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MECHANISM OF DEHYDRODIMERIZATION OF AROMATIC SUBSTRATES BY ALUMINIUM CHLORIDE–CUPRIC CHLORIDE[1]

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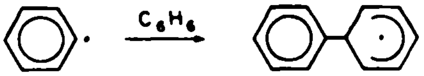
Abstract—The following results were obtained from oxidation of the appropriate aromatic hydrocarbons with $AlCl_3$–$CuCl_2$: 1-(2,4,6-trimethylphenyl)naphthalene from naphthalene-meistylene, 2,2′-bifluorene from fluorene, 2,2′-bifluorene from fluorene-mesitylene, and bimesityl and 3,3′-dichlorobimesityl from mesitylene. Mechanistically, radical cations are presumed to function as intermediates. Generally, coupling seems to proceed by cation attack on an aromatic molecule. Other pathways may pertain in certain cases, e.g. radical dimerization of radical cations.

The mechanism of oxidative coupling of aromatic nuclei to biaryls in catalyst-oxidant systems has not yet been completely elucidated. For the reaction in the presence of a Lewis acid and oxidant, there are three types of initiating species which have been proposed,[4-7] namely, cation, radical cation, or radical. The cationic type of initiation involves formation of a sigma complex which can arise by simple protonation of the aromatic substrate.

Concerning the radical cation pathway, generation of such intermediates has been observed (ESR) in the reaction of aromatics with Co(III) and Tl(III) trifluoroacetates.[8,9] Nyberg,[10] who compared the coupling reactions of naphthalene and polymethylbenzenes (ferric chloride oxidant) to the electrochemical route, proposed that the two processes may take place by a common mechanism.

Radical initiation might arise from deprotonation of an initially generated radical cation, as proposed by Mano and Alves,[5] a transformation which has been noted in the prior literature.[11,12]

Two different modes of propagation have been proposed for these initially formed intermediates: radical or cationic. Propagation by a radical-type mechanism might result either from the radical (2) [eqn (1)] or the radical cation (3) [eqn (2)].



(1)

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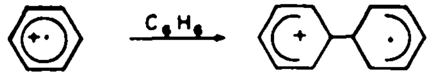
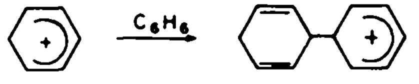


(2)

3 4

Further chain extension with 4 would involve the radical end of the species. The idea of propagation by radical pathways was put forth by Mano and Alves[5] for benzene polymerization by $AlCl_3$–$CuCl_2$. Norman *et al.*[13] proposed involvement of the radical portion of the intermediate radical cation in the oxidative coupling of benzenoid compounds by lead(IV) acetate.

Propagation by a cationic pathway, involving either a sigma complex (5) [eqn (3)] or the radical cation acting as a cation [eqn (2)], has been postulated. The cationic mechanism [eqn (3)] was advanced for the polymerization of aromatics[14] in the presence of Lewis acid catalyst and oxidant. Evidence suggests that such a course is likely being followed in the polymerization of thiophene.[15]



(3)

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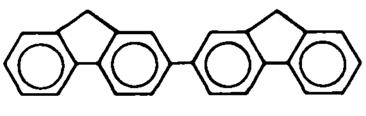
Alternatively, a radical cation mechanism with cation-like propagation [eqn (2)] has been presented[16] and is currently favored.[4] A similar scheme was suggested by Nyberg[10,17] ($FeCl_3$), and apparently by Taylor and McKillop[18] [Tl(III)] for related systems. Recently, pertinent evidence concerning this area has been reported for benzene polymerization by $AlCl_3$–$CuCl_2$.[4] These data, togeter with the relationship between nature of the monomer and degree of propagation,[14,19-21] all suggest that the polymerization is associated with a positively charged propagating species, not a radical type.[22] However, the possibility exists that Norman's system[13] may be an exception to the general rule (*vide infra*). The mode by which radical cations react electrophilically to form coupled products has been discussed in some detail.[4,10,23]

A third type of entity, namely an aryl cation, appears to participate in the case of coupling which involves an aryllead species.[24]

RESULTS AND DISCUSSION

Naphthalene-mesitylene. The coupled product from exposure of the aromatics to $AlCl_3$–$CuCl_2$ consisted of a mixture of five components according to TLC. Separation was not attempted, the yield (10%) being determined by GLC with authentic 5 as the reference standard, which was prepared according to the method of Nyberg.[10] The m.p. was in agreement with the literature value, and the NMR data were consistent with structure 5.

