

was treated with a 1:1 mixture of ethanolamine and acetaldehyde in aqueous solution to afford the following products.

**3-[(*p*-Nitrophenyl)azo]-2-methyl-1,3-oxazolidine (8):** 28%; mp 75–78 °C (ether/petroleum ether, yellow prisms); <sup>1</sup>H NMR 1.68 (3 H, d, *J* = 5 Hz, CH<sub>3</sub>), 3.8–4.5 (4 H, m, CH<sub>2</sub>CH<sub>2</sub>), 5.4 (1 H, q, *J* = 5 Hz, CH), 7.6, 8.3 (4 H, AA'BB', arom, *J*<sub>AB</sub> = 9 Hz) ppm.

**3-[(*p*-Cyanophenyl)azo]-2-methyl-1,3-oxazolidine (9):** 7%; mp 65–67 °C; <sup>1</sup>H NMR 1.64 (3 H, d, *J* = 5.3 Hz, CH<sub>3</sub>), 3.78 (1 H, dt, *J* = 12.2, 7.9 Hz), 3.92 (1 H, m) (NCH<sub>2</sub>), 4.07 (1 H, dt, *J* = 8.7, 7.0 Hz), 4.35 (1 H, ddd, *J* = 3.35, 7.44, 8.93 Hz) (OCH<sub>2</sub>), 5.32 (1 H, q, *J* = 5.3 Hz, CH), 7.50, 7.62 (4 H, AA'BB', arom, *J*<sub>AB</sub> = 8.6 Hz) ppm; <sup>13</sup>C NMR 20.55 (CH<sub>3</sub>), 46.25 (NCH<sub>2</sub>), 65.94 (OCH<sub>2</sub>), 89.15 (NCHO), 109.61 (C≡N), 120.28, 122.20, 134.01, 154.91 (arom) ppm. This product was obtained as an oil, which was purified by column chromatography on Hi/Fosil silica gel (60/200 mesh). Elution of the column began with pure naphtha, and the polarity slowly increased with naphtha/chloroform mixtures (up to 30% CHCl<sub>3</sub>). The fractions of the oxazolidine were combined and evaporated to afford an oil, which crystallized slowly after 2 days. The crystals were separated by washing with cold pentane to give the pure product. Anal. C, H, N.

**1,3-Oxazolidino[3,2-*c*]-3,4-dihydrobenzo-1,2,3-triazine (21).** 2-Aminobenzaldehyde (0.10 mmol) was dissolved in CHCl<sub>3</sub> (30 ml) and the mixture added to a solution of sodium nitrite (0.10 mmol) in water (20 ml). The two-phase mixture was cooled to 0 °C and stirred vigorously, while a solution of concentrated hydrochloric acid (2.5 mL) in water (25 mL) was added dropwise. The resulting mixture was stirred for 1 h, and the two layers were separated; the chloroform layer was extracted with water (20 mL). The combined aqueous fractions, containing the *o*-formylbenzenediazonium salt, were cooled to 0 °C and treated slowly with a cold solution of ethanolamine (0.11 mmol) in water (10 mL) neutralized with hydrochloric acid. The cold aqueous mixture was then rendered basic with a saturated solution of sodium carbonate (20 mL), and the oil which separated was extracted into chloroform. The chloroform extracts were washed with water, dried, and evaporated to afford the oxazolidinotriazine **21**: 0.36 g (20%); oil; δ (CDCl<sub>3</sub>) 3.04 (1 H, dd, *J* = 4.6 and 9.3 Hz), 3.41 (1 H, ddd, *J* = 3.2, 9.4, 12.5 Hz) (NCH<sub>2</sub>), 3.60 (1 H, dd, *J* = 2.3 and 15 Hz), 4.51 (1 H, ddd, *J* = 4.7, 12.5, 14.8 Hz) (OCH<sub>2</sub>), 6.18 (1 H, s, CH), 7.41 (d, *J* = 8.0 Hz), 7.52 (t, *J* = 7.4 Hz), 7.56 (t, *J* = 7.9 Hz), 7.71 (d, *J* = 7 Hz) (4 H, arom) ppm; <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) 55.84 (NCH<sub>2</sub>), 61.5 (OCH<sub>2</sub>), 78.2 (CH), 115.85, 125.5, 126.8, 130.2, 137.9, 156.9 (arom) ppm.

