in 62 ml of 80% aqueous ethanol, 0.2 *N* in sodium hydroxide, was refluxed with stirring for 1.5 hr. The volume was reduced *in vacuo* and the residue was dissolved in ether and water. The ether solution was washed with water until neutral, washed with saturated sodium chloride solution, dried (K_2CO_3), and stripped in nitrogen stream, and the residue was dried *in vacuo*, giving 1.71 g (99.5%) of **6**. Material that had been recrystallized several times from ethyl acetate, 0.1% in triethylamine, melted at 148–150°; ir (CCl_4) 2.70, 3.26 (shoulder), and 3.33 μ; nmr ($CDCl_3$) δ (rel area) 4.36 (d, J = *ca.* 8.5 Hz, 0.73), 0.20–2.6 (19.27); mass spectrum m/e (rel intensity) 204 (100), 202 (89), 186 (296).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.46; H, 9.83.

1,2,3,4,4aβ,5,6,8,10,10aβ-Decahydro-7α,8aα-cyclo-2β-acetoxyanthracene (16).—The alcohol **6** (1.71 g) was dissolved in 34 ml of acetic acid, 2% in sodium acetate, with brief heating on a steam bath. After 3 hr at room temperature, the solution was poured into 150 ml of water and extracted with ether. The ether solution was washed with water, 5% sodium bicarbonate solution, water, and saturated sodium chloride solution, dried ($MgSO_4$), stripped to a small volume in a nitrogen stream, seeded, and taken to dryness in nitrogen. The residue was dried briefly *in vacuo*, giving 2.05 g (99.5%) of **16**. Material that had been recrystallized several times from methanol melted at 65.0–66.5°; ir (KBr) 3.24, 5.77, 6.05 (very weak), 8.00 μ; nmr (CCl_4) δ (rel area) 5.08 (0.94), *ca.* 4.5 (0.89), 1.97 (sharp s), *ca.* 0.5 (complex m, 2.05).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.06; H, 8.97.

1,2,3,4,4aβ,5,6,8,10,10aβ-Decahydro-7α,8aα-cycloanthran-2β-ol (1).—A solution of 2.05 g of **16** in 50 ml of 10% methanolic potassium hydroxide was stirred for 1.5 hr at room temperature. The volume of the solution was reduced *in vacuo* and the viscous liquid was poured into water and extracted with ether. The ether solution was washed with water until neutral and then with saturated sodium chloride solution, dried ($MgSO_4$), and stripped in nitrogen stream, and the residue was dried briefly *in vacuo*, tiving 1.69 g. The product was recrystallized from ethyl acetate to give 1.66 g (97.3%) of **1**, mp 117–119°. Analytical material was obtained by several recrystallizations from ethyl acetate and melted at 117–119°; ir (KBr) 3.02 μ; nmr (CCl_4) δ (rel area) 4.98 (0.95), *ca.* 3.4 (1.23), and 0.25–0.80 (complex m, 2.36); uv (cyclohexane) λ_{max} 218 mμ (ϵ 12,300).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.18; H, 9.88.

Registry No.—**1**, 20843-76-9; **3**, 20843-77-0; **5**, 20843-78-1; **6**, 20843-79-2; **7**, 20843-80-5; **7** (methanesulfonate), 20843-81-6; **8**, 20843-82-7; **9**, 20843-83-8; **10**, 20843-84-9; **11**, 20843-85-0; **12**, 20843-86-1; **13**, 20843-87-2; **16**, 20843-88-3; 1,4,4aβ,5,8,8aα,9,9-aα,10,10aβ-decahydroanthran-9-ol, 20843-89-4.

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Arynes *via* Aprotic Diazotization of Anthranilic Acids[1]

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Aprotic diazotization of anthranilic acids generates the corresponding benzenediazonium-2-carboxylates which decompose *in situ* to give arynes, carbon dioxide, and nitrogen. Moderate to excellent yields of aryne-derived products are obtained when the reaction is conducted in the presence of suitable acceptors.

Arynes have been generated under a variety of conditions by fragmentation of suitable *ortho*-disubstituted benzenes.[3] Most of the methods suffer from either limited availability of benzyne precursor, involved experimental techniques, and/or low yields of benzyne-derived products. One of the more attractive benzyne precursors is benzenediazonium-2-carboxylate,[3f] in that benzyne formation can be effected in neutral aprotic media at moderate temperatures. However, this compound is extremely shock sensitive and hazardous to use. As a result, benzyne has not been utilized to the full extent that it could be.