Fluorene-mesitylene. A mixture of fluorene and mesitylene was treated in a similar fashion. In contrast to the result from the naphthalene-mesitylene system, the major product (40% yield) was a homo "dimer," 2,2′-bifluorene (6). Structural assignment was based on IR and mass spectra, in addition to comparison with literature data.[25,26]



6

The mother liquor from recrystallization, when subjected to TLC, was shown to contain an appreciable number of components. The mass spectrum (10 ev) exhibited ion at *m/e* 416, 402, 330, 298 and 284. Although these minor products were not isolated for structural determinations, mass spectral data and comparison with other, similar reactions[27] suggest the presence of mixed dehydrodimers and dehydrotrimers, joined either through the nucleus or side chain.

The coupling reactions were carried out at room temp. in chlorobenzene. Monomer ratios were varied in order to obtain optimum conditions for formation of products from mixed coupling (Table 1).

The yield and appearance of the crude products were quite insensitive to the molar ratio of fluorene to mesitylene. Decreasing the amount of solvent also did not alter the yield. The major product, regardless of conditions, was 6 (~40%) with only minor amounts of mixed "dimers" and "trimers" (~5%). When the amount of mesitylene was increased, the yield of these byproducts increased slightly, but 6 still predominated. It is ing that the pathway leading to 6 still predominated. It is surprising that the pathway leading to 6 was favored even when a large excess of mesitylene (molar ratio of mesitylene/fluorene = 12/1) was used.

Fluorene. Fluorene, on treatment with $AlCl_3$ and $CuCl_2$ in chlorobenzene, afforded 6 identified on the basis of m.p., mixture m.p., IR and mass spectra. The reaction was investigated under several different conditions in order to optimize the yield (Table 2).

A 71% yield of product was obtained when the molar ratio of fluorene/$CuCl_2$/$AlCl_3$ was 1/3/6. Since inexpensive, readily available starting materials, mild conditions, and relatively uncomplicated techniques are involved, this provides a very convenient, one-step synthesis of 6. Previous preparative procedures include coupling of 2-iodofluorene by the Ullmann condensation,[25] or reduction of 2,2'-bifluorenone, prepared from 2-iodofluorenone.[28] The present, or cosely related, method has been investigated earlier[26] (52% yield: fluorene-$AlCl_3$-$CuCl_2$-H_2O and fluorene-$FeCl_3$-H_2O). We judge the $CuCl_2$-$AlCl_3$ technique superior to other preparative methods.

Mesitylene. When mesitylene was coupled in chlorobenzene solvent, the product mixture was quite complicated according to GLC analysis. The major component was 3,3'-dichlorobimesityl (~15% yield based on mesitylene), accompanied by minor amounts of the mono and trichloro analogs, according to the mass, IR and NMR spectra, as well as m.p. The IR spectrum is essentially the same as the one reported for 3,3'-dichlorobimesityl,[21] except for an additional strong band at 1450 cm^{-1}.

However, when neat mesitylene was treated with $AlCl_3$ and $CuCl_2$, the major product was bimesityl (~40% yield based on cupric chloride), identified by m.p., NMR, IR and mass spectra. The liquid byproduct, which displayed four peaks in GLC analysis, is apparently a mixture of bimesityl and chlorinated material. Evidently, the competing pathways are quite sensitive to reaction variables. The reaction was carried out under three different conditions in order to examine the effects of solvent and time (Table 3).

The reaction course was critically influenced by the solvent. It was shown that 3,3'-dichlorobimesityl was the major product, with no dimesityl, in the presence of chlorobenzene. In the neat system, bimesityl was the major product with no trace of 3,3'-dichlorobimesityl.

Table 1. Fluorene-mesitylene reaction[a]

Fluorene (mol)	Mesitylene (mol)	Chlorobenzene (ml)	Crude Product[b] (g)
0.1	0.1	120	9.5
0.1	0.1	60	9.5
0.1	0.2	120	9.4
0.1	0.4	120	8.7
0.1	1.2	--	9.3

[a] $CuCl_2$ (0.1 mol), $AlCl_3$ (0.2 mol), room temp, 2 hr. [b] Mustard colored solid which turned coffee-brown when dried at 110° under vacuum.

