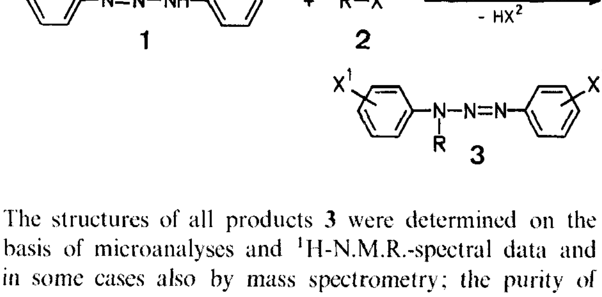
A Convenient General Synthesis of 3-Alkyl-1,3-diaryltriazenes from 1,3-Diaryltriazenes using Phase-Transfer Catalysis

Gaston Vernin*, Jacques Metzger

Laboratoire de Chimie Moléculaire, Associé au C.N.R.S. L.A. N° 126, Faculté des Sciences et Techniques de Saint-Jérôme, Rue Henri Poincaré, F-13397 Marseille Cédex 4, France

Recently, we reported a general synthesis of 1,3-diaryltriazenes by aprotic decomposition of arylamines in the presence of isoamyl nitrite[1]. The biological importance of triazenes[2] prompted us to describe a simple and rapid method for the *N*-alkylation of these compounds, using phase-transfer catalysis conditions according to Mąkosza's method[3]. A limited number of examples of the preparation of 3-alkyl-1,3-diaryltriazenes (**3**) is mentioned in the literature[4]. The classical procedure which consists of the reaction of an arenediazonium salt with a secondary amine in buffered medium[5] is simple but it does not afford good yields and the starting *N*-alkylarenamines are not always easily accessible; further, the crude triazenes have to be purified by column chromatography.

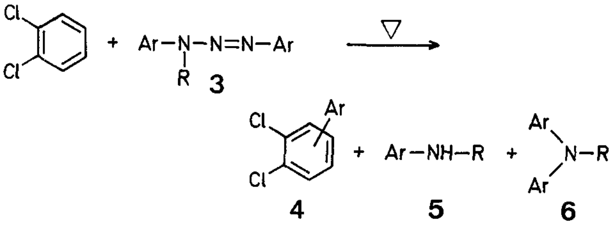
The procedure described here is simple and fast. For example, a solution of an 1,3-diaryltriazene (**1**) in 50 % aqueous sodium hydroxide and benzene is stirred for a few minutes at 50–60° in the presence of a catalytic amount of triethylbenzylammonium chloride (TEBA) and excess alkyl halide (**2**). The reaction, as monitored by T.L.C., proceeds fast. We observed first a red color, corresponding to complex formation of the triazene anion with the ammonium cation, which soon disappears to give a clear solution; work-up of this solution affords the pure triazene **3**.



The structures of all products **3** were determined on the basis of microanalyses and ^{1}H-N.M.R.-spectral data and in some cases also by mass spectrometry; the purity of the products was checked by T.L.C. on silica gel.

The 3-alkyl-1,3-diaryltriazenes **3** possess a number of interesting properties some of which are discussed below.

3-Alkyl-1,3-diaryltriazenes (**3**) may serve as a convenient *source of aryl radicals*. Thus, the thermal decomposition of compounds **3** (X^1 = 4-Cl) in *o*-dichlorobenzene leads to arylation of *o*-dichlorobenzene to give a mixture of isomeric dichlorobiphenyls (**4**) along with the secondary and tertiary amines **5** and **6**, respectively.



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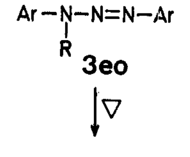
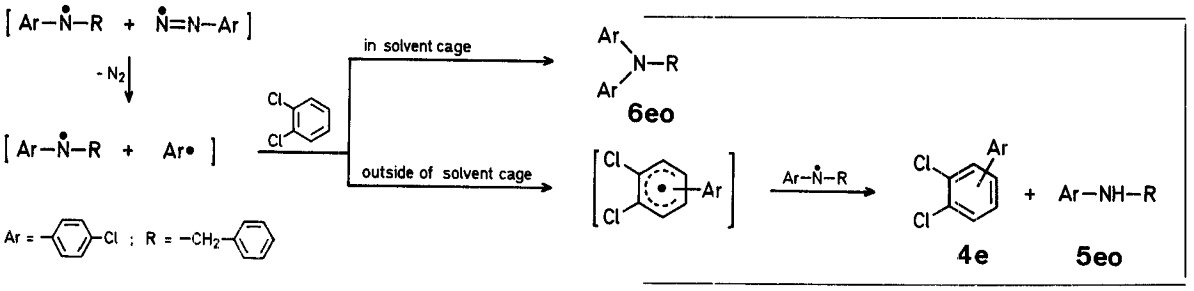
The reaction is assumed to proceed via intermediate formation of aryl radicals as formulated below for the thermolysis of **3eo**.

