Me_3SiC{\equiv}CSiMe_3$ and α-pyrone carried out in benzene medium at 150° (sealed tube) for 4.5 days gave a mixture (in 69% yield) containing 73% 1,2-, 2% 1,3- and 5% 1,4-bis(trimethylsilyl)benzene. The presence of acidic impurities, indicated by these experiments, is understandable, since in one step of the α-pyrone synthesis, malic acid is converted to coumalic acid by treatment with fuming sulfuric acid[9].

If acidic impurites are responsible for the formation of 1,3-bis(trimethylsilyl)benzene as major product in the α-pyrone/$Me_3SiC{\equiv}CSiMe_3$ reaction, then basic additives should prevent such isomerization from occurring. Such was found to be the case. As the comparative results in Table 3 show, *only* 1,2-bis(trimethylsilyl)benzene was produced when the α-pyrone/$Me_3SiC{\equiv}CSiMe_3$ reaction in benzene or bromobenzene was carried out in the presence of 10 mole % of triethylamine. Similarly, no

TABLE 3

INFLUENCE OF TRIETHYLAMINE UPON THE DIELS–ALDER REACTION OF α-PYRONE WITH GROUP IV-SUBSTITUTED ACETYLENES



RC≡CR'	Medium	GLC yield (%)	Isomer distribution		
			1,2	1,3	1,4
$Me_3SiC{\equiv}CSiMe_3$	PhH	58±5	74	26	Trace
$Me_3SiC{\equiv}CSiMe_3$	PhH/10 mole % Et_3N	60±3	100		
$Me_3SiC{\equiv}CSiMe_3$	PhBr	73±4	41	56	3
$Me_3SiC{\equiv}CSiMe_3$	PhBr/10 mole % Et_3N	61±5	100		
$Me_3SiC{\equiv}CSiMe_3$	PhCl/10 mole % Et_3N	66±3	100		
$Me_3SiC{\equiv}CSiHMe_3$	PhBr	61±3	79	21	Trace
$Me_3SiC{\equiv}CSiHMe_2$	PhCl/10 mole % Et_3N	61±3	100		

isomerization occurred when the Diels-Alder addition of $Me_3SiC{\equiv}CSiMe_2H$ to α-pyrone was carried out in the presence of triethylamine.

Thus the observed formation of 1,3-bis(trimethylsilyl)benzene in the α-pyrone/$Me_3SiC{\equiv}CSiMe_3$ reaction as originally carried out[3] is explained*. However, an explanation also must be given for the lack of isomerization in the reactions of α-pyrone with the other acetylenes in Table 1. In view of the known chemistry of the Ge–C and Sn–C bonds in alkynyl derivatives of germanium[10] and tin[11], a ready explanation is at hand. Cleavage of the carbon–metal bonds in alkynylgermanium and -tin compounds by protonic acids is a facile process. The rate of M–C≡C bond cleavage decreases as M is changed in the order $Pb > Sn \gg Ge > Si$[12,13]. Thus the acidic impurities in the case of the reactions of α-pyrone with $Me_3GeC{\equiv}CGeMe_3$ and $Me_3SnC{\equiv}CSnMe_3$ (but not with $Me_3SiC{\equiv}CSiMe_3$) are consumed in reaction with the acetylenic starting material and thus no isomerization is observed. We have found that the initial products of the reactions of α-pyrone with $Me_3GeC{\equiv}CGeMe_3$ and $Me_3SnC{\equiv}CSnMe_3$, 1,2-bis(trimethylgermyl)- and 1,2-bis(trimethyltin)benzene, also are readily cleaved by strong acids[14], and so these also should be scavengers for acidic impurities in these Diels–Alder reactions. Such is indeed the case: 1,2-bis(trimethylgermyl)benzene acts as an effective inhibitor of the acid-catalyzed isomerization of 1,2-bis(trimethylsilyl)benzene simply by consuming the acid present via rapid Ge–C(aryl) cleavage[14]. However, it is likely that most of the acidic impurities are scavenged by the germanium- and tin-substituted acetylenes during these Diels–Alder reactions, rather than by the 1,2-$(Me_3M)_2$-C_6H_4 products. That this is so is suggested by the observation that no isomerization is observed in the reaction of α-pyrone with $Me_3GeC{\equiv}CGeMe_3$, but that a minor, but observable amount of isomerization occurs when 1,2-bis(trimethylgermyl)benzene is heated in the presence of a catalytic amount of trifluoroacetic acid.

