Cathodic *t*-Butylation of Pyrene

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Cathodic reduction of pyrene in N,N-dimethylformamide in the presence of *t*-butyl chloride yields 1-*t*-butylpyrene in 52 % yield. Besides this compound minor amounts of 4-*t*-butyl-4,5-dihydropyrene, 1,6-di-*t*-butylpyrene and 1,8-di-*t*-butylpyrene are formed. Autoxidation of the intermediately formed dihydropyrenes is observed. Variations in the product composition have been noted depending on supporting electrolyte and water content.

The reaction between aromatic anion radicals, formed by reduction of the aromatic compound with alkali metal [1-7] or electrolytically,[8] and alkyl halides has been studied extensively. The reaction mechanism for the chemical and electrochemical reductive alkylation has been shown generally to involve a coupling between the alkyl radical and the aromatic anion radical.

The coupling reaction and the reduction of the alkyl radical by the anion radical are competing reactions,[7,8] and it has been shown that during the electrolytic reductive coupling the catalytic reduction of the alkyl halide is more pronounced for primary alkyl halides than for tertiary.[8]

Tertiary halides are thus well suited for reductive alkylation reactions, and anthracene, stilbene, and naphthalene have previously been *t*-butylated by this means.[8]

1-*t*-Butylpyrene (*1*) has been found difficult to prepare by classical methods; thus Friedel-Crafts alkylation of pyrene with *t*-butyl chloride leads exclusively to 2,7-di-*t*-butylpyrene,[9] whereas a Friedel-Crafts reaction using pivaloyl chloride gives a mixture of 2-*t*-butylpyrene and 1-pivaloyl pyrene.[10] Attempts to prepare *1* from 1-fluoropyrene and *t*-butyllithium following a procedure analogous to the one used by Huisgen [11] to prepare 1-*t*-butylnaphthalene

gave only a very small amount of a difficultly separable mixture of 1- and 2-*t*-butylpyrene.[10]

The purpose of the present study was to investigate whether compounds which could easily be transformed into 1-*t*-butylpyrene could be prepared by electrolytic reductive alkylation.

RESULTS AND DISCUSSION

Pyrene gives in cyclic voltammetry in N,N-dimethylformamide (DMF) two cathodic peaks [$E_\mathrm{p}^1 = -2.13$ V; $E_\mathrm{p}^2 = -2.74$ V (SCE)]; to the first one corresponds an anodic peak, whereas it has not yet been possible to obtain an anodic peak corresponding to the reoxidation of the pyrene dianion. The first redox reaction, the formation and reoxidation of the anion radical, is reversible, and the anion radical is stable for a long time as most other anion radicals of aromatic hydrocarbons.[12]

Addition of *t*-butyl chloride to pyrene in DMF containing tetrabutylammonium iodide (TBAI) gave only a small increase in the peak height of the first wave, indicating that the reaction between the pyrene anion radical and *t*-butyl chloride is a rather slow one. A new peak at -2.6 V may be due to a coupled product or may be a prepeak to the second peak.

Controlled potential reduction in anhydrous DMF/0.1 M TBAI of pyrene in the presence of *t*-butyl chloride at -2.0 V (SCE) gave a mixture of 1-*t*-butylpyrene (*1*), 4-*t*-butyl-4,5-dihydropyrene (*2*), 1,6-di-*t*-butylpyrene (*3*), and 1,8-di-*t*-butylpyrene (*4*), which were subjected to column chromatography.

1 − *4* were identified by ^{1}H NMR, IR,[13] and

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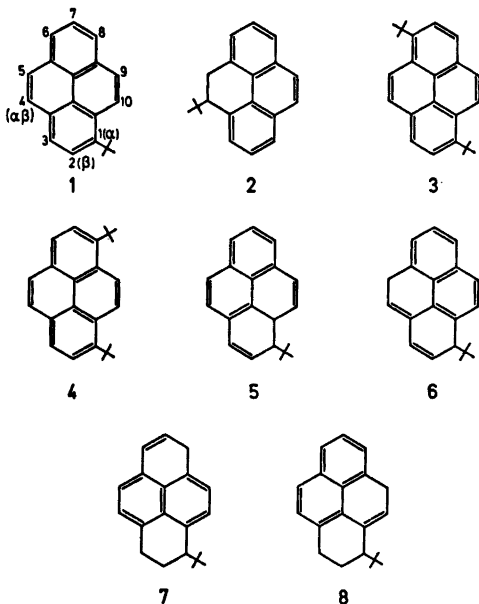
MS spectroscopy, and *2* was, furthermore, oxidized to 4-*t*-butylpyrene by 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ).