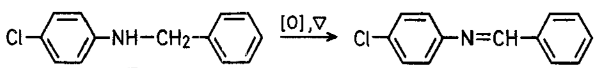




The triazenes **3** undergo thermal decomposition with formation of alkylarylamino- and arylazo radicals. Elimination of nitrogen from the arylazo radicals yields aryl radicals which then either migrate out of the solvent cage and substitute the substrate homolytically to give an intermediate σ-complex which reacts with the alkylarylaminyl radical to give **4** and **5**, or which in the solvent cage recombines with the aminyl radical to give the tertiary amine **6**.

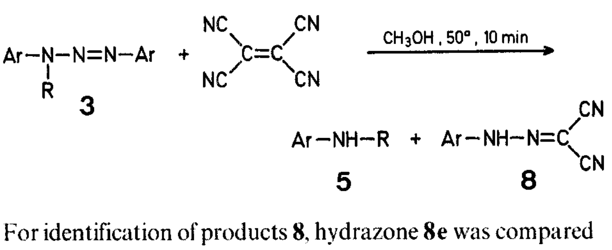
The biaryls **4** were identified by comparison of their G.L.C. retention times and their mass spectra with those of the products obtained by aprotic decomposition of the corresponding arenamines (or triazenes **1**) in *o*-dichlorobenzene. Distinction between the isomers of **4** (2,3- and 3,4-dichlorobiphenyls) was based on the well known fact that on non-polar chromatography columns the *o*-isomers have a shorter retention time than the *m*-isomers. The *N*-alkylanilines **5** were identified by comparison of their G.L.C., T.L.C., and mass-spectral properties with those of authentic samples prepared from anilines and alkyl halides under phase-transfer conditions. The tertiary amines **6** were identified on the basis of their G.L.C. and mass-spectral data.

In the case of triazene **3eo**, the imine **7** (identified by comparison with an authentic sample[7]) is obtained as a side product of the thermal decomposition, probably via oxidation of the amine **5eo** in the silicon column at 200°.



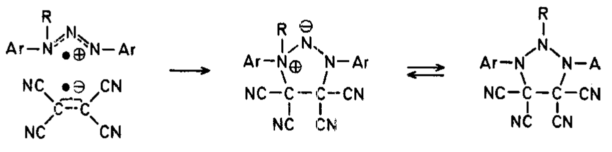
5eo **7**

The triazenes **3** react with tetracyanoethylene in methanol to give *N*-alkylanilines (**5**) and mesoxalodinitrile arylhydrazones (**8**, 80% yield).



For identification of products **8**, hydrazone **8e** was compared with the products obtained from 1-(4-chlorophenyl)-3-methyl-3-(4-methylphenyl)-triazene and tetracyanoethylene in methanol[6].

The reaction leading to **8** is assumed to proceed via the initial formation of the charge-transfer complex **9** (cf. Ref. [6]) which causes the observed green color of the mixture.



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^{1}H-N.M.R. spectra were recorded at 100 MHz using a Varian XL 100 spectrometers; I.R. spectra were recorded on a Perkin Elmer 225, and Mass spectra on a MS 50.

3-Alkyl-1,3-diaryltriazenes (3):

To a stirred solution of the triazene **1** (5 mmol) in 50% aqueous sodium hydroxide (20 ml) and benzene (40 ml) containing TEBA (0.5 mmol), the alkyl halide **2** (10 mmol) is added in one portion at 50–60°. The reaction (as monitored by T.L.C.) proceeds fast, requiring 10–20 min for completion. Color change of the organic layer indicates complete alkylation. The benzene layer is separated, washed twice with water, and dried with magnesium sulfate. The benzene is evaporated in vacuo, the yellow residue which solidifies on cooling is washed with petroleum ether, isolated by suction, and dried in the air. Some products (**3ao**, **3bl**, **3bp**, **3dp**) are sensitive to light (fast brown coloration) and must be stored in the dark.

In the case of alkyl halides of poor reactivity, considerable decomposition of the phase-transfer catalyst (TEBA) with formation of the corresponding 3-benzyl-1,3-diaryltriazenes is observed. This drawback may be partially overcome by carrying out the reaction (100–120°, 1 h) in xylene in the presence of excess powdered sodium hydroxide.

