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ARYNE FORMATION VIA A HINDERED ARYL CARBONIUM ION

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We wish to report evidence for the partitioning of an arylcarbonium ion **8** between S_N1 (solvent capture) and E1 (elimination to aryne) pathways. Our experimental difficulties in isolating 2,5-di-*t*-butylbenzenediazonium salts (**1**), and a recent report[1] of possible aryne formation through decomposition of *o*-*t*-butyl-N-nitrosoacetanilide, prompted an effort to detect di-*t*-butylbenzyne (**2**). When 2,5-di-*t*-butyl aniline[2] with one equivalent of carboxylic acid in methylene chloride was added to a refluxing solution of furan and butyl nitrite in methylene chloride, instantaneous gas evolution was observed. The reaction product was chromatographed on silica gel and afforded 2,5-di-*t*-butylchlorobenzene (**3**) (hexane elution), 2,5-di-*t*-butylphenyl ester (**4**) (hexane-benzene elution), and 5,8-di-*t*-butyl-1,4-dihydronaphthalene-1,4-endoxide (**5**) (benzene elution) in yields recorded in Table I.

TABLE I

Product Yields (%) From Decomposition of Diazonium Salt

	Products		
Acid catalyst	**3**	**4**	**5**
Acetic acid	36	29	22
Mesitoic acid	35	32	25
Pivalic acid	32	19	41

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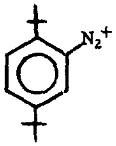
The chloro compound 3, m.p. 27.5-28.5° (lit.[3] 32°) (Anal. Found: C, 75.0%; H, 9.3%; Cl, 15.8%) was unexceptional. The acetate 4, m.p. 51-52° (Anal. Found: C, 77.4%; H, 9.6%) was identified by infrared (C=O, 5.68 μ), nmr Table II) and by synthesis from 2,5-di-t-butylphenol (with acetic anhydride). The mesitoic and pivalic esters, although homogeneous by vpc, could not be crystallized. Their attempted synthesis from the phenol was not successful. Their structures were derived from spectral data and by saponification to the starting phenol and the acids. The structure of the Diels-Alder adduct 5, m.p. 115-116° (Anal. Found: C, 84.4%; Hm 9.5%) was implicit from the simple nmr spectrum suggestive of a symmetrical molecule (Table II). An infrared band, 13.95 μ could be the C-H out-of-plane deformation of cis double bonds. The structural assignment was confirmed by its catalytic hydrogenation (97% yield) to dihydro compound 6,



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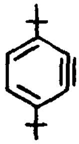

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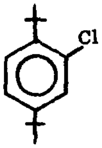

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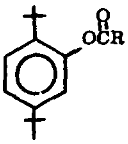

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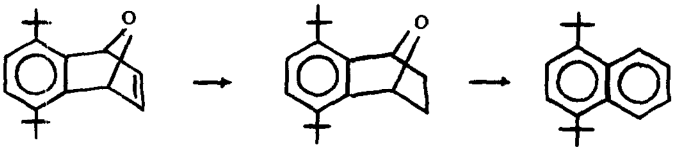

5 6 7

m.p. 134.5-135.5° (Anal. Found: C, 83.8%; H, 10.0%). The simple nmr spectrum suggestive of symmetry (Table II) is consistent with this assignment.

TABLE II

NMR Spectra of Compounds Isolated[a]

Protons	**3**[b]	**4**[c]	**5**[d]	**6**[e]	**7**[f]
t-butyl	1.28 s 1.46 s	1.32 s 1.36 s	1.30 s	1.37 s	1.61 s
aromatic	7.10 m	6.91 H_6d 7.05 H_4dd 7.26 H_3d	6.77 s	7.02 s	7.37 $H_{2,3}$ s 7.39 $H_{6,7}$ dd 8.50 $H_{5,8}$dd
other	-	2.25 s	5.95 m 6.87 m	1.37 m 2.00 m 5.66 dd	

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[a] Shifts reported for CCl_4 with TMS = 0.00 ppm, s=singlet, d=doublet, dd=doubled doublet, m=multiplet.

[b] aromatic protons unresolved.

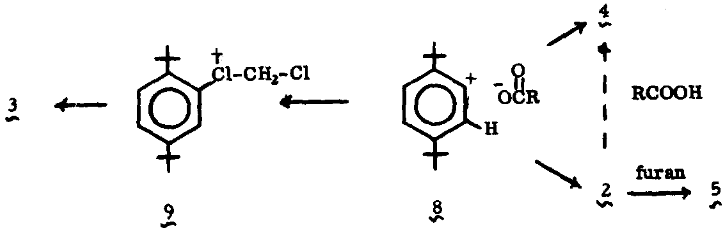
[c] J_{46}2.0 cps, J_{34}8.0 cps, J_{36} not resolved.

[d] The multiplets although unresolved were identical in appearance.

[e] Benzylic protons at 5.66 with different endo-exo coupling, either J 3 and 1.7 cps or J 2.8 and 2.0 cps. Either the *exo* or *endo* methylene protons are a broad base under the sharp *t*-butyl signal.

[f] Naphthalene protons are identical doubled doublets, J *ortho* 6.8 cps, J *meta* cps.

Ethanol-hydrogen chloride catalyzed dehydration of dihydro compound **6** afforded 1,4-di-*t*-butylnaphthalene (**7**)[4] (94% yield), m.p. 61-62° (*Anal.* Found: C, 89.8%; H, 10.2%). This product had a typical 1,4-dialkylnaphthalene uv spectrum[5] $[\lambda_{max}^{isooctane}$ 221 mμ, log ε 4.90; 286 mμ, log ε 3.96 (center of complex Band II), 316 mu, log ε 2.72] and a simple nmr suggestive of symmetry (Table II) which has the interesting feature of compression deshielding[6] of the peri protons. A trapping experiment was performed with DOAc and amine-ND_2 to determine if ester 4 arose via attack on a symmetrical intermediate. A mass spectrum of the isolated acetate revealed a 1% enrichment of the P + 1 fragments at M-15 and M-42 and a 2% enrichment of the P + 1 of the parent ion (as compared in successive determinations to that of an authentic sample). When strong acids were used to catalyze diazonium salt formation, trace amounts of Diels-Alder adduct 5 were detected. This result suggests that a basic counterion is necessary for aryne formation. These observations can be simply accounted for by postulating the arylcarbonium ion 8 as a critical intermediate. Attack on solvent would generate the intermediate chloronium 9 which would be unstable relative to chloro compound 3.[7] Direct attack of carbon by counterion would form ester 4, whereas less hindered abstraction of the ortho proton would generate the aryne 2 which could be trapped by the furan (and, to a small extent, by the carboxylic acid).



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