405(17), 329(100), 328(100), 327(33), 326(29), 252(17); **3l**: 406(100), 405(26), 380(2), 329(53), 328(21), 327(16), 326(16), 252(5); **2m**: 304(100), 303(43), 302(13), 278(49), 277(63); **3m**: 304(100), 303(50), 302(21), 278(14), 277(18).

Hydrogenation of 3h and 3j.—Hydrogenations were carried out using the internal method for the Brown[2] hydrogenation apparatus.[12] To a 250-ml flask were added absolute ethanol (20 ml), decolorizing carbon (0.5 g), and 0.2 *M* chloroplatinic acid in ethanol (0.5 ml). By the use of a hypodermic syringe, 1.00 *M* sodium borohydride in ethanol (3.0 ml) was added, followed 1 min later by glacial acetic acid (2.5 ml). Then a solution of **3h** or **3j** (100 mg) in ethanol (100 ml) was added and the hydrogenation mixture was stirred for 6 hr at room temperature. The reaction mixture was filtered, the carbon was washed with methylene chloride, and the solvents were removed from the filtrate. The residue was treated with methylene chloride and dilute sodium bicarbonate solution, the organic layer was dried with sodium sulfate, and the solvent was removed. The residue was recrystallized from heptane or benzene–heptane.

5,12-Dihydro-5,12-ethanonaphthacene had mp 169–171°; nmr ($CDCl_3$) τ 2.15–3.01 (m, 10), 5.61 (m, 2), and 8.22 (m, 4); mass spectrum *m/e* 256 (molecular ion peak).

Anal. Calcd for $C_{20}H_{16}$: C, 93.7; H, 6.3. Found: C, 93.4; H, 6.6.

6-Cyano-5,12-dihydro-5,12-ethanonaphthacene had mp 170–171°; nmr ($CDCl_3$) τ 1.80–2.96 (m, 9), 5.08 (m, 1), 5.59 (m, 1), and 8.22 (m, 4); mass spectrum *m/e* 281 (molecular ion peak).

Anal. Calcd for $C_{21}H_{15}N$: C, 89.6; H, 5.4; N, 5.0. Found: C, 89.3; H, 5.5; N, 4.9.

Center-Ring Adduct *vs.* End-Ring Adduct (B/A) Ratio Experiments.—Reactions were carried out at 70° for 3–5 hr with 2 mmol of an anthracene, 4–8 mmol of 2-carboxybenzenediazonium chloride,[3,13] 40 ml of stock solvent solution (19:1 v/v 1,2-dichloroethane–propylene oxide), and an internal standard where applicable. Internal standards were employed when direct comparisons between reaction mixtures and mixtures of authentic adducts **2** and **3** could be made. See the next section for procedural details.

Vpc analyses were made on the worked-up reaction mixtures. For isolated pairs of adducts where thermal-conductivity differences could be calculated, the differences ranged from 0 to 15%. For the other pairs of adducts, the thermal conductivities of a given pair were assumed to be the same.

Competition Experiments.—Anthracene (356 mg, 2.00 mmol), a substituted anthracene (2.00 mmol), and an internal standard (octadecane, docosane, tetracosane, or octacosane) for vpc analysis were placed in a 100-ml one-neck flask equipped with a reflux condenser and a magnetic stirring bar operated by a water-driven magnetic stirrer. A solvent stock solution (20 ml), prepared by adding 1,2-dichloroethane (1520 ml) to propylene oxide (80 ml), was added to the flask, which was then placed in a constant-temperature bath at 70 ± 1°. A small aliquot was removed when complete solution was achieved.

Solid 2-carboxybenzenediazonium chloride (368 mg, 2.00 mmol) was added to the reaction mixture, and an additional 20 ml of the stock solvent solution, which had been maintained at 70°, was added. The heterogeneous reaction mixture was rapidly stirred for 3 hr, during which time it changed to a red-brown solution.

An equal volume of water was added to quench the reaction, and the organic layer was dried with magnesium sulfate and concentrated in preparation for vpc analysis.