**5-Methyl-1,3-oxazolidino[3,2-*c*]-3,4-dihydrobenzo-1,2,3-triazine (22).** Reaction of the *o*-formylbenzenediazonium salt, as for **21**, with 1-amino-2-propanol affords **22** (51%): oil; <sup>1</sup>H NMR 1.18 (d, *J* = 6.0 Hz), 1.38 (d, *J* = 5.3 Hz) (3 H, CH<sub>3</sub>), 3.30–5.00 (3 H, m, OCHCH<sub>2</sub>N), 5.45, 5.58 (1 H, singlets, CH), 7.25–7.90 (4 H, m, arom) ppm. The doubling of the C-5 methyl and C-2 proton in **22** arises from the diastereoisomerism of this compound.

**Tetrahydro-1,3-oxazino[3,2-*c*]-3,4-dihydrobenzo-1,2,3-triazine (23).** Reaction of the *o*-formylbenzenediazonium salt, as for **21**, with 3-amino-1-propanol affords **23** (50%): mp 76–78 °C; <sup>1</sup>H NMR δ 1.72 (1 H, dq, *J* = 1.3, 12.3 Hz), 2.33 (1 H, m) (CCH<sub>2</sub>C), 3.85 (1 H, dt, *J* = 3.2, 16.1 Hz), 4.12 (1 H, m) (NCH<sub>2</sub>), 4.12 (1 H, m), 4.53 (1 H, dd, *J* = 4.85, 13.7 Hz) (OCH<sub>2</sub>), 5.79 (1 H, s, OCHN), 7.27 (1 H, d, *J* = 7.1 Hz), 7.44 (1 H, t, *J* = 7.5 Hz), 7.53 (1 H, t, *J* = 8.5 Hz), 7.68 (1 H, d, *J* = 8.1 Hz) (aromatic) ppm. Anal. C, H, N.

**Acknowledgment.** The financial assistance of the Natural Sciences and Engineering Research Council of Canada (K.V.) is gratefully acknowledged. We also thank the Atlantic Regional Magnetic Resonance Centre at Dalhousie University, Halifax, for high-resolution <sup>1</sup>H and <sup>13</sup>C NMR spectra, in particular to Dr. D. L. Hooper for helpful discussion. Anti-tumor evaluation of the oxazolidine (**7**) on the TLX5 tumor was carried out at the Department of Pharmaceutical Sciences, University of Aston in Birmingham, U.K., and in vitro assay of **7** was performed by Ms. Lynn Cameron in the laboratory of Dr. R. Rajaraman in the Department of Microbiology at Dalhousie University.

**Registry No.** **2a**, 96228-94-3; **2b**, 96228-95-4; **2c**, 96228-96-5; **5**, 96228-78-3; **6**, 96228-79-4; **7**, 96228-80-7; **8**, 96228-81-8; **9**, 96228-82-9; **10**, 96228-83-0; **11**, 96228-84-1; **12**, 96228-85-2; **13**, 96228-86-3; **14**, 96228-87-4; **15**, 96228-88-5; **21**, 96228-89-6; *cis*-**22**, 96228-91-0; *trans*-**22**, 96228-92-1; **23**, 96228-93-2; H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH, 141-43-5; MeCH(NH<sub>2</sub>)CH<sub>2</sub>OH, 78-91-1; MeCH(OH)CH<sub>2</sub>NH<sub>2</sub>, 78-96-6; 2-aminobenzaldehyde, 529-23-7; *o*-formylbenzenediazonium chloride, 96228-90-9; 3-amino-1-propanol; 156-87-6; 4-chlorobenzeneamine, 106-47-8; 4-chlorobenzenediazonium chloride, 2028-74-2; 4-nitrobenzeneamine, 100-01-6; 4-nitrobenzenediazonium chloride, 100-05-0; 4-aminobenzonitrile, 873-74-5; 4-cyanobenzenediazonium chloride, 25102-85-6; acetaldehyde, 75-07-0; formaldehyde, 50-00-0.

## Synthesis of Biaryls from Aryltriazenes

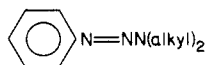
Timothy B. Patrick,\* Richard P. Willaredt, and David J. DeGonia

Department of Chemistry, Southern Illinois University at Edwardsville, Edwardsville, Illinois 62026

Received October 12, 1984

Aryltriazenes react with aromatic solvents in the presence of trifluoroacetic acid to produce biaryls. The mechanism of the reaction involves the formation of arenediazonium trifluoroacetates which lose nitrogen to give mainly aryl radicals.