In 1962, it was reported[4] that arylamines could be diazotized by amyl nitrite in excess benzene to give diazonium species which decompose *in situ* to give biaryls. If anthranilic acids[5] could be diazotized in a similar manner, the products would be benzenediazonium-2-carboxylates, which could, in principle, decompose as formed to arynes, nitrogen, and carbon dioxide.

Results and Discussion

It was found that anthranilic acids are readily diazotized by alkyl nitrites in aprotic media to give benzenediazonium-2-carboxylates, which undergo fragmentation to benzyne, nitrogen, and carbon dioxide. The intermediacy of benzyne[6] was demonstrated by trapping with anthracene (to give triptycene), furan (to give 1,4-dihydro-1,4-epoxynaphthalene), tetracyclone (to give 1,2,3,4-tetraphenylnaphthalene), iodine (to give diiodobenzene), and cyclopentadiene (to give benzonorbornadiene). This technique avoids the isolation and handling of the hazardous benzenediazonium-2-carboxylates and is a convenient preparative source of arynes.

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[1] Part of this work was reported in a preliminary communication, L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963).

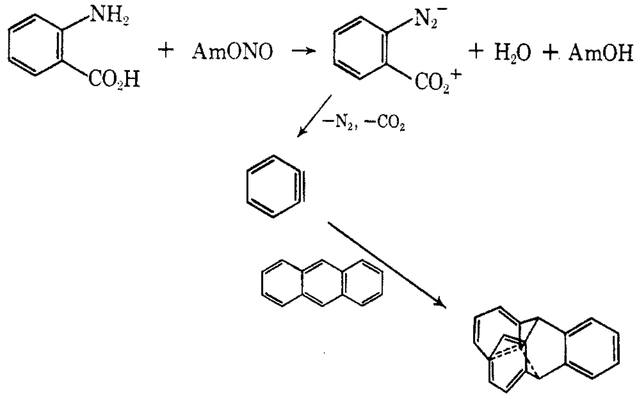
[2] (a) Abstracted in part from the Ph.D. Thesis of F. M. Logullo, Case Institute of Technology, June 1965.

[3] (a) E. LeGoff, *J. Amer. Chem. Soc.*, **84**, 3786 (1962); (b) L. Horner and H. Bruggerman, *Ann.*, **635**, 22 (1960); (c) J. A. Kampmeier and E. Hoffmeister, *J. Amer. Chem. Soc.*, **84**, 3787 (1962); (d) M. Stiles and R. G. Miller, *ibid.*, **82**, 3802 (1960); (e) R. S. Berry, G. N. Spokes, and M. Stiles, *ibid.*, **82**, 5240 (1960); **84**, 3750 (1962); (f) M. Stiles, U. Burckhardt, and A. Haag, *J. Org. Chem.*, **27**, 4715 (1962); (g) G. Wittig and H. F. Ebel, *Angew. Chem.*, **72**, 564 (1960); *Ann.*, **650**, 20 (1961); (h) G. Wittig and R. W. Hoffmann, *Angew. Chem.*, **73**, 435 (1961); (i) E. McNelis, *J. Org. Chem.*, **28**, 3188 (1963), and references contained therein; (j) F. M. Beringer and S. J. Huang, *ibid.*, **29**, 445 (1964); (k) L. Verbit, J. S. Levy, H. Rabitz, and W. Kwalwasser, *Tetrahedron Lett.*, 1053 (1966); (l) C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 296 (1964); *Chem .Commun.*, 192 (1965); (m) E. K. Fields and S. Meyerson, *ibid.*, 474 (1965); 275 (1966); (n) M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Lett.*, 2947 (1966); (o) R. F. C. Brown and R. K. Solly, *Chem. Ind.* (London), **181**, 1462 (1965); *Australian J. Chem.*, **19**, 1045 (1966).

[4] J. I. G. Cadogan, *J. Chem. Soc.*, 4257 (1962).