Table 2. Fluorene reaction[a]

$CuCl_2$ (mol)	$AlCl_3$ (mol)	Crude Product[b] (g)	2,2-Bifluorene Yield[c] (%)
0.1	0.2	7	25.4
0.2	0.4	14.2	58.4
0.3	0.6	16.5	71.3

[a] Fluorene (0.1 mol), chlorobenzene (120 ml), room temp, 2 hr. [b] Mustard colored solid when dried at 110° under vacuum. [c] Recrystallized material, yield based on monomer.

Table 3. Mesitylene reaction[a]

Mesitylene (mol)	Chlorobenzene (ml)	Crude Product (g)	Bimesityl Yield (%)
0.1	120	3.5	--
0.6	--	9	30
0.6[b]	--	16.2	40

[a] $CuCl_2$ (0.2 mol), $AlCl_3$ (0.4 mol); room temp, 1.5 hr. [b] 3 hr.

When the reaction time was increased in the neat system, the yield of bimesityl was enhanced, but not remarkably. In a previous investigation of mesitylene and ferric chloride, the principal products were bimesityl, and chloromesitylene, accompanied by minor amounts of material believed to be 3,3'-dichlorobimesityl.[21]

Mechanism. Based on previous work, it was assumed that the oxidative coupling reactions in this study were also occurring via a radical cation intermediate. An important consequence of this mechanistic approach is that the oxidation potential of an aromatic substrate should be a major factor governing the reaction course. Miller *et al.* have reported a simple, comprehensive correlation of organic oxidation, effected by various reagents, and ionization potential.[29] The data in Table 4 are concerned with two such processes: gas-phase ionization potentials and the polarographic oxidation potentials. Other measures[30,31] of ease of oxidation comprise the lowest energy absorption maxima and association constants for charge-transfer or donor–acceptor complexes. Table 5 includes relative rate data for electrophilic substitution and basicity constants. The ease of attack by an electrophilic species is determined by the nucleophilicity or basicity of the aromatic substrate (Table 5), as well as the nature of the intermediate σ complex. Table 6 lists relative rates of homolytic phenylation of aromatic compounds.

Table 4. Ionization and polarographic oxidation potentials

Benzenoid Compound	IP[a] (ev)	$E_{1/2}$[b] (v)
Fluorene	7.93[c]	1.25
Naphthalene	8.12	1.34
Biphenyl	8.27	1.48
Mesitylene	8.39	1.53
Benzene	9.24	2.04

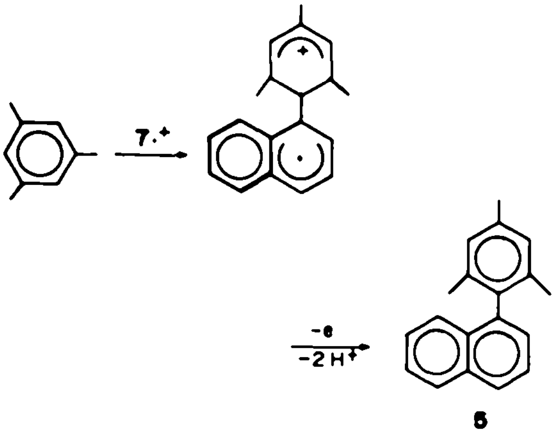
[a] Ref. 32. [b] Ref. 29. [c] Ref. 33.

Naphthalene-mesitylene. Nyberg proposed a mechanistic scheme based on his results with ferric chloride.[10] From the difference in oxidation potentials one can conclude that naphthalene (7) would be more readily oxidized to radical cation $(7^{+\cdot})$ than mesitylene. The relative reactivity and basicity (Table 5) show mesitylene to be about 10^3 more susceptible to electrophilic attack than naphthalene. The unsymmetrical biaryl (5) is then formed by attack of the positive portion of the naphthalene radical cation on mesitylene (Scheme 1).