The aryltriazenes, 1-aryl-3,3-dialkyltriazene (**1**), have a



**1**

long and interesting background dating to 1875.<sup>1</sup> The early chemical studies of aryltriazenes involved their synthesis, structure, and decomposition with mineral

acids.<sup>2-5</sup> Aryltriazene chemistry heightened in the 1940s when Hey<sup>6</sup> et al. and later Rondestvedt<sup>7a</sup> et al. discovered the use of aryltriazenes as diazonium salt equivalents for

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Table I. Yields and Properties of Biaryls

triazene subst	solv	mp, °C	lit. <sup>a</sup> mp, °C	yield, <sup>b</sup> %	GB, <sup>c</sup> %	PTGB <sup>d</sup> %
H	benzene	68–69	71	40	22	62
4-CH <sub>3</sub>	benzene	46–47	49–50 47.7	50	22	73
4-OCH <sub>3</sub>	benzene	86	90	41	25	80
4-OC <sub>2</sub> H <sub>5</sub>	benzene	72–74	72–73	65	29 <sup>e</sup>	NR
4-O-N-Bu	benzene	70–72	NR <sup>f</sup>	72	NR	NR
4-C <sub>2</sub> H <sub>5</sub>	benzene	36–37	33–34	39	NR	50
4-F	benzene	71–72	74.5	61	NR	60
2,4-F <sub>2</sub>	benzene	59–61	61–63 <sup>g</sup>	36	NR	NR
4-Cl	benzene	76–77	77	49	40	80
4-Br	benzene	89–90	91	45	44	81
4-I	benzene	112	113–114	63	NR	NR
4-NO <sub>2</sub>	benzene	112–113	114	66	60	85
4-COCH <sub>3</sub>	benzene	119–120	121	67	NR	NR
4-CH <sub>3</sub>	thiophene	66–68	63–65 77–78 <sup>h</sup>	26	11	NR
4-CH <sub>3</sub>	nitrobenzene	122–126	NR <sup>i</sup>	17	NR	NR
H	<i>p</i> -xylene	1.5819	NR <sup>b</sup>	78	NR	NR
4-CH <sub>3</sub>	bromobenzene	127–30	133 <sup>j</sup>	35	28	NR
4-CH <sub>3</sub>	pyridine	oil	oil <sup>k</sup>	57	NR	50

<sup>a</sup> Melting points are taken from ref 24 or from the "CRC Handbook of Chemistry and Physics", 59th ed.; CRC Press: Cleveland, 1978–1979. <sup>b</sup> Isolated yields of pure biaryl based on the aryltriazene. <sup>c</sup> Yields reported by Gomberg and Bachmann.<sup>49</sup> <sup>d</sup> Yields of phase-transfer catalyzed Gomberg–Bachmann reaction.<sup>50</sup> <sup>e</sup> Haworth, J. W.; Hey, D. H. *J. Chem. Soc.* 1940, 361. <sup>f</sup> New compound gave satisfactory analytical data. NR = not reported. <sup>g</sup> Utne, T.; Johnson, R.; Lowell, H. U.S. Patent 3992 459, 1976. <sup>h</sup> 2-*p*-Tolythiophene: Hartough, D. "Thiophene and Its Derivatives, The Chemistry of Heterocyclic Compounds"; Interscience: New York, 1954; p 468. <sup>i</sup> Mixture of 90% 4-CH<sub>3</sub>,3'-NO<sub>2</sub> and 10% 4-CH<sub>3</sub>,4'-NO<sub>2</sub>. <sup>j</sup> 4-CH<sub>3</sub>,4-Br exclusively. <sup>k</sup> Mixture of 60%  $\alpha$  and 40%  $\beta$ .

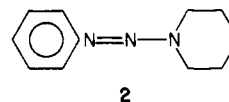
the Gomberg and Pschorr reactions and the Meerwein<sup>7b</sup> arylation, but the reactions were unable to compete synthetically with classical diazonium ion methods.<sup>6–9</sup> Studies also appeared about the use of aryltriazenes as alkylation agents.<sup>10,11</sup> A rebirth began in the 1970s for aryltriazenes when reports appeared about their use in the preparation of radiolabeled aryl fluorides and aryl iodides.<sup>12–17</sup> Tewson and Welch reported the preparation of aryl fluorides from aryltriazenes and cesium fluoride in methanesulfonic acid,<sup>13a</sup> and they further reported the synthesis of <sup>18</sup>F-haloperidol.<sup>13b</sup> Recently, Barrio et al.<sup>14</sup> and Foster, Heindel, et al.<sup>15</sup> reported new methodology for the preparation of aryl iodides from aryltriazenes. These new methods have received attention in the synthesis of radiolabeled aryl iodides of interest as pharmaceuticals and as imaging agents.