[5] A related example is diazotization of an alcoholic solution of sulfanilic acid with nitrous fumes to give the "internal" diazonium salt, benzenediazonium-4-sulfonate. R. Schmitt, *Ann.*, **112**, 118 (1859); **120**, 144 (1861).

[6] For an excellent recent review of benzyne chemistry, see G. Wittig, *Angew. Chem. Intern. Ed. Engl.*, **4**, 731 (1965); *Angew. Chem.*, **77**, 752 (1965).



Reaction can be effected by addition of a solution of the anthranilic acid to a stirred, *refluxing solution*[7] of alkyl nitrite and benzyne acceptor. Gas evolution occurs immediately and ceases within a few minutes after addition is complete. If all of the reactants are mixed at once, a vigorous reaction ensues and the yields of desired products are greatly diminished, *e.g.*, triptycene 9–16% (glpc). This is probably in part a result of reactions of benzyne and benzenediazonium-2-carboxylate with each other[8a] and with unreacted anthranilic acid to give acridone,[8b] N-phenylanthranilic acid, and other products.[8a] If reaction is attempted at room temperature or below, the diazotization step slowly occurs to give a precipitate of benzenediazonium-2-carboxylate[7,9] which decomposes only very slowly. To avoid buildup and inadvertent isolation of this hazardous intermediate, reactions should be conducted at temperatures > *ca.* 40°. When higher boiling solvents are used (acetonitrile, 2-butanone, dioxane), it is *sometimes* advantageous to add the alkyl nitrite concurrently with the solution of anthranilic acid to minimize the thermally induced decomposition of alkyl nitrite.

In the synthesis of triptycene, it was found that unreacted anthracene is conveniently removed from the reaction mixture by formation of its Diels–Alder adduct with maleic anhydride[10] in diethyl carbitol (diethylene glycol diethyl ether) or diglyme (diethylene glycol dimethyl ether) followed by treatment with aqueous methanolic potassium hydroxide to precipitate, almost quantitatively, triptycene free of anthracene.

The results from the aprotic diazotization of anthranilic acid and substituted derivatives in the presence of anthracene to form triptycenes are listed in Table I. Since the yield of triptycene obtained is a measure of available benzyne, the reaction conditions were evaluated by relating the yields of triptycene. Best yields of triptycene were obtained by the rapid (*ca.* 0.5 hr) addition of a diglyme[11] or diethylcarbitol solution of anthranilic acid to a stirred refluxing mixture of anthracene and isoamyl or *n*-butyl nitrite in ethylene chloride.[12] The water-soluble high-boiling ethers were used because of their utility in the work-up procedure. Ethylene chloride was found to be the reaction medium of choice, since (a) its higher boiling point[12] decreases the reaction time necessary for diazotization to occur; (b) it facilitates the clean decomposition of benzenediazonium-2-carboxylate;[2] and (c) it is an exceedingly good solvent for anthracene and triptycene. The use of a molar excess of anthracene gave a 17% increase in yield (70 *vs.* 60%), and the use of a molar excess of anthranilic

Table I

Aprotic Diazotization of Substituted Anthranilic Acids in the Presence of Anthracene[a]

Run	Anthranilic acid	Solvent system[b]	Yield of substituted triptycene, %
1	. . .	$D2M^{c}/ClC_2H_4Cl$	60, 70,^{d} 80^{e}
2	. . .	$D2M^{c}/CH_2Cl_2$	60
3	. . .	$D2M/CHCl_3$	55
4	. . .	CH_3CN^{f}	52
5	. . .	Me_2CO	37,^{g} 33^{h}
6	. . .	$MeCOEt^{f}$	53^{i}
7	5-methyl-	$D2M/CHCl_3$	49^{d,j}
8	5-methyl-	CH_3CN^{f}	49^{d}
9	3-methyl-	$D2M/CHCl_3$	58^{d,j}
10	4:5-benzo-	$D2M–THF^{c}/CH_2Cl_2$	10
11	4:5-benzo-	$D2M/THF/CHCl_3$	47^{d}
12	5-chloro-	DEC/ClC_2H_4Cl	39^{j}
13	5-chloro-	$D2M/CH_3CN$	42, 53^{d}
14	5-chloro-	CH_3CN^{f}	20^{i}
15	5-chloro-	$D2M/CHCl_3$	39, 46^{d}
16	3-chloro-	$D2M/CHCl_3$	11^{d}
17	3-chloro-	Dioxane	18^{d}
18	4-chloro-	$D2M/CH_2Cl_2$	19^{j}
19	4-chloro-	$D2M/CHCl_3$	33
20	4-chloro-	$D2M/ClC_2H_4Cl$	55
21	5-bromo-	$D2M/CHCl_3$	54^{d,j}
22	5-bromo-	CH_3CN^{f}	75^{d,j}
23	5-iodo-	$D2M/CHCl_3$	64^{d}
24	5-iodo-	$MeCOEt^{f}$	38^{d}
25	3-nitro-^{k}	$D2M/CH_3CN$	0
26	4-nitro-^{k}	$D2M/CH_3CN$	46
27	5-nitro-^{k}	$D2M/CH_3CN$	44
28	5-nitro-^{k}	$D2M/CH_2Cl_2$	24
29	5-nitro-^{k}	$D2M/ClC_2H_4Cl$	58
30	6-nitro-^{k}	$D2M/ClC_2H_4Cl$	38

