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DISPROPORTIONATION OF ANTHRACENE IN MOLTEN ANTIMONY TRICHLORIDE BY SIMULTANEOUS HYDROGENATION AND SCHOLL CONDENSATION REACTIONS

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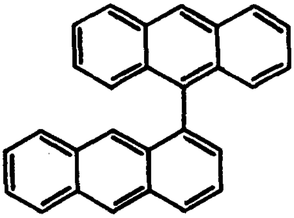
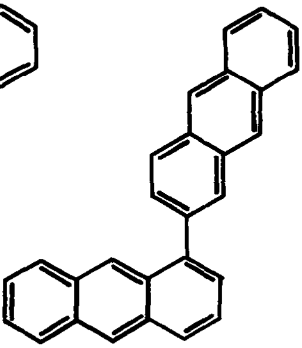
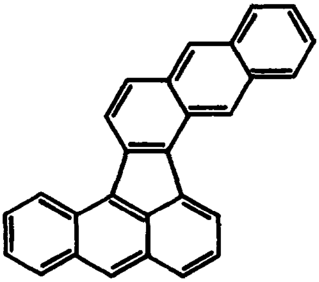
We report that anthracene in solution in molten $SbCl_3$ spontaneously disproportionates at temperatures as low as 100°C. The oxidation steps consist of Scholl reactions[2] in which aryl-bound hydrogen is lost with the formation of 1,9′-bianthracene (I) and anthra[2,1-a]aceanthrylene (II) as major products plus small amounts of 1,2′-bianthracene (III), 2,9′-bianthracene (IV), anthra[1,2-a]aceanthrylene (V) and other oligoanthracenes (but not symmetric bianthracenes). Most, if not all, of the hydrogen released converts other anthracene molecules into



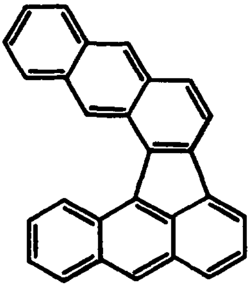
I



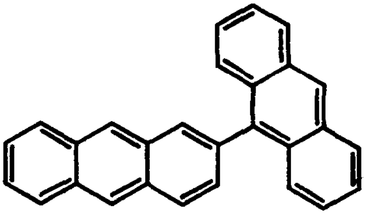
III



II



V



IV

9,10-dihydroanthracene (DHA) and, at a much slower rate, into 1,2,3,4-tetrahydroanthracene (THA). Similar reactions occur for naphthacene but not for naphthalene. The catalytic role of the solvent's Lewis acidity is evident from the fact that the addition of a few mole % of a strong chloride ion donor, KCL or $(CH_3)_4NCl$, reduces the reaction rates by a large factor. These reactions were run on purified compounds, handled in a glove box under purified Ar and sealed in glass ampoules or nmr tubes.

The fact that anthracene serves as an efficient hydrogen acceptor for its own Scholl reactions is a novel aspect of Friedel-Crafts chemistry. Usually, when Scholl reactions occur in the absence of oxidizing agents, it has been supposed (without evidence) that gaseous hydrogen is liberated.[2] Our results demonstrate an alternative. Also noteworthy are the selectivity for asymmetric bianthracenes, which have not previously been prepared, and the fact that so mild a Lewis acid as $SbCl_3$ serves effectively to catalyze Scholl reactions,[3] for which strong acids, like $AlCl_3$, are normally employed. Molten $SbCl_3$ is not difficult to handle and is amenable to study by a variety of electrochemical and spectroscopic tools. For these reasons we are using this aprotic medium to investigate the poorly understood mechanisms of the Scholl reaction.