For each competition experiment, vpc comparisons were made between the amounts of anthracenes in the reaction mixture prior to and subsequent to the reaction with 2-carboxybenzenediazonium chloride. The average value of triplicate vpc determinations was used in each case.

The relative reactivities were calculated using the expression

$$\log[(X)/(X_0)]/\log[(Y)/(Y_0)] = k_{X/Y}$$

where (X) and (Y) refer to final concentrations of substituted anthracene and anthracene, respectively, and (X_0) and (Y_0) refer to initial concentrations.

Registry No.—Benzyne, 462-80-6; **2a**, 15254-35-0; **2b**, 793-39-5; **2c**, 21372-89-4; **2d**, 21372-90-7; **2e**, 17417-17-3; **2f**, 21372-92-9; **2g**, 21372-93-0; **2h**, 477-75-8; **2i**, 20466-07-3; **2j**, 1092-87-1; **2k**, 797-67-1; **2l**, 21372-98-5; **2m**, 4044-52-4; **3a**, 21373-00-2; **3b**, 21373-01-3; **3c**, 21373-02-4; **3e**, 21373-03-5; **3f**, 21373-04-6; **3g**, 21373-05-7; **3h**, 4044-73-9; **3i**, 21373-07-9; **3j**, 4044-74-0; **3k**, 21373-09-1; **3l**, 21373-10-4; **3m**, 4044-75-1; **4e**, 21373-12-6; 5,12-dihydro-5,12-ethanonaphthacene, 10117-59-6; 6-cyano-5,12-dihydro-5,12-ethanonapthacene, 21373-14-8.

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(12) C. A. Brown and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 2829 (1962).

(13) Enough 2-carboxybenzenediazonium chloride was added such that essentially all starting anthracene was converted into products. The more unreactive anthracenes necessitated a larger excess of benzyne precursor.

Azides and Amines from Grignard Reagents and Tosyl Azide

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Grignard reagents react with tosyl azide to form salts of tosyltriazenes, which can be reduced to amines by Raney nickel alloy and aqueous base. Fragmentation of the triazene salts to form aryl or alkyl azides takes place best in aqueous sodium pyrophosphate at 0–20°. Yields are moderate to good with aromatic reagents, poor with aliphatic. *o*-Tolyl and *o*-*t*-butylphenyl Grignard reagents react with tosyl azide under some conditions to give the azobenzene and toluenesulfonamide instead.

The traditional methods for converting organic halides to amines or azides involve displacement reactions with ammonia, metal amides, or metal azides, and thus are unsatisfactory or fail altogether with unreactive halides, including most aryl halides. Grignard reagents react with a variety of nitrogenous reagents to give products in which the aryl or alkyl group of a Grignard reagent has become attached to a nitrogen atom (chloramine,[2] alkoxyamines,[3] nitrosyl chloride,[4] and alkyl nitrates[5]), providing potential alternative routes to amines and azides. Some instances of preparative utility have been reported, but none of these

(1) From the doctoral dissertations of L. B. Bruner, 1957, and C. D. Rowe, 1968.

(2) (a) G. H. Coleman and C. R. Hauser, *J. Amer. Chem. Soc.*, **50**, 1193 (1928); (b) G. H. Coleman, H. Soroos, and C. B. Yager, *ibid.*, **55**, 2075 (1933).

(3) N. I. Sheverdina and K. A. Kocheshkov, *Zh. Obshch. Khim.*, **8**, 1825 (1938).

(4) (a) E. Müller and H. Metzger, *Chem. Ber.*, **89**, 396 (1956); (b) B. Oddo, *Gazz. Chim. Ital.*, **39I**, 660 (1909).

(5) (a) H. Gilman and J. Robinson, *Rec. Trav. Chim. Pays-Bas*, **48**, 328 (1929); (b) J. Bewad, *Ber.*, **40**, 3065 (1907).

reactions can be regarded as generally satisfactory. In this paper we report an alternative method for converting Grignard reagents to amines and azides which seems to have some useful advantages.