[a] In general, reaction was effected by the addition of a solution of the anthranilic acid to a stirred, refluxing mixture of anthracene (1 equiv), isoamyl or *n*-butyl nitrite (excess), and solvent; in lower boiling reaction solvents, *e.g.*, CH_2Cl_2, maximum yields were obtained only when anthranilic acid solution was added slowly (*ca.* 3–4 hr). [b] First solvent refers to that used to form the anthranilic acid solution; the second, the reaction medium. [c] D2M = diglyme; DEC = diethyl carbitol; THF = tetrahydrofuran. [d] 2 equiv of anthracene used. [e] 0.5 equiv of anthracene. [f] Solution of the alkyl nitrite added concurrently with the anthranilic acid. [g] *t*-AmONO used. [h] *t*-BuONO used. [i] *Ca.* 1.5 equiv of anthracene. [j] New compound; for melting point and analytical data, see Table II. [k] Data from D. F. Lindow.

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[7] Diazotization of anthranilic acid in tetrahydrofuran (and other solvents) with isoamyl nitrite at ambient temperatures or lower slowly gives benzenediazonium-2-carboxylate *via* the brick-red precursor, 2,2′-dicarboxydiazoaminobenzene. In the presence of catalytic amounts of trichloro- or trifluoroacetic acid, almost quantitative yields of benzenediazonium-2-carboxylate are obtained in about 1 hr.[2]

[8] (a) T. Miwa, M. Kato, and T. Tamano, *Tetrahedron Lett.*, 2743 (1968); (b) S. F. Dyke, A. R. Marshall, and J. P. Watson, *Tetrahedron*, **22**, 2515 (1966).

[9] *Cf.* T. F. Mich, E. J. Nienhouse, T. E. Farina, and J. J. Tufariello, *J. Chem. Ed.*, **45**, 272 (1968).

[10] G. Wittig, *Org. Syn.*, **39**, 75 (1959).

[11] (a) Other solvents may be used for anthranilic acid in the aprotic diazotization reaction. The necessary criteria are stability toward amyl nitrite, a poor benzyne trap, and, obviously, a good solvent. The following solvents (with solubility of anthranilic acid in grams/100 ml at 25–28°)[11b] were found to be useful: acetonitrile (12), acetone (69), dioxane (62), ethyl acetate (28), glyme (42), methyl acetate (31), methyl ethyl ketone (60), tetrahydrofuran (60), diglyme (40), and diethyl carbitol (40). (b) Determined by L. R. Rice and D. M. Smith.

[12] When methylene chloride was used as the reaction solvent, addition of the anthranilic acid solution had to be extended to *ca.* 4 hr to obtain comparable yields of triptycene. The yield dropped to 44% when the time of addition was decreased to 1 hr. This is probably a result of the side reactions of unreacted anthranilic acid with benzyne or benzenediazonium-2-carboxylate.[8]

acid gave a 33% increase in yield (to 80%). Thus, for maximum yields, an excess (*ca.* 1 equiv) of either benzyne acceptor or precursor is suggested. The choice is dictated by the availability of the reactants and economics. Lower yields of triptycene (run 5) were obtained with *t*-alkyl nitrites, probably as a result of their decreased stability.