Nuclear magnetic resonance spectroscopic studies of aryltriazenes have been directed toward understanding the rotational barriers<sup>18–19</sup> and electronic characteristics<sup>20–22</sup>

of the intriguing triazene system.

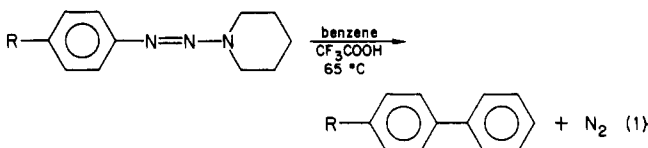
The Gomberg–Bachmann biaryl synthesis uses arenediazonium ions in an aqueous heterogeneous mixture of the aromatic reactant and base.<sup>23</sup> The erratic yields of the Gomberg–Bachmann reaction are at least in part because of the instability of arenediazonium salts and the many competing side reactions. Hey et al.<sup>6</sup> and Rondestvedt et al.<sup>7</sup> attempted to use aryltriazenes as arenediazonium ion synthons in reactions that produced biaryls. Their reactions also gave low yields of biaryls because of heterogeneous conditions and high reaction temperatures.

We have observed that biaryls can be prepared in moderate to good yields by the reaction of 1-aryl-3,3-(pentanediy)triazenes (2) with an aromatic solvent in a



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homogeneous reaction at 65 °C promoted by trifluoroacetic acid (eq 1). The results for 18 triazenes, given in Table



I, show that yields are better than those obtained by the Gomberg–Bachmann reaction and approach the yields obtained recently by Gokel in a phase-transfer catalyzed Gomberg–Bachmann reaction.<sup>24</sup> Furthermore the handling of aryltriazenes is completely safe as contrasted with the hazards of handling arenediazonium salts, and the aryltriazenes can be stored conveniently for long durations. Also the nonaqueous acidic conditions used with aryltriazenes prevent many of the side reactions, phenol and

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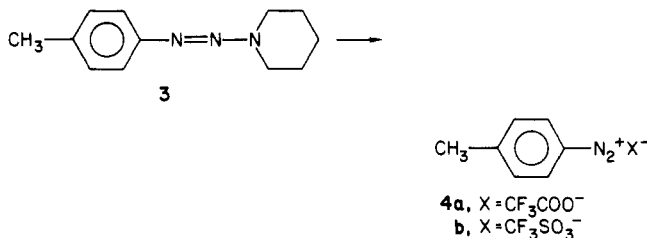
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indazole formation, observed under the aqueous basic conditions of the Gomberg-Bachmann reaction. Although isolation of an aryltriazene requires an additional step, it assures that impurities in the starting amine will be removed. Furthermore, the yields reported in Table I may be improved by the additions of certain reagents, e.g., palladium and iodine, which were studied subsequent to our initial conditions as described later in this paper.

### Mechanism

Arenediazonium ions are well-known to decompose through aryl cations and aryl radicals.<sup>24,25</sup> Similarly, aryltriazenes are thought to produce arenediazonium ions which react by loss of nitrogen to produce aryl cations and radicals.<sup>6,7</sup> Barrio et al. studied the decomposition of aryltriazenes in acidic medium and showed that the relative proportions of the two species were affected by the reaction solvent. Their results suggest that a nonpolar solvent would favor formation of aryl radicals.<sup>14b</sup>

The reaction of 1-*p*-tolyl-3,3-(pentanediyl)triazene (**3**) in benzene solution at 65 °C produces 1 equiv of nitrogen gas within 3 h, and 4-methylbiphenyl can be isolated in 65% yield. When the reaction is conducted in cold benzene (6–10 °C), a white crystalline diazonium salt, *p*-toluenediazonium trifluoroacetate (**4a**), is isolated in 80% yield when trifluoroacetic acid is used, and the *p*-toluenediazonium trifluoromethanesulfonate (**4b**) is isolated in 79% yield when trifluoromethanesulfonic acid is used, but a diazonium salt cannot be obtained from methanesulfonic acid. Both salts shows remarkable stability and can be kept in a freezer without apparent deterioration for several months. Reaction of the salts with warm benzene (60 °C) produces 4-methylbiphenyl in 20% yield from only the trifluoroacetate, but the trifluoromethanesulfonate fails to produce 4-methylbiphenyl.



