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N-Alkyldiarylamines from 3-Alkyl-3-aryl-1-(2-carboxyphenyl)triazenes

Jyuzo Nakayama, Masayuki Yoshida, and Osamu Simamura
Department of Chemistry, Faculty of Science, Tokyo University, Hongo, Tokyo 113

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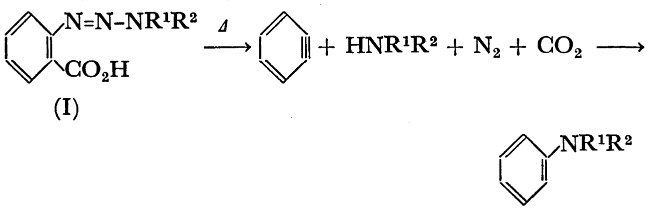
Synopsis. Heating 3-alkyl-3-aryl-1-(2-carboxyphenyl)triazenes in organic media afforded *N*-alkyldiarylamines in good yields, thus providing a useful synthetic route to this type of amines.

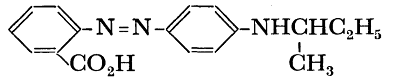
We have shown that 3-substituted 1-(2-carboxyphenyl)triazenes (I) are decomposed in boiling chlorobenzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone to afford 1,2,3,4-tetraphenylnaphthalene, a benzyne adduct, in good yields,[1] while in the absence of the cyclopentadienone 1-(2-carboxyphenyl)-3,3-dimethyltriazene (I; $R^1=R^2=CH_3$) gave *N*,*N*-dimethylaniline (32%) and *N*-methyldiphenylamine (37%) the, products suggestive of the benzyne reaction with dimethylamine and *N*,*N*-dimethylaniline, respectively, in view of the work by Lepley and his co-workers.[2] Furthermore, heating 1-(2-carboxyphenyl)-3-methyl-3-phenyltriazene (Ia; $R^1=CH_3$, $R^2=C_6H_5$) gave *N*-methyldiphenylamine in 72% yield as the sole product. We, therefore, examined the formation of *N*-alkyldiarylamines (II) from 3-alkyl-3-aryl-1-(2-carboxyphenyl)triazenes (I) as a new synthetic route.



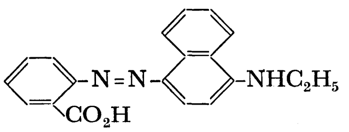
(I)

(II)

The triazenes (I) listed in Table 1 were prepared in excellent yields by diazotization of anthranilic acid by means of sodium nitrite and hydrochloric acid followed by treatment with potassium acetate and *N*-alkylarylamines. With *N*-*sec*-butylaniline and *N*-ethyl-1-aminonaphthalene, however, the azo-coupling reaction took place under the same reaction conditions, affording 4-(*sec*-butylamino)-2′-carboxyazobenzene (III) and 1-(2-carboxyphenylazo)-4-ethylaminonaphthalene (IV), respectively. Weakly basic amines such as diphenylamine and *N*-methyl-4-nitroaniline did not yield any amount of the expected triazenes (I).



(III)



(IV)

Decomposition of the triazenes (I) by heating in organic solvent under reflux gave *N*-alkyldiarylamines (II), and the results are summarized in Table 2. Generally, the yields of *N*-alkyldiarylamines (II) are satisfactory, but 1-(2-carboxyphenyl)-3-phenyltriazene[3] (I; $R^1=H$, $R^2=C_6H_5$) yielded, on being decomposed in boiling chlorobenzene, a mixture of chlorobiphenyls (69%), but no diphenylamine. Evidently, it decomposed homolytically in chlorobenzene to generate phenyl radicals, presumably *via* a diazocarboxylate (V).

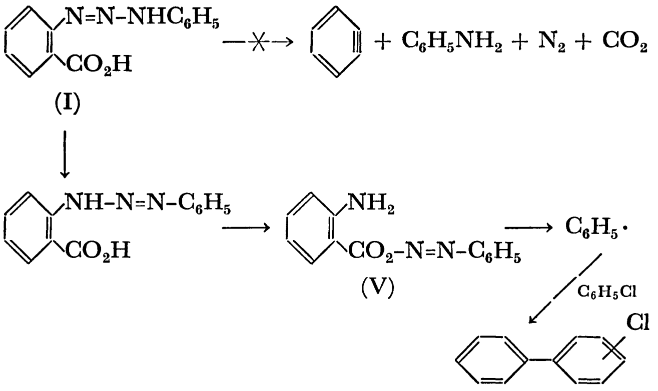


Table 1. 3-Alkyl-3-aryl-1-(2-carboxyphenyl)triazenes (I)

Compound	R^1	R^2	Mp (°C)	Yield (%)	Formula		Elementary analysis (%) C	H	N
Ia	CH_3	C_6H_5	137 (dec)	96	$C_{14}H_{13}N_3O_2$	Found	66.12	4.89	16.73
						Calcd	65.87	5.13	16.46
Ib	C_2H_5	C_6H_5	118 (dec)	93	$C_{15}H_{17}N_3O_2$	Found	67.06	5.51	15.31
						Calcd	66.90	5.61	15.61
Ic	n-C_4H_9	C_6H_5	72— 73 (dec)	94	$C_{17}H_{19}N_3O_2$	Found	68.43	6.40	14.34
						Calcd	68.66	6.44	14.13
Id	$C_6H_5CH_2$	C_6H_5	135—136 (dec)	85	$C_{20}H_{17}N_3O_2$	Found	72.45	5.09	12.98
						Calcd	72.49	5.17	12.68
Ie	C_2H_5	p-$CH_3C_6H_4$	124—125 (dec)	93	$C_{16}H_{17}N_3O_2$	Found	67.95	6.05	14.62
						Calcd	67.82	6.05	14.83
If	$C_6H_5CH_2$	p-ClC_6H_4	152 (dec)	68	$C_{20}H_{16}ClN_3O_2$	Found	65.92	4.49	11.20
						Calcd	65.67	4.41	11.49