The yields of substituted triptycenes formed from substituted anthranilic acids and anthracene vary from 11 to 75%[13] (runs 7–30, Table I). It was found that the diglyme–methylene chloride solvent system did not work well with several substituted anthranilic acids, apparently due to the low boiling point of the mixture; *i.e.*, the diazotization of the anthranilic acid is slow and/or the rate of decomposition of the diazonium carboxylate formed *in situ* decreases, and apparently side reactions predominate. However, higher yields were obtained in the solvent system diglyme–chloroform (or in the system diglyme–ethylene chloride) than in the system diglyme–methylene chloride (*cf.* runs 11 and 19 *vs.* 10 and 18), which also obviated the necessity of concurrent addition of alkyl nitrite. Apparently, with these solvents, the rates of diazotization and decomposition of the diazoniumcarboxylate are favorably increased, while alkyl nitrite decomposition is still relatively slow.

Slow addition of a solution of 0.109 mol of anthranilic acid to a stirred, refluxing solution of tetracyclone (0.100 mol) and isoamyl nitrite in methylene chloride[15] discharged the purple color of the solution and gave, upon work-up, a 95% yield of 1,2,3,4-tetraphenylnaphthalene. Assuming that the starting materials were pure, the efficiency of the formation and capture of benzyne from anthranilic acid in this instance is at least 92%.

Aprotic diazotization of anthranilic acid in the presence of excess furan gave a 65% yield of the Diels–Alder adduct, 1,4-dihydro-1,4-epoxynaphthalene. In a similar manner, benzyne adducts of 2-methyl- and 2,5-dimethylfuran are also easily prepared.

The preparation of benzonorbornadiene by aprotic diazotization of anthranilic acid in the presence of cyclopentadiene was beset by concurrent tar formation, and initially low yields (12–13%) were obtained. In addition, there was discrepancy between glpc yields (29–68%) obtained from small-scale runs and those obtained by isolation upon preparative scale-up. In part, this may have been a result of concurrent dimerization of cyclopentadiene during the longer reaction times or destruction of product during work-up. However, reasonably good yields were obtained by slightly modifying the reaction conditions. Thus, instead of conducting the reaction in the usual way, an acetone or dioxane solution of anthranilic acid and cyclopentadiene was added to a refluxing solution of isoamyl nitrite and methylene chloride. The product was easily separated from the accompanying tar by extraction with petroleum ether or steam distillation. Pure benzonorbornadiene was obtained in 50–60% yield.[16] Larger scale runs (> 0.5 mol) gave lower yields. Attempts to overcome this shortcoming were unsuccessful.

The reaction of arynes (from benzenediazonium-2-carboxylate) with iodine to give *o*-diiodoarenes[17] can also be accomplished *via* aprotic diazotization. For example, addition of a dioxane solution of anthranilic acid to a refluxing mixture of iodine and isoamyl nitrite in chloroform conveniently gave *o*-diiodobenzene in *ca.* 50% yield.

The results described are indicative of the preparative usefulness of generating arynes from benzenediazonium-2-carboxylates prepared and decomposed *in situ.* Since the preliminary report,[1] the technique of aprotic diazotization of anthranilic acids has been widely utilized to safely extend the range of benzyne chemistry.[8b,9,18]

Experimental Section

Triptycene.—To a mechanically stirred, mildly refluxing solution of anthracene (75 g, 0.42 mol), *n*-butyl nitrite (48 g, 0.46 mol) or isoamyl nitrite (59 g, 0.46 mol), and ethylene chloride (1.2 l.) contained in a 3-l., three-necked flask, a filtered solution of anthranilic acid (60 g, 0.44 mol) in diethylcarbitol (300 ml) was added dropwise over a period of about 0.5 hr. When the addition was completed, the mixture was refluxed for 20 min and the flask was refitted for distillation. Distillation was continued until a head temperature of 150–160° was reached. The mixture was cooled somewhat, maleic anhydride (30 g) was added, and the mixture was then brought to reflux for 2–3 min. The heating mantle was then replaced by an ice bath, and a solution of methanol (1 l.), water (500 ml), and potassium hydroxide (120 g) was added to the almost black, stirred reaction mixture. The cold (0–10°) mixture was then suction filtered and the crude, tan product was washed with 80% methanol–water (4:1 v/v) until the washings were colorless (200–400 ml). The almost-white to light tan triptycene, after drying at 100°, weighed 60.9–64.2 g (57–60%), mp 251–254°.