Table 6. Relative rates of homolytic phenylation of aromatic compounds[a]

Compound	Relative Rate[b]
Biphenyl	4.0
Naphthalene	24
Mesitylene	6.2

[a] Ref. 37, p. 57. [b] Benzene = 1.



Scheme 1.

Since similar results were obtained with aluminum chloride-cupric chloride, it is reasonable to assume that both systems follow the same pathways. Table 6 demonstrates that naphthalene is more prone to bomoly-

Table 5. Relative rates of electrophilic aromatic substitution

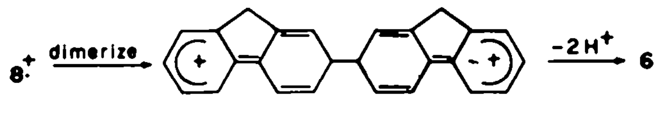
Aromatic Substrate	Relative Rate[a]		pK_B[b]
	Chlorination	Bromination	
Naphthalene	6.6×10^4	1.19×10^5	4.0
Biphenyl	422	1.06×10^3[c]	5.5
Mesitylene	--	1.89×10^8	0.4
Fluorene	1.13×10^5	2.11×10^6[c]	--
Benzene	1.00	1.00	9.2

[a] Ref. 34 and 35. [b] Ref. 31. [c] Ref 36.

tic substitution than mesitylene. Hence if the hypothesis is correct that the radical cation attacks via the radical portion, one would expect appreciable amounts of binaphthyl. Nyberg reported[10] less than 2% yields of the naphthalene homo "dimer" in all cases with this system (29–41% of mixed dimer).

Fluorene–mesitylene. In this system, the situation is more puzzling. The IP and $E_{1/2}$ values (Table 4) and association constants[30,31] indicate that fluorene is more susceptible to one-electron loss. Once the fluorene radical cation is formed, it can conceivably attack either fluorene or mesitylene via an electrophilic reaction. Table 5 shows that the relative rate for electrophilic attack of mesitylene is about 10^2 times greater than fluorene for bromination. These data suggest that one of the principal pathways of the coupling reaction should be formation of unsymmetrical biaryls. However, we found **6** to be the major product, rather than unsymmetrical biaryls or bimesityl, even when twelvefold excess of mesitylene was used.

Because of bifunctionality, radical cations are capable of undergoing a wide variety of reactions. Unfortunately, relatively little is known concerning their chemical behavior in comparison with the better known reactive intermediates. There are at least three reasonable routes for nuclear coupling via cation radicals:[38] (1) combination (ECE reaction) with an aromatic molecule (e.g. Scheme 1), (2) pairing by radical coupling, e.g. Scheme 2, with fluorene radical cation ($\mathbf{8}^{+\cdot}$), and (3) conversion to a dication followed by attack on an aromatic molecule. The ECE pathway seems to be the one usually followed.[38] However, for the formation of **6**, the evidence does not rule out Scheme 2. In the behavior of sulfur-containing aromatic radical cations toward electron donating aromatics, kinetic data suggest initial conversion to a dication.[38] The rather rigid coplanarity of fluorene and favorable delocalization may be important factors. In contrast, the major product from biphenyl and mesitylene is 2,4,6,2″,4″,6″-hexamethyl-*p*-quaterphenyl.[23]



Scheme 2.

Side chain coupling. A competing reaction in the nuclear coupling of alkylbenzenes is side-chain attack to form diarylmethanes. The pathway for this type of transformation has been discussed mainly in relation to electrochemical processes.[39,40] Examples of side chain participation in alkylbenzenes are recorded in the literature.[27] This route increases in importance in those cases in which the aromatic radical cation has a high positive charge density in a substituted ring position,[17] thereby facilitating conversion into benzylcations. In the coupling reaction of biphenyl–mesitylene and fluorene–mesitylene, small amounts of products were formed which were tentatively assigned diarylmethane structures. Their formation could originate from joining of biphenyl with benzyl-type cations derived from mesitylene radical cations. In this radical cation, however, only 37% of the positive charge is located in the substituted positions.[17] As a result these diarylmethane products would be expected to be formed in only very minor amounts, as was observed.