Reaction products were isolated for identification by dissolving solidified reaction mixtures in 6 N HCl and CH_2Cl_2, extracting the aqueous phase with additional CH_2Cl_2, and separating the organics recovered upon evaporation of CH_2Cl_2 with preparative-scale TLC (silica gel). Additional purification of TLC fractions was done by HPLC (DuPont Zorbax ODS column) and recrystallization. A comparison with literature values[6] of the mass and complex uv spectra of II and V and the melting point of II provided identification of these products. Identification of I as an asymmetric bianthracene rests on a comparison of its mass, uv, and ^1H nmr spectra with those of anthracene, 9,9′-bianthracene and the phenylanthracenes.[7] Its identification as 1,9′-bianthracene is based on the following analysis of its ^1H nmr spectrum: unique 1H singlets at $\delta = 8.58$, 8.54, 8.47 ppm for the 10, 10′, 9 hydrogens; 5H multiplets at $\delta = 8.24$-7.96 ppm for the 4, 5, 8, 4′, 5′ hydrogens; 2H doublet, J = 8 Hz, at $\delta = 7.78$ ppm for the 1′, 8′ hydrogens; 8H multiplet at $\delta = 7.60$-7.24 ppm; relative to $CHCl_3$ at $\delta = 7.25$ ppm. The mass and uv spectra of two minor fractions showed them to be bianthracenes different from I and the symmetric bianthracenes.[6] Hence, they must be III and IV.

For routine analyses, the organics were extracted as described above, separated by HPLC, and characterized by their mass and uv spectra. In general the weight of organics recovered from CH_2Cl_2 was greater than 97% of the initial weight of anthracene. A typical product analysis (90 min at 125°) showed 43% unreacted anthracene, 24% DHA, 13% II, 10% I, 3% THA with the balance (7%) made up of small amounts each of III, IV, V and at least 12 other products with mass spectra indicative of oligoanthracenes formed from 2 to 6 anthracene units.

We were also able to obtain useful information on the course of reactions from the ^1H nmr spectrum of the melt. In a typical run at 125°, the bands in the anthracene spectrum were initially broadened in a selective way by a trace of anthracene radical cations[8] but these radicals decayed rapidly (confirmed by esr at 80°, where the decay rate was slower) and, as they did, the anthracene spectrum sharpened while the bands of DHA appeared and grew. After somewhat more than an hour the bands of THA appeared and grew. Except for the first few minutes of reaction time, the anthracene, DHA and THA spectra were well resolved and closely similar to the corresponding spectra for solutions in $CDCl_3$. However, the spectrum of condensed products consisted only of a broad, featureless band in the aromatic region. In general we found that the rates at which DHA and THA formed varied but little with changes in the initial anthracene concentration from 2 to 10 mole %, whereas the addition of a few mole % KCl or $(CH_3)_4NCl$ reduced these rates by a large factor. In a typical experiment (125°) these rates were reduced by a factor of 20 upon addition of 2 mole % $(CH_3)_4NCl$.

In mechanisms proposed for Scholl reactions, areneonium ions and radical cations serve as intermediates.[2] These mechanisms can be extended to include the hydrogenation steps in disproportionation. Previous research has shown that aromatic radical cations are readily formed in $SbCl_3$ by oxidation with O_2 or $SbCl_5$ and that the oxidizing power of these substances is suppressed by added chloride ion donors.[4,9,10] Likewise, there is indirect evidence for the protonation of perylene by HCl in $SbCl_3$ via a reaction that should be suppressed by added chloride ion donors.[10] Thus adventitious protonic acids and oxidants may play a key role in the reactions we report. However, this is not necessarily the case. There is electrochemical evidence[9] (albeit disputed evidence[4]) that the more oxidizable aromatics can reduce $SbCl_3$ by a reaction that is suppressed by added chloride ion donors, and we have shown (in a study to be reported elsewhere) that anthracene in $SbCl_3$ can be protonated in stoichiometrically significant amounts by reactions in which the ultimate proton source is anthracene, itself.

These results make it quite clear that there exists in liquid $SbCl_3$ a previously unrecognized sequence of oxidation-reduction reactions involving hydrogen transfer between aromatics. The synthetic utility and mechanisms of these reactions continue under investigation.

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3. Most prior research on the behavior of polycyclic aromatics in liquid $SbCl_3$ was done at 74-99°C[4] where we found that anthracene disproportionates quite slowly. Some

research at higher temperatures[5] encountered unspecified reactions. No prior effort to separate and identify reaction products has been reported.

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