The triptycene can be further purified by dissolving 25 g in 2-butanone (250 ml) (slight warming), treating with charcoal (2-3 g), filtering, concentrating to 175 ml, adding methanol (200 ml), and cooling in ice. The almost-white to white triptycene was suction filtered and washed with cold methanol (70 ml). The first crop weighed 19.4–19.7 g, mp 254–255.5°. Concentrating the combined filtrates to 120 ml gave a second crop of off-white triptycene, 3.2–3.7 g, mp 253.5–255.0°. Addition of two volumes of water to the filtrates gave a third crop of less pure material, 1.3–1.6 g, mp 248–253.5°. Total recovery was about 97%. The triptycene obtained was glpc pure (20% silicon grease on 60–80 mesh Chromosorb P, 180°); however, a somewhat whiter product could be obtained by recrystallizing from methylcyclohexane (19 ml/g).

Known triptycenes reported in Table I were identified by melting point and nmr comparison to literature data. Data for new compounds are listed in Table II.

1,2,3,4-Tetraphenylnaphthalene.—A solution of anthranilic acid (16.0 g, 0.117 mol) in tetrahydrofuran (85 ml) was added dropwise to a stirred, refluxing solution of tetraphenylcyclo-

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[13] With the exception of anthranilic acid, no attempt was made to find the optimum conditions for aprotic diazotization. However, the data in Table I are typical and indicate that some anthranilic acids[14] are better aryne precursors than others and that, with a given anthranilic acid, better yields would be expected in ethylene chloride or acetonitrile.

[14] The low yields of triptycenes from 3-chloro- and 3-nitroanthranilic acids *via* aprotic diazotization and from the corresponding isolated diazoniumcarboxylates will be discussed elsewhere.

[15] The reaction (*i.e.*, addition time) can be shortened to *ca.* 0.5 hr when ethylene chloride is used.

[16] *Cf.* ref 9.

[17] L. Friedman and F. M. Logullo, *Angew. Chem.*, **77**, 217 (1965).

[18] For example: (a) R. K. Hill and R. M. Carlson, *Tetrahedron Lett.*, 1157 (1964); (b) W. Ried and M. Silion, *Angew. Chem. Intern. Ed. Engl.*, **3**, 67 (1964); (c) G. A. Reynolds, *J. Org. Chem.*, **29**, 3733 (1964); (d) F. Minisci and A. Quilico, *Chim. Ind.* (Milan), **46**, 428 (1964); (e) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 1596, 5584 (1964); (f) C. Paget and A. Burger, *J. Org. Chem.*, **30**, 1329 (1965); (g) E. C. Kornfeld, P. Barney, J. Blankley, and W. Faul, *J. Med. Chem.*, **8**, 342 (1965); (h) C. F. Wilcox, Jr., and F. D. Roberts, *J. Org. Chem.*, **30**, 1959 (1965); (i) L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 1599 (1965); (j) E. Wolthuis and W. Cody, *Angew. Chem. Intern. Ed. Engl.*, **6**, 555 (1967); (k) T. D. Petrova, T. I. Savchenko, G. G. Yacobson, *Zh. Obshch. Khim.*, **37**, 1170 (1967) (Engl. Trans., p 1110); (l) B. H. Klanderman and J. W. H. Faber, *J. Polym. Sci., Part A-1*, **6**, 2955 (1968); (m) H. Heaney and B. A. Marples, *J. Chem. Educ.*, **45**, 801 (1968); (n) J. P. N. Brewer, H. Heaney, and T. J. Ward, *J. Chem. Soc.*, C, 355 (1969).