Nuclear chlorination. Another process which may compete with coupling is nuclear substitution. The mechanistic features have been treated.[39,40] In the present case, nuclear chlorination also occurred, particularly in the mesitylene case. This type of reaction has been observed previously with alkylbenzenes and various redox metal halides.[27,41]

EXPERIMENTAL

Fluorene (98%) and naphthalene (99%) were obtained from Aldrich Chemical Co. Other materials and analytical procedures are presented elsewhere.[23]

Procedures for dehydrodimerization

Fluorene–mesitylene. (a) A mixture of fluorene (16.6 g, 0.1 mol), mesitylene (13.6 ml, 0.1 mol), chlorobenzene (120 ml), $AlCl_3$ (13.36 g, 0.2 mol) and $CuCl_2$ (13.46 g, 0.1 mol) was stirred under N_2 at room temp. for 2 hr. The mixture then was poured into 400 ml of ice-cold 6 M HCl and steam distilled. The residue was pulverized with water in a blender, triturated with 6 M HCl until the filtrate became colorless, and finally washed with boiling water until a negative test ($AgNO_3$) for chloride ion was obtained. The light brown crude product (9.5 g) darkened when dried at 110° under reduced pressure.

(b) A mixture of fluorene (16.6 g, 0.1 mol), mesitylene (120 ml, 1.2 mol), $AlCl_3$ (13.36 g, 0.2 mol), and $CuCl_2$ (13.46 g, 0.1 mol) was stirred at room temp. for 2 hr. The mixture was then worked up as in (a), yielding 9.3 g of a fine, light brown powder which turned to a coffee-brown solid when dried at 110° under reduced pressure.

Fluorene. Fluorene (16.6 g, 0.1 mol), dissolved in chlorobenzene (120 ml), was treated with $AlCl_3$ (40.08 g, 0.6 mol) and $CuCl_2$ (40.38 g, 0.3 mol) under N_2 at room temp. for 2 hr. The usual workup afforded a mustard yellow, crude product in essentially quantitative yield, after being dried at 110° under reduced pressure.

Mesitylene. (a) $AlCl_3$ (26.72 g, 0.4 mol) and $CuCl_2$ (26.92 g, 0.2 mol) were allowed to react with mesitylene (12 g, 0.1 mol) dissolved in chlorobenzene (120 ml) at room temp. under N_2. After 1.5 hr the mixture was poured into ice-cold 6 M HCl and extracted with ether. The ether extract was washed successively with 6 M HCl, sat $NaHCO_3$aq and water, and dried over Na_2SO_4. The ether was evaporated and the residue was vacuum distilled to remove chlorobenzene and unreacted mesitylene, yielding 3.5 g of crude product.

(b) Mesitylene (72 g, 0.6 mol) was treated with $AlCl_3$ (26.72 g, 0.4 mol) and $CuCl_2$ (26.92 g, 0.2 mol) as described in (a). Workup in the usual way yielded 9 g of crude product.

(c) The procedure was the same as for (b), except that the reaction time was prolonged to 3 hr. Workup in the usual way yielded 16.2 g of crude product.

Naphthalene–mesitylene. Naphthalene (12.8 g, 0.1 mol) was dissolved in mesitylene (83.6 ml, 0.6 mol). After $AlCl_3$ (26.7 g, 0.4 mol) and $CuCl_2$ (26.9 g, 0.6 mol) were added to the soln, stirring under N_2 at room temp. was continued for 2 hr. The mixture was then poured into 400 ml of ice-cold 6 M HCl. The product was extracted with benzene and the soln washed successively with 6 M HCl, sat. $NaHCO_3$aq and water, and then dried over $CaCl_2$. The filtered soln was concentrated, and unreacted naphthalene and mesitylene were removed by vacuum distillation (140° at 30 mm). The crude product was a brown sticky solid, 19.6 g (80% based on naphthalene).

Purification of products

Fluorene–mesitylene. A portion of the dried crude product

(1.21 g) was subjected to fractional sublimation. Below 140° (0.1–0.05 mm), 0.029 g of light yellow solid was collected which was identified as unreacted fluorene and a trace of bimesityl, from the mass spectrum (*m/e* 166 and 238). Continued sublimation at 140–190° (0.1–0.05 mm) gave 0.35 g of a white shiny solid mixed with some yellow material. This was recrystallized from toluene to give white, fluorecent platelets of 6, 0.24 g, m.p. 304–305° (lit.[25] m.p. 307°); IR (KBr): 1445 (m, d), 1400 (m, d), 945 (w), 855 (w), 815 (m), 760 (s), 721 (s); MS (*m/e*): 330 (10 eV), *m/e* 330 (M^+, 56), 165 (10), 148 (59), 146 (100), 111 (18), 105 (36), 91 (21).