Thermal Decomposition of 3-Benzyl-1,3-bis[4-chlorophenyl]-triazene (3eo) in o-Dichlorobenzene:

A solution of triazene **3eo** (100 mg) in *o*-dichlorobenzene (5 ml) is heated at 120–130° for 10–15 min. Excess solvent is then removed in vacuo. The residue is separated into two fractions by preparative T.L.C. on silica gel (PF 254+366) using benzene as eluent. The *first fraction* (Rf≥0.90; 45 mg) is a mixture of 2,3,4′- (57%) and 3,4,4′-trichlorobiphenyl (43%) (**4e**) as evidenced by G.L.C. (10% Silicone SE 30 column) and G.L.C./M.S. (Mat 111, 80 *e*V) analysis. [The mass spectra of the two isomers **4e** (m/e = 260, 258, 256, 188, 186) were identical with those observed for the products obtained by aprotic decomposition of the corresponding 4-chloroanilines or triazenes in *o*-dichlorobenzene].

Distinction between the two isomers **4e** was based on the well-known fact that on non-polar chromatographic columns the *o*-isomers have a shorter retention time (α_r relative to biphenyl = 3.8 in this case) than the *m*-isomers (α_r=4.8). Further, the *o*-position is generally the most reactive one in homolytic aromatic substitution[8].

From the *second fraction* (Rf≈0.70–0.85), *N*-benzyl-4-chloroaniline (**5eo**, Rf: 0.78) is obtained as colorless oil (40 mg) [identified by comparison with an authentic sample prepared from 4-chloroaniline and benzyl chloride under phase-transfer conditions] which is purified by preparative T.L.C.

$C_{13}H_{12}ClN$	calc.	C 71.72	H 5.55	N 6.43
(217.7)	found	71.45	5.40	6.28

Table. Synthesis of 3-Alkyl-1,3-diaryltriazenes (**3**) from 1,3-Diaryltriazenes (**1**) and Alkyl Halides (**2**) under Phase-Transfer Conditions