Consistently, only trifluoroacetic acid is effective in biphenyl production from aryltriazenes, as neither trifluoromethanesulfonic acid nor methanesulfonic acid is successful. A solution of trifluoroacetate in D<sub>2</sub>O decomposes with nitrogen evolution over a period of 4 days to produce deuterated *p*-cresol and trifluoroacetic acid quantitatively.

A study of the effect of reaction temperature and additives on the yield of 4-methylbiphenyl from **3** is presented in Table II. Most notable, radical inhibitors are observed to reduce the yield of 4-methylbiphenyl by up to 35%. But curiously trace iodine actually increases the yield of biaryl by 17%. Palladium additives, which can operate by catalyzing the loss of nitrogen,<sup>26</sup> improve the reaction yield 10–15%. We did not apply the additive study to all the compounds shown in Table I, but it is likely that those yields would be improved by the inclusion of additives, especially palladium acetate.

The results thus indicate that a free radical process involving aryl radicals is involved in the reaction mecha-

Table II. Additive Effect on Biaryl Yield

additive <sup>a</sup>	% yield <sup>b</sup>	additive <sup>a</sup>	% yield <sup>b</sup>
UV light	55	I <sub>2</sub> (150 mg)	30
dark	28	I <sub>2</sub> (732 mg)	20
25 °C	16	5% Pd on Carbon	65
40 °C	31	Pd(OAc) <sub>2</sub>	60
65 °C	50	Zn dust	57
O <sub>2</sub>	35	Th(OAc) <sub>2</sub>	50
hydroquinone	15	Zn(ClO <sub>4</sub> ) <sub>2</sub>	50
I <sub>2</sub> (10 mg)	67		

<sup>a</sup> Compound **3** (6.09 g, 0.03 mol), additive (10 mg), trifluoroacetic acid (4.6 mL, 0.06 mol), 3 h; benzene, 300 mL; temperature, 65 °C unless otherwise stated. <sup>b</sup> Isolated yield of 4-methylbiphenyl.

nism. Several further results also substantiate this conclusion. When **3** is allowed to react with trifluoroacetic acid in a equal molar mixture of benzene and hexane, the yield of 4-methylbiphenyl is reduced to 20%, and toluene is obtained in 30% yield. Toluene is likely produced through hydrogen abstraction from hexane by the *p*-tolyl radical.

Furthermore, reactions of **3** with benzene or of 1-phenyl-3,3-(pentanediyl)triazene with toluene do not produce radical dimerization products, diphenylmethane or bibenzyl. A similar reaction reported by Rondestvedt<sup>7</sup> et al., who decomposed the phenyltriazene in toluene solution with acetic acid at 160 °C, did produce both diphenylmethane and bibenzyl. Apparently, our reaction conditions produce free radicals at a much lower concentration than do the conditions reported by Rondestvedt and could be the reason for the improvement of yields in our case.

In a study of the relative reactivity of the intermediate species generated from the phenyltriazene, pairs of reactants are allowed to compete in the reaction. The results show that toluene reacts 1.5 times the rate of benzene while chlorobenzene reacts 0.42 times the rate of benzene. In electrophilic reactions relative reactivities are much more amplified. For example, the review by Brown and Stock<sup>27</sup> shows that toluene reacts 1.6–1650 times faster than the rate of benzene whereas chlorobenzene reacts 0.01–0.2 times slower than the rate of benzene. More consistent with our results are the aromatic phenylation results of Hey et al.,<sup>28</sup> who observed reactivity of 1.23 for toluene and 1.06 for chlorobenzene relative to benzene. Thus the overall results of our studies clearly show that aryl radicals are produced as intermediates in our reaction. However this does not rule out the possibility that a small portion of the reaction still proceeds through aryl cations.

The selectivity of biaryl formation was studied by using several substrate solvents which could yield several possible isomers. In the cases of thiophene or bromobenzene as substrates only one isomer was obtained. However, nitrobenzene and pyridine gave mixtures of isomers. Thus, in comparison with Gomberg-Bachmann methods, which always produce mixtures, the aryltriazene method shows some selectivity. Although both of the methods involve aryl radicals, it is likely that the aryltriazene method generates radicals at lower concentrations and could be the reason for selectivity differences.

