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REACTION OF BENZYNES WITH 9-t-BUTYLTHIOANTHRACENE TO AFFORD 9-t-BUTYLTHIOTRIPTYCENES

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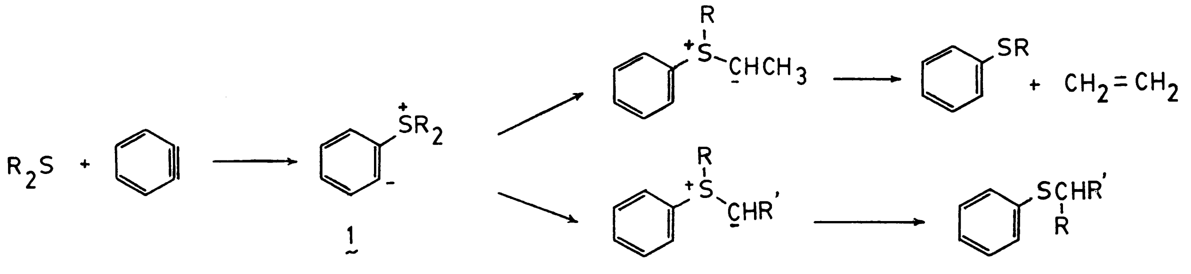
Reaction of benzynes (3a, c, d) with 9-t-butylthioanthracene (2d) resulted in formation of the corresponding 9-t-butylthiotriptycenes (5a, c, d) and 5-t-butylthio-6,11-dihydro-6,11-ethenonaphthacenes (6a, c, d), while that of 1,4-dimethoxybenzyne (3b) with 2d did not give the corresponding adducts (5b, 6b).

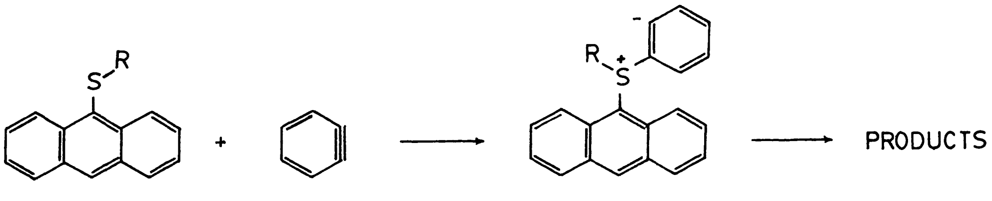
Organic sulfides are well known to react with benzyne to provide initially the corresponding sulfonium betaines 1, which then collapse, by elimination or rearrangement reactions depending on the substituents of the sulfides, to final products.1,2)



Scheme 1.

These results are explained in terms of electrophilic nature of benzyne. Synthetic applications of such reactions have been reported.3) On the other hand, benzyne exhibits dienophilic character also to perform Diels-Alder reaction, one of typical examples of which is formation of triptycene from benzyne and anthracene.4) In the course of the studies on rotational isomerism, the present author has encountered a chance to let benzyne (3a) react with 9-alkylthioanthracenes (2a-d), and has found an interesting example that the benzynes (3a, c, d) do not attack the sulfur atom of 9-t-butylthioanthracene (2d) but do the anthracene nucleus of 2d. In this communication, the author wishes to report the preliminary results on the above observations.

9-Alkylthioanthracenes (2a-d)5) were reacted, at first, with an excess of benzyne (3a) generated in situ under aprotic conditions at a reflux temperature of the reaction mixture. Inspection of the reaction products by nmr and TLC indicated almost complete consumption of the starting sulfides 2a-c and the absence of the triptycene derivatives. One of the reaction products from 2b and 3a was confirmed as 9-phenylthioanthracene.5) These facts may probably be accounted for by the "normal" reaction pathway via the anthrylsulfonium betaine 4 formed by electrophilic attack of benzyne to the sulfur atom (Scheme 2).



