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SYNTHESIS AND REACTIONS OF 2-NAPHTHYLTELLURIUM TRICHLORIDE†

JAN BERGMAN and LARS ENGMAN*
Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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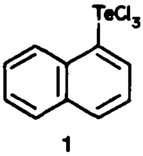
Abstract—$TeCl_4$ and naphthalene, when heated to 110° in the absence of a solvent, yielded 2-naphthyltellurium trichloride (2), which on treatment with degassed Raney Ni afforded 2,2'-binaphthyl in excellent yield. Reaction of 2 with propene and *cis*-2-butene produced the corresponding 1:1-adducts, which however could not be coupled to 2-(2-chloroalkyl)naphthalenes with this reagent.

Existing methods for the syntheses of 1- and 2-naphthyltellurium trichlorides (1, 2) are based either on the reaction of naphthyl mercury chlorides with $TeCl_4$[1,2] or on the direct interaction of naphthalene with $TeCl_4$ in toluene.[3] The latter reaction yielded only the 1-substituted product, which is in accord with the general pattern of electrophilic substitutions on naphthalene. Thus mercuration, bromination, and nitration gave 95[4], 99[5] and 90[6]% yield respectively of the 1-substituted product. Sulphonation of naphthalene, on the other hand, is a reversible process. At lower temperatures the kinetically controlled product, naphthalene-1-sulphonic acid, is the main product. At higher temperatures, e.g. 160°, the thermodynamically more stable product, naphthalene-2-sulphonic acid, predominates.[7]

We have found that $TeCl_4$ and naphthalene at 110° without any solvent gives 2-naphthyltellurium trichloride (2). A similar preference for 2-substitution has previously been observed for the reaction of thallium(III)-isobutyrate with naphthalene at 112° without any solvent yielding 2-naphthylthallium diisobutyrate.[8]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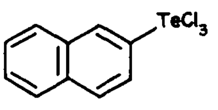
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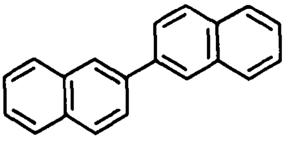
It has recently been shown[9,10] that diaryltellurium dichlorides and diaryl tellurides can be converted to biaryls with degassed Raney Ni. We have found that 2-naphthyltellurium trichloride, not unexpectedly, can be coupled to 2,2'-binaphthyl (3) in good yield with degassed Raney Ni. Binaphthyls are of interest for the synthesis of condensed ring systems such as perylenes and they occur in nature when suitably substituted.[11,12] Other synthetic methods for binaphthyls like the Ullman reaction[13] and the different variants of the Grignard coupling[14-16] require halogen-substituted aromatics which often has to be done indirectly, especially for the 2-substituted derivatives.

RESULTS AND DISCUSSION

When $TeCl_4$ and naphthalene were heated in a 1:3 molar ratio for 12 hr at 110°, 2-naphthyltellurium trichloride was obtained as the only product (54%) identical in all respects with the compound described.[2] However, when the same reaction is performed in the presence of toluene 1-naphthyltellurium trichloride is formed.[3] When 1-naphthyltellurium trichloride is heated to 110° without solvent or with naphthalene in a 1:3 molar ratio it can *not* be converted to the 2-substituted derivative. Consequently, the electrophilic addition of $TeCl_4$ is not a reversible process at this temperature, a fact that could have explained the 2-substitution by a migration of the $TeCl_3$ group at elevated temperatures from the kinetically favoured 1-position to the thermodynamically favoured 2-position. The explanation to this anomalous 2-substitution may be a steric one due to charge-transfer complexation[17] of $TeCl_4$ in the absence of a solvent and preference for attack at the least hindered position.

Treatment of 2-naphthyltellurium trichloride with degassed Raney Ni[10] in diglyme afforded 2,2'-binaphthyl in excellent yield (*cf* the coupling of 2-naphthyl radicals generated by thermolysis of 2-naphthylsulphonyl chloride in the presence of cuprous chloride).[18] Attempted coupling of 1-naphthyltellurium trichloride in the same manner however resulted in formation of 1,1'-dinaphthyl telluride and 1,1'-dinaphthyl ditelluride as indicated from analysis by mass spectrometry.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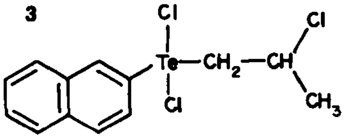
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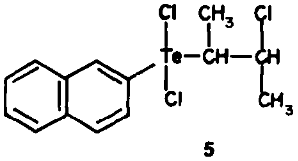
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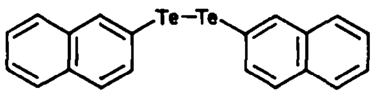
† Part 6 in the series "Tellurium in Organic Synthesis". For part 5 see Ref. 20.

2-Naphthyltellurium trichloride could be added in a sealed tube to propene and *cis*-2-butene yielding the adducts **4** and **5** respectively in good yield.