### Experimental Section

Melting points were taken on a Hoover melting point apparatus and were uncorrected. <sup>1</sup>NMR spectra were obtained on a Perkin-Elmer R24B (60 MHz) instrument in CDCl<sub>3</sub> solution with internal tetramethylsilane (δ 0.0) as a reference standard. Infrared

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Table III. Yields and Properties of 1-(4R-Aryl)-3,3-(pentanediy)triazene

R	% yield	mp, °C
H	81	30-40
CH <sub>3</sub>	86	41-43
C <sub>2</sub> H <sub>5</sub>	75	46-47
OCH <sub>3</sub>	83	29-31
OC <sub>2</sub> H <sub>5</sub>	82	51-53
OC <sub>4</sub> H <sub>9</sub>	69	37-39
COCH <sub>3</sub>	65	65-66
Cl	87	39-41
Br	87	55-56
I	72	61-62
F <sup>a</sup>	67	26-27
2,4-F <sub>2</sub> <sup>b</sup>	79	58-60
NO <sub>2</sub>	79	87-88

<sup>a</sup><sup>19</sup>F NMR (84.26 MHz)  $\phi$ -117.9 vs. CFC<sub>3</sub>. <sup>b</sup><sup>19</sup>F NMR (84.26 MHz)  $\phi$ -115.3, -124.1 vs. CFC<sub>3</sub>.

spectra were obtained on a Perkin-Elmer 710-B spectrophotometer. Refractive indexes were taken on a Bausch and Lomb refractometer with the sodium D line as reference at a temperature of 20 °C.

Aromatic amines were used as obtained from commercial sources. Trifluoroacetic acid was obtained in 99% purity from Aldrich Chemical Co. Benzene was dried by distillation from lithium aluminum hydride and then stored over 4-Å molecular sieves.

**Aryltriazenes. General Method.** Aniline (9.11 mL, 0.10 mol) was added to 300 mL of 1 M hydrochloric acid at room temperature. The solution was stirred and cooled to 0 °C. After 15 min, sodium nitrite (6.90 g, 0.10 mol) in 50 mL of water was added slowly to the stirred mixture. After 30 min at 0 °C, the mixture contained a yellow solid. Piperidine (11 mL, 0.11 mol) was added dropwise. After 30 min at 0 °C, the yellow-orange precipitate was collected by suction filtration. The solid was dissolved in ether, dried over MgSO<sub>4</sub>, and concentrated to give the triazene. Recrystallization from ether, petroleum ether, or ethanol gave 1-phenyl-3,3-(pentanediy)triazene (15.31 g, 81%), mp 39-40 °C.

Structure proof for the triazene was obtained through conversion to known biaryl and a characteristic <sup>1</sup>H NMR absorption for the piperidyl ring at  $\delta$  1.7 and 3.7. Yields and properties for the triazenes, RPhN=NN(CH<sub>2</sub>)<sub>5</sub>, are given in Table III.

**(p-Toluenediazonium Trifluoroacetate (4a).** 1-(p-Tolyl)-3,3-(pentanediy)triazene (6.09 g, 0.03 mol) was placed in a 500-mL three-necked round-bottomed flask containing 250 mL of anhydrous benzene. The solution was cooled to 5 °C causing some benzene to freeze on the walls of the flask. Trifluoroacetic acid (4.62 mL, 0.06 mol) was added dropwise. The precipitated diazonium salt was filtered by suction through a fritted-glass funnel. The salt was washed with cold dry ether to give a white diazonium salt which was freed of excess solvent under reduced pressure. The salt **4a** weighed 5.6 g (80%); mp 71-73 °C; <sup>1</sup>H NMR (D<sub>2</sub>O)  $\delta$  2.2 (s, CH<sub>3</sub>), 7.22 (d, *J* = 8 Hz, Ar), 7.75 (d, *J* =

8 Hz, Ar); <sup>13</sup>C NMR (15 MHz, D<sub>2</sub>O)  $\delta$  0.0 (CH<sub>3</sub>), 93.26 (q, *J* = 289 Hz, CF<sub>3</sub>), 109, 111, 134 (Ar), 139 (q, *J* = 37 Hz, C=O); <sup>19</sup>F NMR (84.26 MHz, D<sub>2</sub>O)  $\phi$ -69.9 ( $\alpha$ , CF<sub>3</sub>); IR (Nujol) 2260 cm<sup>-1</sup> (N<sup>+</sup>=N).

