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A PREPARATION OF 3-ARYL-2,5-DIHYDROTHIOPHENE-1,1-DIOXIDES FROM ARYL IODIDES

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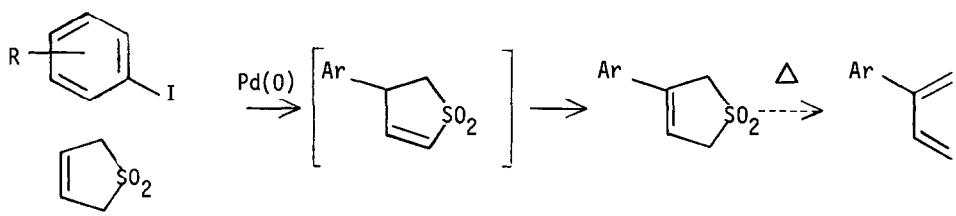
As part of our synthetic program we sought an efficient preparation of 1-aryl-4-substituted-1-cyclohexenes that would provide flexibility in both the nature of the aryl and cyclohexenyl substituents. An ideal approach would involve [4+2] cycloaddition if a versatile synthesis of the requisite 2-aryl-1,3-butadienes were available. Several syntheses of 2-phenyl-1,3-butadiene have been reported. There are two general approaches: 1) classical methods involved a pyrolysis of an alcohol or alcohol derivative as a final step [1,2]; 2) more recent methods utilize a transition metal-mediated coupling of a preformed diene [3,4]. The coupling with chloroprene grignard [3] would appear to provide greatest flexibility. However, prompted by the low catalyst activity with aryl halides as well as the probable carcinogenicity and cost of chloroprene, we sought a more convenient method.

While palladium-mediated coupling of aryl halides with 1,3-dienes results in arylation of a terminal diene carbon [5], we envisioned coupling with sulfolene and subsequent thermolysis would result in arylation of a central diene carbon [6].



The thermolysis of sulfolenes to provide dienes for [4+2] cycloaddition is precedented [7]. We now report our preliminary results on the arylation of sulfolene.

Two factors dictated the choice of reaction conditions:

1) Since sulfolene and 3-arylsulfolenes are thermally labile, we used a phase transfer catalyst to facilitate oxidative addition-olefin insertion-reductive elimination [8].

2) As an allylic sulfone, sulfolene should be capable of forming a π-allyl complex when palladium-phosphine complex is used [9]. Aryl iodides, which do not require phosphine

Supplementary Material:

4-H: 60MHz ^{1}H NMR ($CDCl_3$) δ: 3.95-4.25 (s, 3H), 6.2-6.5 (m, 1H), 7.30 (m, 4H); IR (KBr) 3088, 1497, 1454, 1310-1298, 1236, 1125, 1112, 1105, 752, 686 cm^{-1}.

4-Me: 60MHz ^{1}H NMR ($CDCl_3$) δ: 2.38 (s, 3H), 3.9-4.2 (m, 4H), 6.2-6.5 (m, 1H), 7.30 (m, 4H); IR (KBr) 2960, 2930, 1525, 1430, 1293, 1276, 1246, 1123, 784 cm^{-1}.

4-OMe: 60 MHz ^{1}H NMR ($CDCl_3$) δ: 3.84 (s, 3H), 3.9-4.2 (m, 4H), 6.15-6.4 (m, 1H), 6.98 (d, 2H), 7.38 (d, 2H); IR (KBr) 3080, 2842, 1608, 1518, 1465, 1452, 1310-1300, 1264, 1239, 1124, 1109, 803 cm^{-1}.

4-OAc: 60 MHz ^{1}H NMR ($CDCl_3$) δ: 2.34 (s, 3H), 3.9-4.2 (m, 4H), 6.25-6.5 (m, 1H), 7.19 (d, 2H), 7.46 (d, 2H); IR (KBr) 3080-3060, 2980, 2965, 2940-2920, 1770-1750, 1603, 1514, 1317-1300, 1238, 1205, 1188, 1170, 1117, 851, 787 cm^{-1}.
Analysis: Cal. C (57.13), H (4.79); Obs. C (57.30), H (4.69).