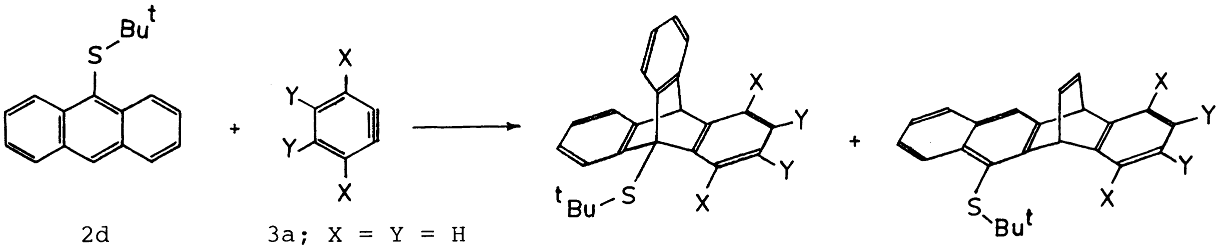
2a; R = Me
b; R = Et
c; R = CH_2Ph

3a

4

Scheme 2.

In contrast to these observations, the sulfur atom of 9-t-butylthioanthracene[5] proved to be intact under the reaction conditions, and benzyne behaved as a dienophile to afford 9-t-butylthiotriptycene (5a)[6] (9,10-adduct) and 5-t-butylthio-6,11-dihydro-6,11-ethenonaphthacene (6a)[7] (1,4-adduct) along with considerable amount of the starting sulfide 2d (Scheme 3).



2d

3a; X = Y = H
b; X = OMe, Y = H
c; X = H, Y = Me
d; X = Y = Cl

5a-d
a; X = Y = H
(b; X = OMe, Y = H)

6a-d
c; X = H, Y = Me
d; X = Y = Cl

Scheme 3.

Typical procedure is as follows: To a refluxing solution of 9-t-butylthioanthracene (10 mmol) in 1,2-dimethoxyethane (DME, 30ml) were simultaneously added a solution of isopentyl nitrite (30 mmol) in DME (5 ml) and that of anthranilic acid (20 mmol) in DME (40 ml) over a period of 2 h . After further 15-min stirring under a reflux, the solvent was removed under a reduced pressure and the residue was chromatographed on silica gel (500 g) with a 5:1 mixture of hexane and dichloromethane, yielding 9-t-butylythioanthracene (1.34 g, 51 %, R_f 0.68), 9-t-butylthiotriptycene (1.23 g, 36 %, R_f 0.23), and 5-t-butylthio-6,11-dihydro-6,11-ethenonaphthacene (0.44 g, 13 %, R_f 0.38).

Table 1. Reaction of Benzynes with 9-t-Butylthioanthracene[a]

	Benzyne (3)		9,10-Adduct (5)	1,4-Adduct (6)	Recovered 2d
	X	Y	Yield (mol%)	Yield (mol%)	Yield (mol%)
a	H	H	36	13	51
b	OMe	H	0	0	100
c	H	Me	24	14	62
d	Cl	Cl	21 (23)[b]	26 (25)[b]	53 (52)[b]

a) Benzynes were generated in situ from the corresponding anthranilic acid and isopentyl nitrite in DME at a reflux temperature of the reaction mixture (heating-bath temperature was controlled at 100 °C).

b) Values in parenthesese were obtained using hexachlorobenzene and butyllithium in ethereal solvent according to the reported procedure.8)

Similarly, the reaction of the substituted benzynes (3b-d) with the sulfide 2d was also examined: The reaction of 2,3-dimethylbenzyne (3c) and tetrachlorobenzyne (3d) with 2d again afforded both the corresponding 9,10- and 1,4-adducts, but that of 1,4-dimethoxybenzyne (3b) with 2d resulted in complete recovery of the starting sulfide 2d.9,10) The results are summarized in Table 1 and the characteristic nmr signals of the triptycenes (5a, c, d) are shown in Table 2.