The reaction of Grignard reagents with azides is vigorous and gives rise to magnesium salts of 1,3-disubstituted triazenes (eq 1).[6] The magnesium-attached group thereby becomes attached to nitrogen; conversion

$$RMgX + R'N_3 \longrightarrow [RNNNR']MgX \quad (1)$$

into an amine can be brought about by reduction. However, the group attached to the original azide also becomes an amine, and separation of the resulting mixture of amines may be tedious. Sulfonyl azides, however, would be converted by the over-all sequence into nonbasic sulfonamides, from which the desired amine would be readily separable. Published reports indicate that the expected intermediate sulfonyltriazenes (or their salts) are prone to fragmentation in two ways: cleavage to a sulfonamide and a diazo compound (eq 2), and cleavage to a sulfinic acid and an azide (eq 3). The first of these is in fact the basis of a

$$(RNNNSO_2R')^- \xrightarrow{H_2O} RN_2^+ + {}^-HN{-}SO_2R' \quad (2)$$

$$[RNNNSO_2R']^- \longrightarrow RN_3 + {}^-SO_2R' \quad (3)$$

synthesis of diazo compounds from active methylene compounds,[7] particularly diazocyclopentadiene.[8] It is in principle reversible, for sulfonyltriazenes can be prepared by coupling diazonium salts to sulfonamides. The second is the basis of a synthesis of aryl azides from diazonium salts and sulfonamides.[9,10]

Nevertheless, we have obtained arylamines in yields as high as 82% (see Table I). Arylmagnesium halides, prepared in tetrahydrofuran, were treated with *p*-toluenesulfonyl azide; reaction was immediate and exothermic. Treatment of the reaction mixtures with Raney nickel alloy and cold aqueous sodium hydroxide produced the corresponding anilines, which were isolated by steam distillation and precipitation as hydrochlorides. The possibility that unsubstituted aniline might have been produced by reductive removal[11] of chloro or methoxy substituents was eliminated when no evidence, spectroscopic or from melting points, could be obtained for the presence of such contaminants. The other products of the principal reaction were ammonia and *p*-toluenesulfonamide (eq 4); the latter was not generally isolated once its formation had been established in the early experiments.

$$(ArNNNSO_2C_7H_7)MgX \xrightarrow[Al\text{-}Ni]{aq\ NaOH} ArNH_2 + C_7H_7SO_2NH_2 \quad (4)$$

Preliminary attempts to prepare aliphatic amines by this procedure were not encouraging, for the triazene salts appeared to be too unstable. Only one example, β-phenylethylamine, was therefore pursued diligently, and gave at best only 25% yield.

TABLE I

AMINE HYDROCHLORIDES FROM GRIGNARD REAGENTS

Amine hydrochloride	Yield, %
o-Toluidine	82
m-Toluidine	79
p-Toluidine	66
2,5-Dimethylaniline	76
o-*t*-Butylaniline	19
o-Aminodiphenylmethane	71
m-Chloroaniline	41
p-Chloroaniline	49
o-Anisidine	63
p-Anisidine	51
Neophylamine	25
β-Phenylethylamine	25
p-Aminobiphenyl	62[a]
9-Aminophenanthrene	54[a]

[a] As free base.

The fragmentation leading to an azide (eq 3) offers the possibility of a direct synthesis of aryl (and perhaps alkyl) azides, from which primary amines could be obtained by reduction. In order to repress the competing fragmentation to sulfonamide and diazonium compound (eq 2), we warmed the sulfonyltriazene salts with an excess of toluenesulfonamide in aqueous sodium hydroxide. Yields of aryl azides were at best moderate, and a red–brown contaminant was produced. Fragmentation was slow, probably because of the formation of complexes (known to occur with metal ions[12]), and heat brought about undesirable side reactions.

Thermolytic fragmentation of the magnesium salt of 1-phenyl-3-*p*-toluenesulfonyltriazene by dry distillation at 120–130° (0.1 mm) has recently been reported by Ito.[13] The conditions apparently required confirm the resistance of the magnesium salts to fragmentation. Although phenyl azide was obtained in 82% yield in this way[13], we were concerned about the danger of such a technique, particularly on a preparative scale, and also about the temperatures required, which might preclude use for heat-sensitive azides and those of lower volatility.