On reductive alkylation generally hydro derivatives are obtained; the isolation of *1*, *3*, and *4* points to an oxidative aromatization during work up. Such an oxidation might also be responsible for the observed extensive tar formation that seems to occur on exposure of the reaction mixture to air. Aromatization by chloranil in the reduction cell immediately after reduction leads to good yields of the compounds *(1 – 4)*, and hardly any tar formation is observed.

Work-up under oxygen-free conditions revealed the presence of dihydropyrenes rather than the fully aromatic pyrenes. The dihydropyrenes have tentatively been assigned the structures 1-*t*-butyl-1,10a-dihydropyrene *(5)* and 1-*t*-butyl-1,5-dihydropyrene *(6)* on the basis of ¹H NMR spectra. They are stable under oxygen-free conditions, but are oxidized in contact with air within a few hours. Besides the stable 4,5-dihydropyrene only the unstable 1,9-dihydropyrene, prepared by reduction of pyrene with lithium in liquid ammonia, is known.[14]

The formation of *1* (through *5* and/or *6*) and *2* from pyrene is easily explained from the general reaction scheme given previously.[8]

This scheme is supported by the fact that in the presence of a 4-fold excess of naphthalene no butylated naphthalene derivatives were formed. This observation makes reactions of the *t*-butyl radical with the nonreduced aromatic species less probable.

Addition of small amounts of water (0.2 – 1.0 %) did not change the product composition much although more highly reduced compounds occurred and a decrease in the amount of *2* with increasing amounts of water is observed. When D₂O was added (1 %) instead of water no incorporation of deuterium in the products *1 – 4* occurred. These findings support the assumption that *t*-BuCl is the proton donor.

The mechanism of the formation of the dibutylated pyrenes is less clear. The anion, *t*-BuPy⁻, Py = pyrene, could react with *t*-BuCl in a S_N-manner with subsequent aromatization, but it seems more likely that it is oxidized to *1*, which could then be reductively alkylated following the general scheme. The latter possibility was strongly supported by the fact that *3* and *4* besides a series of *t*-butylated dihydropyrenes were produced by reductive alkylation of *1*. However, no evidence of the mechanism of an aromatization in the catholyte is available.

When LiCl was used as supporting electrolyte the product distribution changed because of the different ion pairing and solvation properties of Li⁺ as compared with Bu₄N⁺. Besides *2* the only major compounds were the *t*-butyl derivative of each of the two tetrahydropyrenes: 1,2,3,8 and 1,2,3,9, respectively, as shown by the ¹H NMR spectra. They are formed in the ratio 2:1. The *t*-butyl group is not in an aromatic or vinylic position. Most probably it occupies position 1 in both compounds as shown in *7* and *8*. On exposure to air, a solution of these compounds turns green to greenish brown. In the oxidized mixture considerable amounts of *1* are formed.

Compounds with similar properties are formed on reduction of pyrene by sodium in liquid ammonia:[15] 1,2,3,8-tetrahydropyrene and 1,2,3,9-tetrahydropyrene are formed in the ratio 2:1. Exposure to air of these compounds leads, however, to a stable 6,7,8-trihydropyrenyl radical.[14]

Reductive alkylation of pyrene in DMF/0.1 M LiCl with 0.5 % D₂O added gave *1 – 4* with 20 – 40 % incorporation of deuterium (MS,

¹H NMR), reflecting the competition between *t*-BuCl and hydrated Li⁺ as proton donors. The occurrence of deuterium in position 9 in *1* points towards 1-*t*-butyl-1,9-dihydropyrene as a likely intermediate in this reaction. In *2* incorporation took place in position *5*.

About the same ratio of α- to α,β-substituted compounds was found whether TBAI (4:1) or LiCl (3:1) served as supporting electrolyte. Thus, coupling takes place preferentially at the position of highest electron density [16] in the pyrene radical anion.

Steric factors have been observed to be important in the reductive alkylation of naphthalene and anthracene.[8] Steric effects, therefore, would be expected to make coupling at the β-positions in pyrene more favourable, but no β-substituted products are observed.

The results reported indicate that electrolytic reductive alkylation is a feasible method for preparation of 1-*t*-butylpyrene. By variation of the procedure with respect to work-up, supporting electrolyte, water content, or potential, further reduced products can be obtained.

EXPERIMENTAL

Electrolytic reductive alkylation. The electrolytic cell described by Iversen[17] was used. *N,N*-Dimethylformamide (DMF) was dried over Molecular Sieves (4A).

The reduction potential was kept near the polarographic half-wave potential of pyrene rather than at the plateau of the wave in order to avoid further reduction of the dihydropyrenes which are reduced at potentials 0.2 − 0.3 V more negative than that of pyrene.