Attempted coupling of **5** with degassed Raney Ni to form 2 - (2 - chloro - 1 - methylpropyl)napthalene resulted in formation of 2,2'-binaphthyl in 88% yield. Apparently degassed Raney Ni is best suited for the synthesis of biaryls.

Reduction of **4** with aqueous Na_2S yielded 2,2'-dinaphthyl ditelluride (**6**), instead of the expected 2-chloropropyl naphthyltelluride. Compound **6** may be formed *via* the epitelluronium chloride **7** which decomposes into propene and 2-naphthyltellurenyl chloride. Alternatively Na_2S, after reduction of **5** to the corresponding telluride, may attack the 2-halogen atom with expulsion of a 2-naphthyltellurium anion.



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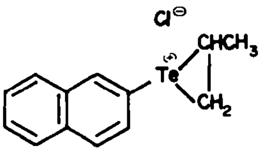

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EXPERIMENTAL

Materials and spectroscopic measurements. $TeCl_4$ was a Merck product. *cis*-2-Butene was obtained from Fluka and propene from AGA Specialgas. Raney Ni was a generous gift from Kema Nord AB. 1-Naphthyltellurium trichloride was synthesised according to the literature.[3]

IR spectra were obtained using a Perkin–Elmer 257 instrument. NMR spectra were recorded on a Varian EM 360 instrument. Mass spectra were obtained with an LKB 9000 mass spectrometer.

2-*Naphthyltellurium trichloride* (**2**). $TeCl_4$ (7.5 g, 27.8 mmol) was added to melted naphthalene (11.0 g, 86 mmol) kept at 110° under dry N_2. After 12 hr at this temp the greenish solid was pulverised in a mortar and washed thoroughly with hot toluene, yield of **1** 5.4 g (54%): m.p. 200–02° (benzene) (lit. 200–02[2]). IR (KBr): 1620(w), 1580(m), 1495(m), 1345(m), 1270(m), 1200(m), 1130(m), 930(m), 885(s), 850(s), 790(s), 735(s), 675(s).

Naphthyl - (2 - chloropropyl)tellurium trichloride (**4**). 2-Naphthyltellurium trichloride (5.4 g, 15 mmol) and propene (1.0 g, 24 mmol) dissolved in acetonitrile (50 ml) were heated in a sealed tube at 70° for 12 hr. Evaporation and recrystalisation from acetonitrile yielded 4.8 g (79%) of **2**, m.p. 136–38°. IR (KBr): 1620(w), 1580(m), 1500(m), 1440(m), 1270(m), 1265(m), 1100(m), 1055(m), 980(m), 960(w), 935(w), 915(w), 900(w), 860(m), 815(s), 760(s), 750(s). NMR ($CDCl_3$) δ 1.8 (d, 3H), 4.1 (d, 2H), 4.8–5.2 (m, 1H), 7.4–8.2 (m, 6H), 8.6 (s, 1H).

Naphthyl - (2 - chloro - 1 - methylpropyl)tellurium dichloride (**5**). 2 - Naphthyltellurium trichloride (2.5 g, 6.9 mmol) and *cis* - 2 - butene (0.6 g, 10.7 mmol) dissolved in $CHCl_3$ (50 ml) were heated in a sealed tube at 70° for 12 hr. Evaporation and recrystallisation from acetonitrile yielded 2.1 g (73%) of **3**, m.p. 114–15°. IR (KBr): 1620(w), 1500(m), 1440(m), 1345(w), 1170(m), 1130(m), 1055(m), 1030(w), 985(w), 970(w), 935(m), 890(w), 860(s), 815(s), 750(s). NMR ($CDCl_3$) δ 1.55 (d, 3H), 1.65 (d, 3H), 4.2–4.8 (m, 1H), 7.3–8.3 (m, 6H), 8.7 (s, 1H).

2,2' - *Binaphthyl* (**3**). 2 - Naphthyltellurium trichloride (0.60 g, 1.65 mmol) in diglyme (40 ml) was added to degassed Raney Ni[10] (1.5 g) and refluxed for 2 hr. Evaporation of the filtered soln afforded **3** 0.21 g (98%), m.p. 184–85° (acetonitrile) (lit. 184[15]). M.S. *m/e* M^+ 254.

Treatment of **3** *with degassed Raney Ni.* 2 - Naphthyl - (2 - chloro - 1 - methylpropyl)tellurium dichloride (0.75 g, 1.80 mmol) in diglyme (40 ml) was added to degassed Raney Ni (1.5 g) and refluxed for 2 hr. Evaporation of the filtered soln afforded **3** 0.20 g (88%), m.p. 184–85° (acetonitrile).

2,2' - *Dinaphthyl ditelluride* (**6**). 2 - Naphthyl - (2 - chloropropyl)tellurium dichloride (0.40 g, 1.0 mmol) was shaken with CH_2Cl_2 (50 ml) and an aqueous soln of $Na_2S \cdot 9H_2O$ (9.0 g) until all material had dissolved. Drying over $CaCl_2$ and evaporation yielded **6** 0.24 g (95%), m.p. 117–18° (EtOH) (lit. 120–22[19]). M.S. *m/e* M^+ 514.

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