TABLE II

NEW TRIPTYCENES. MELTING POINT AND ELEMENTAL ANALYTICAL DATA

			Calcd, %		Found,[a] %	
Substituent	Mp, °C	Formula	C	H	C	H
1-Methyl-	190.5–192.5	$C_{21}H_{16}$	93.99	6.01	94.04	6.06
2-Methyl-	165–166	$C_{21}H_{16}$	93.99	6.01	94.01	6.02
2-Chloro-	168–169	$C_{20}H_{13}Cl$	83.18	4.54	83.32	4.59
2-Bromo-	167.5–169	$C_{20}H_{13}Br$	72.08	3.93	72.12	3.94
2-Iodo-	183–185	$C_{20}H_{13}I$	63.18	3.45	63.01	3.46

[a] Analyses by Galbraith Laboratories, Knoxville, Tenn.

pentadienone (38.4 g, 0.100 mol) and isoamyl nitrite (16.5 g, 0.13 mol) in methylene chloride (300 ml). After 3.5 hr, the purple reaction mixture turned a light orange and addition was stopped. Evaporation of the remaining tetrahydrofuran solution left 1.15 g (0.008 mol) of recovered anthranilic acid.

The reaction mixture was filtered from insolubles and evaporated under reduced pressure to *ca.* 100 ml. Addition of methanol (500 ml) and chilling in ice gave 39.26 g (95%) of 1,2,3,4-tetraphenylnaphthalene, mp 197–198°, remelt mp 205–205.5° (lit.[19] remelt mp 203–204°).

1,4-Dihydro-1,4-epoxynaphthalene.—A solution of anthranilic acid (41.10 g, 0.30 mol) and furan (50 ml, 0.78 mol) in dioxane (100 ml) was added over 4 hr to a stirred refluxing solution of furan (10 ml) and isoamyl nitrite (47 ml, 0.35 mol) in ethylene chloride (250 ml).

Solvents were removed under reduced pressure, and the dark residue was made basic with aqueous potassium hydroxide and extracted with petroleum ether (two 500-ml portions). The extracts were washed twice with water, treated with activated carbon, and dried, and the solvent was removed under reduced pressure to give an oil which partially crystallized on cooling. The oxide was triturated with a little cold petroleum ether and collected on a Büchner funnel. The yield of crude product, mp 48°, was 27.8 g. Recrystallization from petroleum ether gave material of mp 55.5–56° (lit.[20] mp 53–54.5° and 56°).

***o*-Diiodobenzene.**—A solution of anthranilic acid (60 g, 0.44 mol) in dioxane (300 ml) was added over 2 hr to a stirred, refluxing mixture of iodine (107 g, 0.42 mol) and isoamyl nitrite (83 ml, 0.60 mol) in chloroform (1 l.). The solution was then washed successively with 5% aqueous sodium bisulfite, water, 5% aqueous potassium hydroxide, and water, and dried over anhydrous calcium chloride. Solvents were removed by distillation and the residue was distilled under reduced pressure to give *o*-diiodobenzene, bp 132.7° (8-9 mm), 73.6 g (53%). A dark residue, 20 g, remained after distillation. Iodine was removed from the product by washing with aqueous sodium bisulfite. The *o*-diiodobenzene was crystallized from petroleum ether to give white crystals, mp 24° (lit.[21] mp 27°), glpc pure.

Benzonorbornadiene.[22]—A solution of anthranilic acid (68.5 g, 0.5 mol) and freshly distilled cyclopentadiene (33.0 g, 41.0 ml, 0.50 mol) in 300 ml of acetone was added over a period of 1.25–1.50 hr to a refluxing, mechanically stirred solution of isoamyl nitrite (65 g, 74 ml, 0.55 mol) in 700 ml of methylene chloride contained in a 2-l. three-necked flask. After the addition was completed, the dark reaction mixture was refluxed for 0.5 hr (glpc yield *ca.* 57–68%). It was then cooled and made basic with 100 ml of 10% aqueous KOH, and the low-boiling solvents were removed. The residual black oil was steam distilled, and about 300 ml of distillate was collected. The organic layer was separated and the aqueous layer was extracted with two 100-ml portions of ether. The combined material was dried over Na_2SO_4 and ether was removed. The residual yellow oil was fractionated (18-in. packed column) to give a forerun of isoamyl alcohol and dicyclopentadiene and then 35–42 g of benzonorbornadiene (50–60%), bp 78–79° (20 mm), n^{25}_{D} 1.5600. The pot residue (*ca.* 5 ml) is mainly isoamyl phenyl ether.

The yield could not be improved by changing the ratio of reactants or modifying the reaction conditions. On a 2-mol scale, the yield of isolated material drops to 28%.

Registry No.—Triptycene, 477-75-8.

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