Novel aromatizational skeletal rearrangement with 1,5-isomerization of an *exo*-heteroelement *para*-semiquinoid system. Transformation of 4-methyl-4-trichloromethyl-2,5-cyclohexadiene-1-thione into *p*-tolyltrichloromethylsulfide

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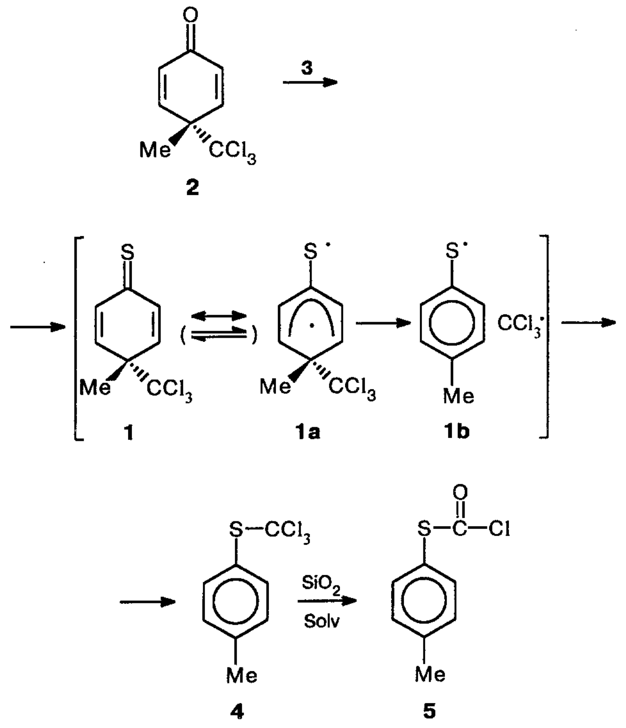
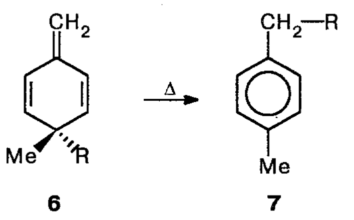
In the course of the study of semiquinoid systems, *i.e.*, cyclohexadienones, alkylidenecyclohexadienes, and their heteroanalogs,[1] we found that thioketone **1**, whose formation was to be expected as the result of the interaction of dienone **2** with Lawesson's reagent ($(p\text{-MeOC}_6H_4P(S)S)_2$ (**3**)[2,3] (a 2 : 1 molar ratio of the reagents, C_6H_6, Ar, 80 °C, 4 h), easily rearranges into *p*-tolyltrichloromethylsulfide (**4**) under the reaction conditions. Sulfide **4** was isolated in the pure form chromatographically (a glass column, d = 1.6 cm, l = 12 cm, Silpearl 029, $CHCl_3$, and then a CH_2Cl_2—hexane mixture (1 : 5) as the eluents). *p*-Tolyl thiochloroformate (**5**) was also obtained as a result of partial hydrolysis of **4** on the column.

Such an isomerization is likely to have a homolytic nature (it probably includes an excited biradical state of *para*-semiquinoid thioketone **1a** with its subsequent transformation into radical pair **1b**). Parallel formation of the "homodimer" of the *p*-thiocresolate radical, di-*p*-tolyldisulfide, isolated in ~5 % yield counts in favor of this mechanism.



In heteroorganic chemistry, the reaction found is the first example of aromatizational skeletal rearrangement of an *exo*-heteroelement *para*-semiquinoid system, which proceeds through a 1,5-shift of the substituent off the geminal center. It is noteworthy that the rearrangement of similar systems with the *exo*-hydrazono substituent (discovered by T. Miller and R. Hollander in 1980) appears to proceed through a 1,6-shift rather than through a 1,5-shift of the substituent off the geminal center and affords a heterocyclic product (see Ref. 4). As for true organic *para*-semiquinoid systems, the closest analog of this reaction found seems to be thermally induced isomerization of 1-methylene-4-methyl-4-dichloromethyl- (**6**, R = $CHCl_2$)[5] and -trichloromethyl- (**6**, R = CCl_3)[6] -2,5-cyclohexadienes (see Ref. 7) into *p*-1,1-dichloro- and *p*-1,1,1-trichloroethyltoluenes **7** (R = $CHCl_2$, CCl_3), respectively (Auwers' rearrangement[8]).