1	X^1	**2**	$R-X^2$	**3**[a]	Yield[b] [%]	m.p.[c]	Molecular formula[d]	T.L.C.[e] R_F	^{1}H-N.M.R. ($CDCl_3$/TMS)[f] δ [ppm]
1a	H	**2o**	$C_6H_5-CH_2-Cl$	**3ao**	90	70–72°	$C_{19}H_{17}N_3$ (287.4)	0.38	7.7–7.0 (m, 15H); 5.48 (s, 2H)
1b	4-CH_3	**2l**	H_3C-J	**3bl**	80	48–50°	$C_{15}H_{17}N_3$ (239.8)	0.48 (A)	7.6–7.0 (m, 8H); 3.52 (s, 3H); 2.32 (s, 3H); 2.28 (s, 3H)
		2p	$H_2C=CH-CH_2-Br$	**3bp**	90	52–54°	$C_{17}H_{19}N_3$ (265.4)	0.53 (A)	7.6–7.0 (m, 8H); 6.1–5.6 (m, 1H); 5.2–4.8 (m, 4H); 2.32 (s, 3H); 2.30 (s, 3H)
1c	4-OCH_3	**2m**	C_2H_5-Br	**3cm**	80	66–67°	$C_{16}H_{19}N_3O_2$ (290.4)	0.30 (A)	7.5 (d, 2H); 7.32 (d, 2H); 6.9 (d, 4H); 4.24 (q, 2H); 3.82 (s, 6H); 1.24 (t, 3H)
1d	4-F	**2p**	$H_2C=CH-CH_2-Br$	**3dp**	85	76–78°	$C_{15}H_{13}F_2N_3$ (235.3)	0.46 (A)	7.7–6.9 (m, 8H); 6.1–5.6 (m, 1H); 5.3–4.7 (m, 4H)
1e	4-Cl	**2l**	H_3C-J	**3el**	80	72–74°	$C_{13}H_{11}Cl_2N_3$ (280.2)	0.35 (A)	7.6–7.3 (m, 8H); 4.65 (s, 3H)
		2m	C_2H_5-Br	**3em**	75	80°	$C_{14}H_{13}Cl_2N_3$ (294.2)	0.50 (A)	7.6–7.3 (m, 8H); 4.34 (q, 3H); 1.3 (t, 3H)
		2p	$H_2C=CH-CH_2-Br$	**3ep**	85	78–80°	$C_{17}H_{13}Cl_2N_3$ (306.2)	0.47	7.6–7.2 (m, 8H); 6.1–5.6 (m, 1H); 5.3–4.7 (m, 4H)
		2n	n-C_4H_9-Br	**3en**	85	72–74°	$C_{16}H_{17}Cl_2N_3$ (322.2)	0.65	7.6–7.3 (m, 8H); 4.28 (t, 2H); 1.9–1.2 (m, 4H); 0.92 (t, 3H)
		2o	$C_6H_5-CH_2-Cl$	**3eo**	80	110°	$C_{19}H_{15}Cl_2N_3$ (356.3)	0.44 (A)	7.55–7.0 (m, 13H); 5.47 (s, 2H)
1f	4-Br	**2p**	$H_2C=CH-CH_2-Br$	**3fp**	80	62–64°	$C_{17}H_{13}Br_2N_3$ (419.1)	0.48 (A)	7.65–7.1 (m, 8H); 6.1–5.6 (m, 1H); 5.4–4.8 (m, 4H)
1g	3,5-di-Cl	**2p**	$H_2C=CH-CH_2-Br$	**3gp**	85	130–132°	$C_{15}H_{11}Cl_4N_3$ (375.1)	0.68 (A)	7.5–7.0 (m, 6H); 6.1–5.6 (m, 1H); 5.3–4.7 (m, 4H)
1h	2,3,4-tri-Cl	**2p**	$H_2C=CH-CH_2-Br$	**3hp**	85	106–108°	$C_{15}H_9Cl_6N_3$ (514.9)	0.82 (A)	7.6–7.0 (m, 4H); 6.2–5.7 (m, 1H); 5.4–5.0 (m, 2H); 4.78 (d, 2H)
1i	2,3,5-tri-Cl	**2p**	$H_2C=CH-CH_2-Br$	**3ip**	85	52–54°	$C_{15}H_9Cl_6N_3$ (514.9)	0.77 (A)	7.55–7.15 (m, 4H); 6.1 (t), 6.0 (t), 5.9 (t), 5.8 (t) 1H; 5.23 (d, 1H); 5.20 (d, 1H); 4.7 (d, 2H)
1j	4-$CO-CH_3$	**2l**	H_3C-J	**3jl**	90	128–130°	$C_{17}H_{17}N_3O_2$ (295.3)	0.33 (C); 0.58 (D)	8.1–7.4 (m, 8H); 3.68 (s, 3H); 2.56 (s, 3H); 2.54 (s, 3H)
		2m	C_2H_5-Br	**3jm**	55	120–122°	$C_{18}H_{19}N_3O_2$ (309.4)	0.35 (C); 0.58 (D)	8.1–7.5 (m, 8H); 4.35 (q, 2H); 2.55 (s, 6H); 1.27 (t, 3H)
		2p	$H_2C=CH-CH_2-Br$	**3jp**	90	103–105°	$C_{19}H_{19}N_3O_2$ (321.4)	0.36 (C); 0.63 (D)	8.1–7.4 (m, 8H); 6.1–5.6 (4t, 1H); 5.3–4.8 (m, 4H); 2.55 (s, 3H); 2.53 (s, 3H)
		2n	n-C_4H_9-Br	**3jn**	70	83–85°	$C_{20}H_{21}N_3O_2$ (335.4)	0.38 (C); 0.66 (D)	8.05–7.4 (m, 8H); 4.32 (t, 2H); 2.6–2.5 (2s, 6H); 2.0–1.3 (m, 4H); 1.1 (t, 3H) (in CCl_4)
		2o	$C_6H_5-CH_2-Cl$	**3jo**	75	144–146°	$C_{23}H_{21}N_3O_2$ (371.4)	0.40 (C); 0.65 (D)	8.1–7.0 (m, 13H); 5.6 (s, 2H); 2.55 (s, 3H); 2.52 (s, 3H)
1k	4-$CO-OC_2H_5$	**2l**	H_3C-J	**3kl**	75	120°	$C_{19}H_{21}N_3O_4$ (355.4)	0.63 (C); 0.86 (D)	8.2–7.4 (m, 8H); 4.35 (q, 4H); 3.63 (s, 3H); 1.35 (t, 6H)
		2m	C_2H_5-Br	**3km**	70	80–82°	$C_{20}H_{23}N_3O_4$ (370.4)	0.65 (C); 0.88 (D)	8.2–7.4 (m, 8H); 4.37 (q, 6H); 1.35 (2t, 6H); 1.27 (t, 3H)
		2p	$H_2C=CH-CH_2-Br$	**3kp**	80	70–72°	$C_{21}H_{23}N_3O_4$ (382.4)	0.68 (C); 0.89 (D)	8.2–7.4 (m, 8H); 6.1–5.6 (m, 1H); 5.3–4.8 (m, 4H); 4.35 (q, 4H); 1.35 (t, 6H)
		2n	n-C_4H_9-Br	**3kn**	70	76–78°	$C_{22}H_{27}N_3O_4$ (396.5)	0.70 (C); 0.90 (D)	8.2–7.4 (m, 8H); 4.6–4.1 (m, 6H); 1.8–1.2 (m, 10H); 1.0 (t, 3H)
		2o	$C_6H_5-CH_2-Cl$	**3ko**	85	124–126°	$C_{25}H_{25}N_3O_4$ (431.2)	0.68 (C); 0.89 (D)	8.2–7.1 (m, 13H); 5.56 (s, 2H); 4.37 (q, 4H); 1.4 (2t, 6H)