We therefore treated the sulfonyltriazene salts with aqueous sodium polyphosphates or sodium pyrophosphate to sequester the magnesium. The results are shown in Table II. The azides were either isolated as such, or assayed by reduction to amine with sodium borohydride followed by benzoylation. Yields of azides were higher than those from the use of sodium hydroxide alone or with toluenesulfonamide (which appears to be unnecessary), and are comparable to those obtained from coupling the corresponding diazonium salt to *p*-toluenesulfonamide. Over-all conversions to amines compare favorably with those obtained by *in situ* reduction of the triazene salt with Raney nickel alloy.

The azides prepared in this way are satisfactory for many purposes, but are contaminated with small

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(7) M. Regitz, *Angew. Chem. Intern. Ed. Engl.*, **6**, 733 (1967).
(8) (a) W. von E. Doering and C. H. DePuy, *J. Amer. Chem. Soc.*, **75**, 5955 (1953); (b) T. Weil and M. Cais, *J. Org. Chem.*, **28**, 2472 (1963).
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(10) H. Bretschneider and H. Rager, *Monatsh. Chem.*, **81**, 970 (1950).
(11) E. Schwenk, D. Papa, B. Whitman, and H. F. Ginsberg, *J. Org. Chem.*, **9**, 1 (1944).
(12) (a) F. E. Brinckman, H. A. Haiss, and R. A. Robb, *Inorg. Chem.*, **4**, 936 (1965); (b) F. P. Dwyer and D. P. Mellor, *J. Amer. Chem. Soc.*, **63**, 81 (1941); (c) F. P. Dwyer, *ibid.*, **63**, 78 (1941); (d) F. P. Dwyer, *Aust. Chem. Inst. J. Proc.*, **6**, 348 (1939); (e) F. E. Brinckman and H. S. Haiss, *Chem. Ind.* (London) 1124 (1963); (f) C. M. Harris, B. F. Hoskins, and R. L. Martin, *J. Chem. Soc.*, 3728 (1959); (g) J. G. Noltes, *Rec. Trav. Chim. Pays-Bas*, **84**, 126 (1965); (h) G. E. Coates and R. N. Mukherjee, *J. Chem. Soc.*, 1295 (1964).
(13) S. Ito, *Bull. Chem. Soc. Jap.*, **39**, 635 (1966).

TABLE II
ARYL AZIDES AND BENZAMIDES FROM GRIGNARD REAGENTS

Aryl bromide	Aryl azide, %	N-Aryl-benzamide, %
Phenyl	50[a]	81[b]
p-Tolyl	73[c]	67[c]
p-Chlorophenyl	70[c], 55[b]	63[c]
p-Anisyl	55[b]	77[c]
Mesityl	63[b]	
o-*t*-Butylphenyl	42[b,d]	
o-Benzylphenyl[e]	49[b]	
p-Biphenylyl	68–79[f]	

[a] Triazene treated with aqueous sodium hydroxide. [b] Triazene treated with tetrasodium pyrophosphate. [c] Triazene treated with sodium polyphosphates and potassium hydroxide. [d] Grignard reagent added to tosyl azide (inverse addition). Oil: bp *ca.* 50° (0.01 mm); ir (neat) 2105 (N_3), 1395, and 1365 cm^{-1} (*t*-butyl); nmr (CCl_4) τ 2.6–3.2 (m, 4, aromatic) and 8.60 (s, 9, *t*-butyl). *Anal.* Calcd for $C_{10}H_{13}N_3$: C, 68.54; H, 7.48; N, 23.98. Found: C, 68.74; H, 7.40; N, 23.83. [e] Oil: bp *ca.* 97° (0.1 mm); ir (neat) 2120 cm^{-1}; nmr (CCl_4) τ 2.9–3.3 (m, 9, aromatic) and 6.22 (s, 2, benzylic CH_2). Reported without physical properties by L. O. Krbechek and H. Takimoto, *J. Org. Chem.*, **33**, 4286 (1968). [f] Triazene treated with sodium hydroxide and *p*-toluenesulfonamide, or with aqueous ammonium chloride.