The complete lack of isomerization in the reaction of α-pyrone with $Me_2HSiC{\equiv}CSiMe_2H$ most likely is due to the consumption of the acidic impurities by the starting

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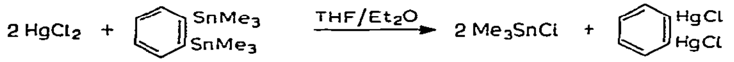
* The tentative explanations given in ref. 3 obviously no longer are applicable. However, the photochemical rearrangement of 1,2-bis(trimethylsilyl)benzene to the 1,3-isomer, described in ref. 3, remains an intriguing observation and this reaction very likely does proceed via non-Kekulé benzene intermediates.

acetylene (Si–H protolysis). The product, 1,2-bis(dimethylsilyl)benzene is itself isomerized to a small extent (ca. 7%) by a catalytic quantity of trifluoroacetic acid at 150° and it does not inhibit the acid-catalyzed isomerization of 1,2-bis(trimethylsilyl)-benzene[15].

The low extent of isomerization of 1,2-bis(dimethylsilyl)benzene on treatment with CF_3CO_2H very possibly is a consequence of diminished vicinal nonbonded interactions in this compound [compared with 1,2-bis(trimethylsilyl)benzene.]

The results which we have observed in our α-pyrone/Group IV element-substituted acetylene reactions thus are a consequence of the acid cleavage rates of the Group IV element–C≡C and –C(aryl) bonds. When the cleavage rate is relatively slow, the acidic impurities survive long enough to cause isomerization of the initially formed 1,2-disubstituted benzene; if the cleavage of the M–C bonds by acid is very rapid, the acidic impurities are destroyed before they can cause isomerization of the initially formed product.

The facile electrophilic cleavage of the Sn–C bonds in 1,2-bis(trimethyltin)-benzene has provided the basis for a useful synthesis of 1,2-bis(chloromercuri)benzene:



The acid-catalyzed isomerization of 1,2-bis(trimethylsilyl)benzene merited further study, and the results of these investigations will be reported in the near future[15].

EXPERIMENTAL

General comments

Infrared spectra were recorded using Perkin–Elmer 237, 257 or 337 grating infrared spectrophotometers, NMR spectra on Varian A60 or T60 spectrometers. Chemical shifts are given in δ units, ppm downfield from tetramethylsilane. Gas–liquid partition chromatography (GLC) was carried out using either MIT isothermal units or F&M model 700, 720 or 5754 temperature-programmed gas chromatographs. Yield determinations were made using the internal standard method.

The bomb tube heater which was used to heat reaction mixtures in sealed tubes was constructed from a 10" length of 1.63" i.d. iron pipe. Both ends of the pipe were threaded and capped with pipe caps. An 1/8th in. hole was drilled in one of these to permit pressure equilibration and to admit an iron–constantan thermocouple for temperature measurement. The pipe was wrapped successively with glass cloth electrical tape, asbestos paper tape, 150 ft. of 0.677 ohm/ft. Chromel A ribbon and several layers of asbestos cloth tape. When in use, the heater was clamped upright on a ring stand and further insulated with fiber-glass aircraft insulation.

The preparation of the Group IV element-substituted acetylenes has been described[5], as has been the preparation of α-pyrone[2,9]. Authentic samples of all isomeric (1,2-, 1,3- and 1,4) di-Group IV element-substituted benzenes were available for comparison. Their preparation and spectroscopic properties will be reported elsewhere[15].

Reactions of Group IV element-substituted acetylenes with α-pyrone

Reactions of bis(trimethylsilyl)acetylene with α-pyrone will be described in order to illustrate the procedures used.

(*a*). *At atmospheric pressure*. A 10 ml, one-necked flask equipped with a reflux condenser topped with a gas inlet tube was charged with 0.96 g (10 mmol) of α-pyrone, 2.30 g (13.5 mmol) of the acetylene and 2 ml of reagent grade bromobenzene. The reaction mixture was heated under an atmosphere of argon at 134–140° for 4.5 days. The reaction mixture then was cooled and trap-to-trap distilled (0.01 mm, pot temperature to 200°, receiver at −198°). GLC examination of the distillate (UC-W98 silicone rubber gum, 10% on Chromosorb W, 100–175° at 10°/min, *o*-dichlorobenzene internal standard) showed the presence of 1,2-bis(trimethylsilyl)benzene (18%). 1,3-bis(trimethylsilyl)benzene (47%) and 1,4-bis(trimethylsilyl)benzene (3%), as well as of unconverted bis(trimethylsilyl)acetylene (48%). The products were identified by comparison of their infrared and NMR spectra with those of authentic samples. (In the initial experiments[3], ultraviolet spectra, refractive indices and b.p. or m.p. also were compared.)