1. *Pyrene. TBAI as electrolyte.* Pyrene (2.02 g, 0.01 mol) was reduced at − 1.5 V (*vs.* Ag/AgI, 0.1 M TBAI) in 170 ml of DMF containing TBAI (0.1 M) and *t*-butyl chloride (20 ml, 0.18 mol); $n = 2 - 2.5$ F/mol. The reduction completed, chloranil (4.92 g, 0.02 mol) was added to the catholyte. The stirred solution was allowed to stand for 2 h and then poured into water and acidified. The mixture was extracted five times with 200 ml portions of toluene. After washing and drying the toluene was evaporated. The dark redbrown oily product was cleared of tarry materials and chloranil hydroquinone on a short column (alumina) and subsequently separated by column chromatography on silica mixed with 10 % caffeine.[18] As eluent served petrol ether (b.p. below 50 °C). The following products were isolated in the order *2, 3, 4, 1* (yields in mol % relative to pyrene):

1-t-Butylpyrene (*1*) (52 %), m.p. 100.0 −

100.5 °C. ¹H NMR (CS₂): δ 1.70 (s, 9 H), 7.4 − 8.1 (m, 5 H), 7.81 (s, 2 H), 7.89 (d, *J* = 9.8, 1 H), 8.57 (d, *J* = 9.8, 1 H). IR (KBr) cm⁻¹ (intensity): 835 (s), 820 (m), 812 (m), 750 (m), 720 (m), 672 (m). MS: 258 (M⁺), 243 (− 15).

4-t-Butyl-4,5-dihydropyrene (*2*, mixed with *3*) (14 %). ¹H NMR (CS₂): δ 0.65 (s, 9 H), 2.87 (1 H), 3.35 (1 H), 3.41 (1 H), 7.10 − 7.75 (m, 6 H), 7.51 (s, 2 H). MS: no molecular ion was observed.

1,6-Di-t-butylpyrene (*3*, mixed with *2*) (2.5 %). ¹H NMR (CS₂): δ 1.71 (s, 18 H), 7.78 (d, *J* = 9.8, 2 H), 7.92 (4 H), 8.57 (d, *J* = 9.8, 2 H). MS: 314 (M⁺), 299 (− 15).

1,8-Di-t-butylpyrene (*4*) (0.8 %) m.p. 186 − 187 °C. ¹H NMR (CS₂): δ 1.77 (s, 18 H), 7.81 (s, 2 H), 7.95 (4 H), 8.58 (s, 2 H). IR (KBr) cm⁻¹ (intensity): 845 (s), 825 (m), 807 (w), 760 (w), 731 (m). MS: 314 (M⁺), 299 (− 15). A reduction was performed with zinc dust in the anode compartment to avoid a possible diffusion of oxidants from the anode compartment to the catholyte, but the yield of dibutylated products did not change.

In order to observe the dihydropyrenes *5* and *6* the catholyte, in a separate experiment, was poured directly into a saturated solution of sodium dithionite. The extraction, washing and evaporation was performed in a nitrogen atmosphere. No separation was attempted.

2. *Pyrene. LiCl as electrolyte.* Pyrene (2.02 g, 0.01 mol) was reduced at − 1.55 V (*vs.* Ag/AgI, 0.1 M TBAI) in 170 ml DMF containing LiCl (0.1 M) and *t*-butyl chloride (20 ml, 0.18 mol); $n = 2.5 - 3$ F/mol. The catholyte was worked up as described above except that no chloranil was added. The reaction mixture was not separated, but investigated as such. Ratios between *2, 7,* and *8* have been estimated from the ¹H NMR integrals of the *t*-butyl groups. No satisfactory integration of the other parts of the spectrum was obtained.

Mixture of *1-t-butyl-1,2,3,8-tetrahydropyrene* (*7*) and *1-t-butyl-1,2,3,9-tetrahydropyrene* (*8*) (75 %). ¹H NMR (CS₂): δ 0.80 (s), 0.82 (s), 1.5 − 2.7 (m), 3.85 (broad s), 5.53 (t, *J* = 4.0), 5.73 (dt, *J*₁ = 9.8, *J*₂ = 4.0), 6.40 (dt, *J*₁ = 9.8, *J*₂ = 2.0), 6.70 − 7.20 (m). Compound *2* (25 %).

3. *1-t-Butylpyrene. TBAI as electrolyte.* *1* (0.525 g, 0.002 mol) was reduced and worked up as for pyrene except for the addition of chloranil after reduction. Separation yielded the following hydrocarbons (yields, in mol %, include also amounts in mixed fractions as estimated from the NMR-spectra): *3* (8 %), *4* (19 %), *1,3,6-tri-t-butylpyrene* (6 %), *1,4-di-t-butyl-4,5-dihydropyrene* (a), *1,5-di-t-butyl-4,5-dihydropyrene* (b), and *1,9-di-t-butyl-9,10-dihydropyrene* (c), a + b + c = 23 %). Traces of the last three compounds were also seen in the products from pyrene.

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