amounts of substances derived from the preparation of the Grignard reagents (aryl halide and biaryl) as well as tosyl azide. Purer azides can be obtained by intermediate isolation of the triazene salts. This is easily accomplished by virtue of the fact that the latter are soluble in tetrahydrofuran, but insoluble in ethyl ether or petroleum ether. They precipitate automatically if their preparation is carried out in ethyl ether, or by addition of petroleum ether if their preparation involves tetrahydrofuran (the contaminants remain in solution).

Although the formation of sulfonyltriazene salts from Grignard reagents and tosyl azide is rapid and generally appears to occur in high yield, a side reaction leading to azobenzenes was unexpectedly encountered in two instances. *o,o'*-Di-*t*-butylazobenzene was obtained in 24% yield from *o*-bromo-*t*-butylbenzene in an experiment in which the ratio to tosyl azide was 2:1 (along with *p*-toluenesulfonamide, 54%). In another experiment, which differed in that the ratio was 1:1 and the Grignard reagent was prepared by the entrainment technique of Pearson, Cowan, and Beckler,[14] using ethylene dibromide and excess magnesium, the yield of azo compound rose to 53% (accompanied by *p*-toluenesulfonamide in 65% yield). Formation of azo compound was avoided by using inverse addition (Grignard reagent to tosyl azide). When *o*-tolylmagnesium bromide prepared in the same way was used, *o,o'*-azotoluene was obtained in 28% yield (the ratio of Grignard reagent to tosyl azide was 2:1), whereas only a high yield of *o*-tolyl azide was obtained when the Grignard reagent was prepared in the ordinary way and added to tosyl azide, even with the same 2:1 ratio of reagents.

This type of reaction has not been reported previously. We have not explored its scope or its dependence on conditions, but it appears to be promoted by the presence of excess Grignard reagent or magnesium bromide, and can be described by eq 5, pending further investigation. It is perhaps analogous to the formation of azobenzene from phenylmagnesium bromide and benzenediazonium chlorozincate. The absence of the orange-red color of the azobenzene structure from most of the reactions listed in Table II suggests that the formation of azobenzenes is not ordinarily a significant reaction.

$$(ArNNNSO_2C_7H_7)MgBr \xrightarrow{ArMgBr} ArN{=}NAr + C_7H_7SO_2NMg_2Br_2 \quad (5)$$

The foregoing reactions are preparatively feasible for synthesis of anilines, within the limitation that the many functional groups that are incompatible with Grignard reagents must be avoided. The required tosyl azide is easily prepared and handled.[8a] However, nearly all simple anilines are as easily obtained by conventional methods. The reactions are relatively more expeditious for the preparation of aryl azides, and may in many instances be competitive with the conventional sequence: nitration, reduction, and diazotization. The actual yields obtained are obviously dependent on the efficiency with which the Grignard reagents are prepared, a factor that can vary considerably with experimental technique. The yields in many instances are probably actually higher, for mechanical losses are high in handling small quantities of liquid products. The principal utility of the syntheses with tosyl azide is with more complex compounds where the corresponding nitro compound or amine cannot be obtained satisfactorily by simple substitution reactions. The method has been particularly useful for *o*-azidostyrene derivatives, the chemistry of which will be described in a forthcoming communication.