TABLE 4

CONTROL EXPERIMENTS WITH 1,2-BIS(TRIMETHYLSILYL)BENZENE

The following samples were heated in sealed tubes in a bomb-tube heater to 150±5° for 4.5 days.

Sample	1,2-$(Me_3Si)_2C_6H_4$	Co-reactant	Bromobenzene[a]	$(Me_3Si)_2C_6H_4$[b]		
				1,2	1,3	1,4
A	76.5 mg (0.303 mmole	α-pyrone 30.8 mg (0.320 mmole)	150 μl	0	82	18
B	68.2 mg (0.306 mmole)	$Me_3SiC{\equiv}CSiMe_3$ 48.4 mg (0.284 mmole)	150 μl	0	97	3
C[b]	15 μl	None		98	2	0
D[c,d]	20 μl	None		≥99	Trace	0
E	15 μl		100 μl	0	96	4

[a] Baker reagent. [b] Normalized yields in %. [c] Run in a melting-point capillary tube. [d] Heated in an oil bath at 134–140°.

TABLE 5

CONTROL EXPERIMENTS WITH 1-DIMETHYLSILYL-2-TRIMETHYLSILYLBENZENE

Same experimental conditions as in Table 4.

Sample	1,2-$Me_2HSiC_6H_4SiMe_3$	Co-reactant	Bromobenzene[a]	$Me_2HSiC_6H_4SiMe_3$		
				1,2	1,3	1,4
A	83.5 mg (0.400 mmole)	α-pyrone 40.7 mg (0.425 mmole)	150 μl	0	91	9
B	81.2 (0.389 mmole)	$Me_2HSiC{\equiv}CSiMe_3$ 64.5 mg (0.412 mmole)	150 μl	2	97	1
C[c]	20 μl			91	9	0
D[c]	15 μl		100 μl	26	74	0

[a] Baker reagent. [b] Normalized yields in %. [c] Run in a melting-point capillary tube.

TABLE 6

INFLUENCE OF α-PYRONE UPON ITS DIELS–ALDER REACTION WITH BIS(TRIMETHYLSILYL)ACETYLENE

Sample	1,2-$(Me_3Si)_2C_6H_4$	α-Pyrone	$Me_3SiC \equiv CSiMe_3$	Benzene[a]	Yield (%)		Isomer ratio $(Me_3Si)_2C_6H_4$		
					$(Me_3Si)_2C_6H_4$	$PhSiMe_3$	1,2	1,3	1,4
A		0.2245 g (2.337 mmoles)	0.5979 g (3.509 mmoles)	1 ml	69±6	1	73	22	5
B		0.2502 g[b] (2.610 mmoles)	0.5250 g (3.081 mmoles)	1 ml	54±4	3	44	53	3
C	45 mg (0.2 mmole)		34 mg (0.2 mmole)	100 μl			100	0	0
D	45 mg	19 mg (0.2 mmole)		100 μl			89	11	0
E	45 mg (0.2 mmole)			100 μl			100	0	0
F	45 mg (0.2 mmole)						100	0	0

[a] Fisher reagent. [b] Chromatographed on neutral alumina.

(*b*). *Sealed-tube reactions.* A 2.5 × 18 cm Pyrex bomb tube was charged with 10 mmol of α-pyrone, 10 mmole of bis(trimethylsilyl)acetylene, 0.01 g of hydroquinone and 3 ml of bromobenzene. The contents of the tube were cooled to −78°, and the tube was evacuated to 1 mm and sealed. The tube then was heated at 145–150° for 4.5 days. Work-up of the reaction mixture follwed the procedure described in (*a*). The yields of the bis(trimethylsilyl)benzene isomers were: 1,2-, 30%; 1,3-, 41%; 1,4-, 2%. A 22% recovery of bis(trimethylsilyl)acetylene was determined.

Other reactions were carried out on a 5–12 mmole scale. In all cases the GLC conditions used were such that the 1,2-, 1,3- and 1,4-isomers to be expected would be resolved.