***p*-Tolyltrichloromethylsulfide (4)** was obtained in 84 % yield (^{1}H NMR). ^{1}H NMR ($CDCl_3$), δ: 2.43 (s, 3 H, CH_3); 7.33 and 7.70 (q, AB-system, 4 H, CH arom., J_{AB} = 8 Hz). MS (70 eV), m/z (I_{rel} (%)): 240 $[M]^+$ (33), 205 [M—Cl] (90), 169 [M—Cl—HCl] (9), 123 $[M—CCl_3]$ (100), 91 $[C_7H_7]$ (33), 45 [CHS] (28).

***p*-Tolyl thiochloroformate (5)** was obtained in 12 % yield (^{1}H NMR). ^{1}H NMR ($CDCl_3$), δ: 2.41 (s, 3 H, CH_3); 7.28 and 7.43 (q, AB-system, 4 H, CH arom., J_{AB} = 8.2 Hz). MS

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(70 eV), m/z (I_{rel} (%)): 186 $[M]^+$ (35), 151 [M–Cl] (10), 123 [M–Cl–CO] (100), 91 $[C_7H_7]$ (6), 45 [CHS] (20).

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Pd and Cu catalyzed synthesis of diarylacetylenes in aqueous-organic emulsion

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Cross-coupling reaction of terminal acetylenes with aryl iodides is usually carried out in polar organic solvents in the presence of tertiary amines, CuI, and Pd complexes.[1,2] To extend the investigation of this reaction to aqueous solutions[3] we have studied the synthesis in a water-alcohol emulsion in the presence of cetyltrimethylammonium bromide (CTAB) as an emulsifier.

We found that phenylacetylene readily reacts with aryl iodides in the presence of $Pd(OAc)_2$ and CuI under the given conditions. The reaction is completed in 4 h upon boiling and stirring of the reagents, yielding the desired acetylenes in high yields (90—95 %).

$$PhC{\equiv}CH + IC_6H_4X \xrightarrow[H_2O{-}BuOH,\ CTAB,\ \Delta]{Pd(OAc)_2,\ CuI,\ K_2CO_3} PhC{\equiv}CC_6H_4X$$

X = H, *p*-Me, *p*-MeO, *p*-Cl, *p*-CN

General procedure. Distilled water (9 mL), *n*-butanol (1 mL), cetyltrimethylammonium bromide (5 g), and K_2CO_3 (0.69 g, 5 mmol) were stirred in a two-necked flask with a magnetic stirrer at 100 °C until a transparent microemulsion was produced. To the microemulsion obtained PhC≡CH (3 mmol), PhI (2.7 mmol), $Pd(OAc)_2$ (0.025 mmol), and CuI (0.05 mmol) were added with stirring under nitrogen. The reaction mixture was refluxed with stirring for 4 h and neutralized with dilute HCl, and butanol was removed. The precipitate was extracted with benzene, dried over Na_2SO_4, and passed through a fine layer of Al_2O_3. The resultant solution was evaporated, and the residue was crystallized from ethanol. Yield of tolan was 95 %, m.p. 60—61 °C.

$4\text{-}CNC_6H_4C{\equiv}CPh$ (90 %), $4\text{-}ClC_6H_4C{\equiv}CPh$ (92 %), $4\text{-}MeC_6H_4C{\equiv}CPh$ (88 %), and $4\text{-}MeOC_6H_4C{\equiv}CPh$ (94 %) were prepared by the same method. The boiling points of the compounds synthesized are in agreement with published data.[4]

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