Experimental Section[15]

Amines from Tosyl Azide.—The amines reported in Table I were prepared by the following procedure or minor modifications of it. All are well-known compounds and were identified by comparison of melting points of the amines, their hydrochlorides, and/or benzoyl derivatives with reported values.

p-Tolylmagnesium bromide was prepared from 17.1 g (0.10 mol) of *p*-bromotoluene (Eastman) and 2.7 g (0.11 g-atom) of magnesium turnings in 100 ml of dry tetrahydrofuran. The solution was then cooled in an ice bath, and 19.7 g (0.10 mol) of *p*-toluenesulfonyl azide[8a] in 25 ml of dry THF was added dropwise with stirring under nitrogen. The stirring was continued an additional 15 min. The solution was poured with stirring into a mixture of 131 ml of 50% sodium hydroxide and 300 g of ice. At 1-hr intervals, 10-, 10-, and 15-g portions of Raney nickel–aluminum alloy (Raney Catalyst Co., Chattanooga, Tenn.) were added slowly to the resulting suspension with vigorous stirring in a flask fitted with an efficient condenser. The mixture was then steam-distilled. The first distillate, mostly THF, was distilled through a Vigreux column (470 mm), and the higher boiling material (water and amine) was combined with the subsequent aqueous steam distillate and was extracted with ethyl ether. The dried (KOH) extract was treated with hydrogen chloride, which precipitated *p*-toluidine hydrochloride, 10.1 g (66%): mp 241–243° (lit.[16] mp 243°). Benz-*p*-toluidide, mp 157–159° (lit.[17] mp 158°), was prepared from a portion of the hydrochloride.

(14) D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

(15) Melting and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 237B instrument, and nmr spectra on a Varian A-60 instrument using tetramethylsilane as internal standard. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

(16) "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965.

(17) L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 95.

Aryl Azides from Grignard Reagents.—The procedure for mesityl azide exemplifies the method used, with variations as noted in Table II. All except *o*-*t*-butylphenyl and *o*-benzylphenyl azides are known compounds, and were identified by comparison of melting points and infrared spectra with authentic samples, and/or by reduction to the amine.

Mesityl Azide.—Mesitylmagnesium bromide, prepared from 39.8 g (0.2 mol) of mesityl bromide[18] in 85 ml of dry ether, was added dropwise to a solution of 19.7 g (0.1 mol) of tosyl azide in 500 ml of dry ether with cooling in an ice bath. Stirring was continued for an additional 30 min, and the tan precipitate was filtered off, washed with dry ether and then petroleum ether, and dried in a vacuum desiccator: wt 50.9 g. The entire amount was suspended in 250 ml of dry ether and cooled in an ice bath; a solution of 44.6 g (0.1 mol) of tetrasodium pyrophosphate decahydrate in 500 ml of distilled water was added dropwise. After stirring overnight, the ether layer was separated, and the aqueous layer was extracted twice with 100-ml portions of petroleum ether. The combined extracts and ether layer were dried ($CaCl_2$) and concentrated, leaving 16.70 g of red oil, which was then passed through a column of alumina (300 g) with petroleum ether (bp 30–60°). Evaporation of the solvent left colorless mesityl azide, pure by thin layer chromatography: 10.16 g (63%); ir (neat) 2130 cm^{-1} ($-N_3$). An analytical sample was distilled in a microstill at *ca.* 65° (0.175 mm): nmr (CCl_4) τ 3.40 (s, 2, aromatic), 7.79 (s, 6, *ortho* methyl), 7.83 (s, 3, *para* methyl).

Anal. Calcd for $C_9H_{11}N_3$: C, 67.05; H, 6.88; N, 26.07. Found: C, 66.98; H, 6.82; N, 26.03.

***o,o'*-Di-*t*-butylazobenzene. A.**—A solution of 2.13 g (0.01 mol) of *o*-bromo-*t*-butylbenzene[18] and 10 ml of dry tetrahydrofuran was refluxed with 0.24 g (0.01 g-atom) of magnesium turnings for 1 hr. After cooling the solution to room temperature, 0.99 g (0.005 mol) of tosyl azide in 5 ml of tetrahydrofuran was added and the mixture was stirred overnight and then concentrated to a red oil. A solid (3.25 g) precipitated when the oil was taken up in chloroform and then diluted with ether. The filtrate was concentrated somewhat and then passed through a column of alumina (25 g) with petroleum ether. Evaporation of the effluent left *o,o'*-di-*t*-butylazobenzene: 0.356 g (24%); mp 89–91°. Recrystallization from chloroform–methanol mixture gave an analytical sample: mp 90.5–91°; nmr (CCl_4) τ 2.6–2.9 (m, 8, aromatic), 8.47 (s, 18, *t*-butyl); ir (Nujol) 1360 and 1380 cm^{-1} (*t*-butyl).

Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.58; H, 8.90; N, 9.51. Found: C, 81.55; H, 9.01; N, 9.46.

The solid that was precipitated by ether was acidified with 10% aqueous hydrochloric acid and extracted with chloroform. Concentration of the dried ($MgSO_4$) extracts left a solid, which was recrystallized twice from chloroform–petroleum ether mixture to give 0.463 g (54%) of *p*-toluenesulfonamide, mp 136–137°, mmp 136–137° (lit.[16] 137°).

(18) P. A. S. Smith and E. P. Antoniades, *Tetrahedron*, **9**, 210 (1960).

B.—A solution of 2.6 g (0.012 mol) of *o*-bromo-*t*-butylbenzene and 12 ml of dry ether was refluxed with 0.6 g (0.024 g-atom) of magnesium turnings while a solution of 2.2 g (0.012 mol) of 1,2-dibromoethane and 12 ml of dry ether was added over a 10-hr period. The solution was cooled and 1.97 g (0.01 mol) of tosyl azide dissolved in 10 ml of dry ether was added dropwise, forming a red solution; no *o*-*t*-butylphenyl azide could be detected by thin layer chromatography, although a medium ir band at 2120 cm^{-1} showed the presence of an azido group. A solution of 4.4 g (0.01 mol) of tetrasodium pyrophosphate decahydrate in 50 ml of distilled water was added dropwise and stirred for 2 hr. The ether layer was separated and the aqueous phase was extracted with ether. The extracts were combined, dried ($CaCl_2$), and concentrated. Addition of petroleum ether precipitated *p*-toluenesulfonamide: 0.55 g (65%); mp 135–137°; mmp 135–137°. Evaporation of the solvent gave 2.83 g of a reddish brown liquid, 1 g of which was chromatographed over 50 g of alumina. The lowest visible band was eluted with petroleum ether (bp 30–60°). Evaporation of the eluate left a solid, which was recrystallized from methanol to give 0.784 g (53%) of red needles, mp 90–91°, spectroscopically identical with the first preparation of *o,o'*-di-*t*-butylazobenzene.

***o,o'*-Azotoluene.**—A solution of 3.42 g (0.02 mol) of *o*-bromotoluene and 20 ml of dry diethyl ether was added to 1.44 g (0.06 g-atom) of magnesium turnings and heated to reflux; 7.52 g (0.04 mol) of 1,2-dibromoethane in 40 ml of ethyl ether was added over a period of several hours. The reaction mixture was cooled and 1.98 g (0.01 mol) of tosyl azide in 10 ml of dry ether was added with constant stirring while keeping the temperature at 0°. After 5 hr, the reaction mixture was hydrolyzed with 25 ml of water and the ether layer was separated, dried ($CaCl_2$), and concentrated. The residue was taken up with petroleum ether and passed through a column of alumina (75 g) with petroleum ether. Evaporation of the solvent left a red liquid (0.944 g) that crystallized from *ca.* 95% aqueous methanol to give 0.594 g (28%) of *o,o'*-azotoluene: mp 48–50°, mmp 48–49° (lit.[16] 55°); nmr (CCl_4) τ 2.4–3.2 (m, 8, aromatic), 7.33 (s, 6, methyl). The infrared spectrum was essentially identical with that of *o,o'*-azotoluene prepared by paralleling the method of Bigelow and Robinson.[19]

Registry No.—Tosyl azide, 941-54-8; mesityl azide, 14213-00-4; *o,o'*-di-*t*-butylazobenzene, 21367-80-6; *o,o'*-azotoluene, 584-90-7; *o*-*t*-butylphenyl azide, 20442-98-2; *o*-benzylphenyl azide, 17691-65-5.

Acknowledgment.—We wish to thank the National Science Foundation for a grant (GP-6463) supporting part of this work.

(19) H. E. Bigelow and D. R. Robinson, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 103.