2,3,4-$(OMe)_3$: 60 MHz ^{1}H NMR ($CDCl_3$) δ: 3.95-4.3 (m, 13H), 6.15-6.4 (m, 1H), 6.75 (d, 1H), 7.04 (d, 1H); IR (KBr) 3012, 2978, 2960, 2938, 1596, 1496, 1462, 1455, 1309, 1220, 1132, 1097, 795 cm^{-1}.
Analysis: Cal. C (54.92), H (5.67); Obs. C (54.81), H (5.86).

4-Br: 60 MHz ^{1}H NMR ($CDCl_3$) δ: 3.95-4.25 (m, 4H), 6.3-6.55 (m, 1H), 7.3 (d, 2H), 7.63 (d, 2H); IR (KBr) 2965, 2923, 1590, 1494, 1292, 1244, 1128, 835, 783, 597 cm^{-1}.

4-COOMe: 60 MHz ^{1}H NMR ($CDCl_3$) δ: 3.98 (s, 3H), 4.0-4.25 (m, 4H), 6.45-6.65 (m, 1H), 7.50 (d, 2H), 8.13 (d, 2H); IR (KBr) 3079, 2979, 2958, 2938, 1718, 1607, 1310, 1284, 1130-1110, 762 cm^{-1}.
Analysis: Cal. C (57.13), H (4.79); Obs. C (57.20), H (4.91).

Thin layer chromatography was performed on **KIESELGEL 60 F 254** plates using Et_2O for development. Rf values are:

Sulfolene		0.38
ArI	4-H	0.82
	4-Me	0.83
	4-OMe	0.80
	4-OAc	0.79
	2,3,4-$(OMe)_3$	0.76
	4-Br	0.84
	4-COOMe	0.81
3-Arylsulfolene	4-H	0.63
	4-Me	0.64
	4-OMe	0.61
	4-OAc	0.52
	2,3,4-$(OMe)_3$	0.52
	4-Br	0.60
	4-COOMe	0.54

for oxidative addition to palladium, were used. A representative procedure (for R=4-H) is as follows: A mixture of 2.040 g (10.00 mmol) iodobenzene, 1.241 g (10.50 mmol) sulfolene, 1.265 g (12.50 mmol) triethylamine, 3.224 g (10.00 mmol) tetrabutylammonium bromide, 112 mg (5 mol %) $Pd(OAc)_2$ and 5 ml of benzene was stirred in a foil-covered, stoppered flask for 163 h. The solvent was removed in vacuo. The residue was mixed with celite then Soxhlet extracted with ethyl ether for 6 h. The ether solution was then concentrated in vacuo. The residual oily brown solid was recrystallized from 20 ml MeOH to afford 1.365 g (69.8 %) of shiny beige plates, m.p. 129-131.5°C (lit. [10] 131.3-131.8°C).

TABLE 1. Sulfolene Arylation

R=	time (h)	Yd. (g)	* Pct.Yd.	** recovered iodide (g)	m.p. (°C) pure
4-H	163	1.356	69.8		131.3-131.8 [10]
4-Me	95	1.350	64.8		150-150.5 [11]
4-OMe	90	1.478	65.9		132-132.5 [11]
4-OAc	170	1.218	55.5		143-144 [12]
2,3,4-$(OMe)_3$	262	1.277	44.9	0.544	100.7-101.3 [12]
4-Br	238	0.767	58.8	1.478	160-160.5 [11]
4-COOMe	215	0.846	52.4	1.412	148.5-149 [12]

* Percent yield is based on iodide not recovered. No attempt was made to recover iodide in the first four cases.

** Iodides were separated from arylsulfolenes by radial chromatography (silica gel). Iodides were recrystallized from hexanes or 30-60°C petroleum ether and arylsulfolenes were recrystallized from MeOH.

No reaction was observed with 1-iodo-4-nitrobenzene. From these few examples it is apparent that the rate is retarded by electron withdrawing substituents and by substituents adjacent to the iodide. Conditions providing faster rates are being sought.

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