The control experiments (stability of products to the reaction conditions) were

TABLE 7

INFLUENCE OF TRIETHYLAMINE[a] UPON THE DIELS–ALDER REACTION OF α-PYRONE WITH BIS(TRIMETHYLSILYL)-ACETYLENE

Sample	$Me_3SiC{\equiv}CSiMe_3$	α-Pyrone	Solvent	Yield (%) $(Me_3Si)_2C_6H_4$	Isomer ratio		
					1,2	1,3	1,4
A	1.0377 g (6.090 mmoles)	0.5744 g (6.090 mmoles)	1 ml PhH	59±4	45	55	Trace
B	1.0302 g (6.056 mmoles)	0.5721 g (5.953 mmoles)	1 ml PhH	60±3	100	0	0
C	1.1140 (6.18 mmoles)	0.6081 g (6.32 mmoles)	1 ml PhBr	61±5	100	0	0
D	0.9656 g (5.667 mmoles)	0.5684 g (5.917 mmoles)	1 ml PhCl	66±3	100	0	0
E	0.8361 g[b] (5.347 mmoles)	0.5516 g (5.741 mmoles)	1 ml PhCl	61±3[c]	100	0	0

[a] Added to samples B–E, 60 mg, (0.6 mmole). [b] $Me_3SiC{\equiv}CSiMe_2H$. [c] $(Me_3Si)(Me_2HSi)C_6H_4$.

TABLE 8

ACID-CATALYZED REARRANGEMENT OF GROUP IV-SUBSTITUTED ARENES IN BENZENE SOLUTION IN SEALED TUBES AT 150° FOR 48 HOURS

Acid	Arene	Normalized % yield of $R_2R'MC_6H_4MR_2R'$		
		1,2	1,3	1,4
p-$MeC_6H_4SO_3H \cdot H_2O$[a]	1,2-$(Me_3Si)_2C_6H_4$[c]	0	76	24
CF_3COOH[b]	1,2-$(Me_3Si)_2C_6H_4$[d]	1.5	94	4.5
CF_3COOH[b]	1,2-$(Me_3Ge)_2C_6H_4$[e]	99	1	Trace
CF_3COOH[b]	1,2-$(Me_2HSi)_2C_6H_4$[f]	93	4	3
CF_3COOH[b]	1,2-$Me_2HSiC_6H_4SiMe_3$[g]	71	27	1

[a] 0.3 mole %. [b] 2.3 mole %. [c] 18% cleavage to $PhSiMe_3$. [d] 13% cleavage to $PhSiMe_3$. [e] < 5% cleavage to $PhGeMe_3$. [f] Minor cleavage to $PhSiMe_2H$. [g] Minor cleavage to $PhSiMe_3$ and $PhSiMe_2H$.

carried out in the same manner, as were the experiments testing the effect of additives such as triethylamine. Full details would be repetitive but they are available in the Ph.D. thesis of D.L.W.[16]. The control experiments in which isomerization was observed are summarized in Tables 4 and 5. Experimental data concerning the effects of additives are given in Tables 6, 7 and 8.

Reaction of 1,2-*bis(trimethyltin)benzene with mercuric chloride*

To 6.14 g (22.6 mmoles) of mercuric chloride (Mallinckrodt reagent) in 50 ml of THF in a 200 ml, three necked, round-bottom flask equipped with a mechanical stirrer, pressure-equalizing addition funnel, and an argon inlet tube, was added dropwise 4.57 g (11.3 mmoles) of 1,2-bis(trimethyltin)benzene in 50 ml of ether (Fisher anydrous reagent). The reaction mixture was stirred ca. 4 h at room temperature. The resulting white precipitate was collected by filtration and washed with 1 l of ether. Drying *in vacuo* (0.5 mm) for two days yielded 5.40 g (87%) of 1,2-bis(chloromercuri)benzene, m.p. 310–311° (dec); IR (KBr disc): 3100(w), 3040(m), 2960(w), 1610(m), 1550(m), 1440(s), 1425(s), 1260(s), 1165(w), 1105(m), 1020(s), 745(s), and 725(s) cm^{-1}. [Lit.[17] m.p. 310–320° (dec.).] (Found: C, 13.21; H, 0.84; Cl, 13.05. $C_6H_4Cl_2Hg_2$ calcd.: C, 13.14; H, 0.75: Cl, 12.93%.)

ACKNOWLEDGEMENTS

The authors are grateful to the National Science Foundation (Grant NSF 6466X) for generaous support of this work and to the IBM Corporation for the award of a fellowship to D.L.W. Gifts of chemicals by the Union Carbide Corporation, Dow Corning Corporation, Eagle Picher Company and M&T Chemicals, Inc. are gratefully acknowledged.

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