[a] These products are yellow or yellow orange. Storage in the dark is not necessary, except for **3ao**.

[b] Yield of isolated product after washing (or recrystallization) with petroleum ether.

[c] Measured on a Kofler Heizbank.

[d] All products gave satisfactory microanalyses with the following maximum deviations from the calculated values: C, ±0.3; H, ±0.21; N, ±0.25. The analyses were carried out by Microanalytical Service, University of St-Jérome, Marseille.

[e] The purity of the *N*-alkyltriazenes **3** was checked by T.L.C. on silica gel HF 254+366; eluents: (A) ether, (B) benzene, (C) benzene/ethyl acetate 9/1, (D) benzene/methanol 9/1.

[f] Measured with Perkin-Elmer R-32 (90 MHz) or Varian XL 100 (100 MHz) spectrometers. In most cases, aromatic protons between 8.4–7.0 ppm appeared as two different AA'BB' systems. **3jn** is too instable in $CDCl_3$ and was measured in CCl_4.

M.S.: $m/e = 219$ (M^{+}, 10%), 217 (M^{+}, 30), 142, 138, 111, 91 (100).
^{1}H-N.M.R. ($CDCl_3$): $\delta = 7.4-7.2$ (m, $5H_{arom}$); 7.10 (d, $2H_{arom}$), 6.55 (d, $2H_{arom}$), A_2B_2 system; 4.86 (s, 1H, N$\underline{H}$); 4.26 ppm (s, 2H, C$\underline{H}_2$).

[G.L.C. analysis (silicone SE 30, 200°) of the unpurified amine **5eo** showed the presence of an additional product (10%) which was isolated by preparative G.L.C. (silicone SE 30) and identified as *N*-benzylidene-4-chloroaniline (**7**) by its mass-spectral and ^{1}H-N.M.R.-spectral data and by comparison with an authentic sample prepared according to Ref. [7]; m.p. 60°.]

Reaction of 3-Alkyl-1,3-diaryltriazenes (3) with Tetracyanoethylene; Typical Procedure:

3-Benzyl-1,3-bis[4-chlorophenyl]-triazene (**3eo**; 357 mg, 1 mmol) is dissolved in methanol (20 ml) and tetracyanoethylene (154 mg, 1.2 mmol) is added with stirring at 50–60°. After a few seconds, a blue-green color appears which fades within 5–10 min. [Monitoring of the reaction by T.L.C. on silica gel (benzene as eluent) shows two major yellow spots at Rf 0.30 and 0.77 and spots of traces at 0.35, 0.50, and 0.60]. After the reaction is complete, the solvent is evaporated in vacuo, the residue allowed to stand at room temperature overnight, the solid product isolated by suction, and recrystallized from petroleum ether/benzene to give pure *4-chlorophenylhydrazonomalodinitrile* (**8**, Ar = 4-chlorophenyl); yield: 102 mg (50%); m.p. 191–192° (Ref. [6], m.p. 189–190°).

$C_9H_5ClN_4$ (204.6)

M.S.: $m/e = 204$ (M^{+}), 177, 139, 126, 111.

I.R. (CH_2Cl_2): $\nu_{max} = 3260$ (NH); 2220, 2200 (C≡N); 1600 (C=N); 1560; 1465 (C=C); 840 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 9.8$ (s, 1H, N$\underline{H}$); 7.32 ppm ($4H_{arom}$, A_2B_2 system).

From the petroleum ether/benzene filtrate, the amine **5eo** (30 mg) is isolated by evaporation, dissolution of the residue in petroleum ether, and preparative T.L.C. on silica gel.

Note added in proof: After completion of this work, we have synthesized by the same method, some interesting *N*-substituted triazenes bearing *n*-propyl, 2-chloroethyl, 2-hydroxyethyl, *iso*-butyl, 2,4-dinitrophenyl, and 2,6-dinitro-4-trifluoromethyl-phenyl groups in the 3-position.

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* Correspondence address.

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