Table 2. Characteristic NMR Signals of the Triptycenes (5a, c, d)a,b)

	^{1}H NMR				^{13}C NMR			
	t-Bu	10-H	peri-H'sc)		t-Bu		9-C	10-C
5a	1.73	5.29	7.83	7.33	34.25	47.07	65.61	54.13
5cd	1.74	5.22	7.80	7.30	34.29	47.03	65.29	53.68
			7.53	7.12				
5d	1.47	5.98	8.28	7.47	33.76	49.10	68.90	52.14

a) Chemical Abstructs numbering for triptycene (9,10-dihydro-9,10-o-benzenoanthracene) is adopted in this paper.11)

b) Spectra were recorded with $CDCl_3$ solutions. Chemical shifts are expressed in δ unit (ppm from internal TMS).

c) peri-Protons on the same side of the substituent in the 9-position resonate at lower field than those on the other side.

d) Aromatic methyl signals appear at δ 2.13 and 2.16 in ^{1}H NMR, and at δ 19.23 and 19.64 in ^{13}C NMR.

As product ratios of 5 to 6 show, a reactive benzyne such as 3d adds non-selectively to anthracene nucleus, while ordinary benzyne adds more selectively to the 9,10- position than to the 1,4-position of the anthracene ring. The ratio (5/6) seems to be almost independent of the methods by which benzyne is generated, as the ratio (5d/6d) obtained from 3,4,5,6-tetrachloroanthranilic acid and isopentyl nitrite and that from hexachlorobenzene and butyllithium are nearly the same value.12) Similar results has been reported in Diels-Alder addition of benzyne to 9,10-diphenylanthracene, the product ratio of the 9,10-adduct relative to the 1,4-adduct being 0.1:1 and independent of the benzyne precursors.13)

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1) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York (1967), Chap. 2, p. 164.
2) V. Franzen, H. I. Joschek, and C. Mertz, Liebigs Ann. Chem., 654, 82 (1962); H. Hellmann and D. Eberle, ibid., 662, 188 (1963).
3) J. Nakayama, T. Fujita, and M. Hoshino, Chem. Lett., 1982, 1777; 1983, 249.
4) M. Stiles and R. G. Miller, J. Am. Chem. Soc., 82, 3802 (1960); L. Friedman and F. M. Logullo, ibid., 85, 1549 (1963).

5) These 9-anthryl sulfides were prepared by sulfenylation reaction of 9,10-dihydroanthracene with an appropriate disulfide and by subsequent dehydrogenation reaction with DDQ. The preparative procedures will be published elsewhere.

6) **5a**: mp 207-208 °C; ^{13}C NMR (CDCl$_3$, δ) 34.25, 47.07, 54.13, 65.61, 122.99, 125.27, 145.23, 146.13.

7) When X and/or Y are not hydrogen, the numbering of the 1,4-adduct (**6**) should be 1,4-X$_2$-2,3-Y$_2$-6-t-butylthio-5,12-dihydro-5,12-ethenonaphthacene. **6a**: oil; ^{1}H NMR (CDCl$_3$, δ) 1.33 (9H, s, t-Bu), 5.20 (1H, m, 11-H), 6.25 (1H, m, 6-H), 6.85-7.10 (4H, m), 7.25-7.45 (3H, m), 7.63 (1H, s, 12-H), 7.55-7.70 (1H, m), 7.73-7.90 (1H, m), 8.67 (1H, m, 4-H).

8) H. Heaney and B. A. Maples, J. Chem. Educ., 45, 801 (1968).

9) As numbering of benzyne is not consistent in the text,$^{1)}$ Chemical Abstructs nubering (1,3-cyclohexadiene-5-yne) is adopted for the substituted benzynes in this paper.

10) In control experiments, 1,4-dimethoxybenzyne generated under the same conditions added smoothly to unsubstituted anthracene, 9-alkylanthracenes and 9-silyl-substituted anthracenes.

11) A. Guenzi, C. A. Johnson, F. Cozzi, and K. Mislow, J. Am. Chem. Soc., 105, 1438 (1983); Y. Kawada and H. Iwamura, ibid., 105, 1449 (1983).

12) Slight difference in the product ratios, if any, is ascribed to the solvent system and accordingly to the acutual reaction temperature employed for generation and addition of the benzynes. At higher reaction temperatures, slight increase in the yield of **6** and slight decrease in the yield of **5** are often observed exprimentally.

13) B. H. Klanderman, J. Am. Chem. Soc., 87, 4649 (1965).

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