The soluble material (0.11 g) left in the mother liquor after recrystallization from toluene, when subjected to TLC (alumina, 98% Skelly C – 2% toluene), revealed 5 components: R_f 0.30,0.21, 0.15, 0.09 and 0.05; MS (*m/e*) (10 eV): 416, 402, 330, 398, 284.

Continued sublimation at 190–220°C (0.1–0.05 mm) gave additional almost white solid, 0.46 g, which upon recrystallization from toluene or chlorobenzene gave white, fluorescent platelets. The m.p. and spectra (mass and IR) were identical to those of authentic 6.

Fluorene. A portion of dried crude product (0.30 g) was sublimed at 190–220° (0.1–0.05 mm) to give a light yellow solid, 0.23 g, which was recrystallized from chlorobenzene (93% recovery) yielding white, fluorescent platelets of 6 (0.214 G, 71% yield based on monomer). The m.p. and spectra (IR and mass) were identical to those of authentic 6.

Mesitylene. (a) The crude product was vacuum distilled up to 60° (25 mm) to remove ether, chlorobenzene, and unreacted mesitylene. Upon cooling, a portion of the pot residue solidified. A brownish solid (1.8 g) was collected by filtration, which on recrystallization from n-propyl alcohol, yielded a white solid (1.6 g), m.p. 137–9° (lit.[21] m.p. 130.5–131.5°); NMR: δ 1.77 (s, 6), 1.92 (s, 6), 2.36 (s, 6), 6.97 (s, 2), MS (*m/e*): 342 (20), 341 (6.7), 340 (20), 310 (15), 309 (17), 308 (67), 307 (23), 306 (100), 271 (10) (10 ev); IR (KBr): 2950 (s), 1450 (s), 1380 (s), 1220 (w), 1190 (w), 1060 (s), 1045 (s), 1000 (m), 960 (m), 870 (m), 720 (w), 705 (w), 660 (s). A green flame was observed in the Beilstein test.

The liquid portion of the pot residue (1.7 g) showed five components on GLC analysis (oven temp. 210°, flow rate 80 ml/min); T_R (min) 1.0, 1.4, 4.7, 8.4, 14.0. No bimesityl was detected in any of the fractions.

(b) The unreacted mesitylene was removed by vacuum distillation at 60° (25 mm). The pot residue partially solidified on cooling. A nearly white solid (7 g) was collected by filtration. Recrystallization from MeOH gave bimesityl (6.5 g, 30%), m.p. 98.5–99.5° (lit.[21] m.p. 100–100.5°); NMR: δ 1.80 (s, 12, *ortho*–Me), 2.25 (s, 6, *para*-Me), and 6.85 (s, 4, $(CH_3)_3C_6H_2$–); IR (CCl_4): 1630 (m), 1450 (s), 1010 (m), 880 (s); MS (*m/e*): 238 (10 ev), 239 (24), 238 (99), 224 (24), 223 (100), 208 (43), 193 (39), 178 (18), 163 (12), 154 (55), 153 (27), 119 (60), 117 (64).

The brown liquid filtrate from the pot residue (2 g) on GLC analysis revealed four peaks (oven temp. 210°, flow rate 80 ml/min): T_R (min) 1.0, 1.4, 2.6 (bimesityl), 4.7.

(c) The pot residue solidified on cooling after vacuum distillation of the unreacted mesitylene. The brown crystalline needles were collected and recrystallized from MeOH to give bimesityl (9.2 g, 40%), m.p. 98.5–99.5°.

Naphthalene–mesitylene. The crude product when subjected to TLC (alumina, n-pentane) showed four spots with R_f 0.50, 0.44, 0.37, 0.20 and a brown spot at the origin. The crude product was dissolved in n-pentane and analyzed by GLC (oven temp. 210°, flow rate 200 ml/min). The yield was calculated by means of authentic 6 as the reference. The overall yield was about 10% (based on naphthalene).

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