**(p-Toluenediazonium Trifluoromethanesulfonate (4b).**

The procedure used was the same that described for **4a** except that trifluoromethanesulfonic acid was used: yield 6.35 g (79%); mp 63-65 °C; <sup>1</sup>H NMR (D<sub>2</sub>O)  $\delta$  2.0 (s, CH<sub>3</sub>), 7.2 (d, *J* = 8 Hz, Ar), 7.7 (d, *J* = 8 Hz, Ar); <sup>13</sup>C NMR (D<sub>2</sub>O)  $\delta$  0.0 (s, CH<sub>3</sub>), 97.98 (q, *J* = 317 Hz, CF<sub>3</sub>), 109.8, 110, 134 (Ar); IR (Nujol) 2230 cm<sup>-1</sup> (N<sup>+</sup>=N).

**Biaryl Preparation. General Procedure.** 1-Phenyl-3,3-(pentanediy)triazene (6.09 g, 0.03 mol) and 300 mL of dry benzene were placed in a 500-mL three-necked flask fitted with an addition funnel and condenser. The solution was heated to 65-70 °C, and trifluoroacetic acid (4.62 mL, 0.06 mol) was added dropwise over 10-15 min. The solution darkened and nitrogen gas evolved over 3 h. The cooled solution was added to 300 mL of 5% sodium carbonate solution, followed by extraction with ether (three 300-mL portions). The ether was removed under vacuum, and the resulting product was chromatographed over a column of alumina (15 in.  $\times$  1 in.) with 3:1 hexane/methylene chloride as eluent. The biaryl was obtained in a long yellow band which eluted first. Removal of the solvent gave pure biphenyl (1.85 g, 40%); mp 68-69 °C. Yields and properties of all the biphenyls prepared in this manner are given in Table I.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

**Registry No.** **2** (R = H), 16978-76-0; **2** (R = 4-CH<sub>3</sub>), 51274-57-8; **2** (R = 4-OCH<sub>3</sub>), 74148-29-1; **2** (R = 4-OC<sub>2</sub>H<sub>5</sub>), 87261-58-3; **2** (R = 4-OBu), 96227-74-6; **2** (R = 4-C<sub>2</sub>H<sub>5</sub>), 96227-75-7; **2** (R = 4-F), 332-01-4; **2** (R = 2-F, R' = 4-F), 96227-76-8; **2** (R = 4-Cl), 62499-15-4; **2** (R = 4-Br), 87261-59-4; **2** (R = 4-I), 96227-77-9; **2** (R = 4-NO<sub>2</sub>), 52010-83-0; **2** (R = 4-COCH<sub>3</sub>), 87261-60-7; **4a**, 49724-60-9; **4b**, 96227-78-0; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 106-49-0; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 644-08-6; *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 104-94-9; *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 613-37-6; *p*-CH<sub>3</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 156-43-4; *p*-CH<sub>3</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 613-40-1; *p*-BuOC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 4344-55-2; *p*-BuOC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 6842-78-0; *p*-C<sub>2</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 589-16-2; *p*-C<sub>2</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 5707-44-8; *p*-FC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 371-40-4; *p*-FC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 324-74-3; 2,4-F<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 367-25-9; 2,4-F<sub>2</sub>C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 37847-52-2; *p*-ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 106-47-8; *p*-ClC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 2051-62-9; *p*-BrC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 106-40-1; *p*-BrC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 92-66-0; *p*-IC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 540-37-4; *p*-IC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 1591-31-7; *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 100-01-6; *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 92-93-3; *p*-CH<sub>3</sub>COC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 99-92-3; *p*-CH<sub>3</sub>COC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>, 92-91-1; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*m*, 53812-68-3; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*p*, 2143-88-6; 2,5-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>C<sub>6</sub>H<sub>5</sub>, 7372-85-2; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Br-*p*, 50670-49-0; aniline, 62-53-3; piperidine, 110-89-4; benzene, 71-43-2; biphenyl, 92-52-4; thiophene, 110-02-1; 2-*p*-tolylthiophene, 16939-04-1; nitrobenzene, 98-95-3; *p*-xylene, 106-42-3; bromobenzene, 108-86-1; pyridine, 110-86-1; 2-*p*-tolylpyridine, 4467-06-5; 3-*p*-tolylpyridine, 4423-09-0.