TABLE 2. *N*-ALYKYLDIARYLAMINES (II) FROM THE TRIAZENES (I)

Compound	Reaction Conditions[a]	II ($PhNR^1R^2$)			
		R^1	R^2	Yield (%)[b]	Bp (°C/mmHg) or [mp (°C)]
Ia	PhCl, refl., 5 hr	CH_3	C_6H_5	72	122—124/2[c]
Ib	PhCl, refl., 5 hr	C_2H_5	C_6H_5	63	127—129/2[d]
	$PhCH_3$, refl., 8 hr			68	
Ic	Xylene, refl., 5 hr	n-C_4H_9	C_6H_5	64	145—147/2[e]
Id	Xylene, refl., 4 hr	$C_6H_5CH_2$	C_6H_5	56	[86— 87][f]
Ie	PhCl, refl., 5 hr	C_2H_5	p-$CH_3C_6H_4$	77	106—108/0.4
If	PhCl, refl., 9 hr	$C_6H_5CH_2$	p-ClC_6H_4	63	[97— 97.5]

a) Refl. stands for heated under reflux. b) By weighing the isolated material. c) 175/31 (Ref. 4). d) 150/13 (Ref. 4). e) 164/11 (Ref. 4). f) [87] (Ref. 5).

Thus, generally the triazenes (I) are prepared easily from diazotized anthranilic acid and appropriate *N*-alkylarylamines in excellent yields and decompose at moderate temperatures to give satisfactory yields of the amines (II); accordingly the present method provides a useful synthetic route to the amines (II), which are otherwise prepared by the alkylation of diarylamines.[4–6]

Experimental

3-Alkyl-3-aryl-1-(2-carboxyphenyl)triazenes (I). Anthranilic acid (13.7 g, 0.1 mol) was dissolved in a mixture of 200 ml of methanol and 25 ml of concentrated hydrochloric acid and diazotized by addition of a solution of sodium nitrite (6.9 g, 0.1 mol) in 15 ml of water at 0—5 °C. To the resulting diazonium solution were added 200 g of crushed ice, 20 g of powdered potassium acetate (0.2 mol), and an appropriate *N*-alkylarylamine (0.1 mol). The mixture was stirred for 1 hr at 0—5 °C and then for 30 min at room temperature. 3-Alkyl-3-aryl-1-(2-carboxyphenyl)triazene (I) was precipitated by adding 200 ml of water, collected, washed with water and recrystallized from benzene or ethanol.

*4-(*sec*-Butylamino)-2′-carboxyazobenzene (III) and 1-(2-carboxyphenylazo)-4-ethylaminonaphthalene (IV).* These azo-compounds (III and IV) were obtained when *N-sec*-butylaniline and *N*-ethyl-1-aminonaphthalene were used in the preparation of triazoles (I).

Compound III (Found: C, 68.44; H, 6.37; N, 14.42%. Calcd for $C_{17}H_{19}N_3O_2$: C, 68.66; H, 6.44; N, 14.13%), mp 156 °C, ν_{max} (KBr) 3370 (N-H), 2800—2300 (O-H), 1715 (C=O), and 828 (*p*-disubstituted benzene ring) cm^{-1}.

Compound IV (Found: C, 71.41; H, 5.47; N, 12.98%. Calcd for $C_{19}H_{17}N_2O_2$: C, 71.45; H, 5.37; M, 13.16%), mp 185—187 °C, ν_{max} (KBr) 3330 (N-H) and 1700 (C=O) cm^{-1}.

N-Alkyldiarylamines (II). A triazene (I, 10 g) was heated under reflux in 200 ml of solvent for several hr. On cooling, the reaction mixture was washed successively with 1 M sodium hydroxide, 1 M hydrochloric acid, and water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by distillation or recrystallization. Elementary analyses and spectral data for new *N*-alkyldiarylamines (II, $PhNR^1R^2$) are shown below.

Compound IIe ($R^1=C_2H_5$, $R^2=p$-$CH_3C_6H_4$) (Found: C, 84.96; H, 7.87; N, 6.86%. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63%), bp 106—108 °C/0.4 mmHg; NMR ($CDCl_3$) δ 1.15 (t, 3H), 2.15 (s, 3H), 3.66 (q, 2H), and 6.5—7.3 (m, 9H).

Compound IIf ($R^1=C_6H_5CH_2$, $R^2=p$-ClC_6H_4) (Found: C, 77.72;, H, 5.74; N, 4.90%. Calcd for $C_{19}H_{16}ClN$: C, 77.68; H, 5.49; N, 4.77%), mp 97—97.5 °C; NMR (CCl_4) δ 1.15 (t, 3H), 2.15 (s, 3H), 3.66 (q. 2H), and 6.5—7.3 (m, 9H).

Decomposition of 1-(2-carboxyphenyl)-3-phenyltriazene (I; $R^1=H$, $R^2=C_6H_5$) in chlorobenzene. A solution of the triazene (I, 0.62 g) in 50 ml of chlorobenzene was heated under reflux for 2 hr. The reaction mixture was washed successively with 1 M hydrochloric acid, 1 M sodium hydroxide, and water, and dried over anhydrous sodium sulfate. After removal of chlorobenzene under reduced pressure, the brown oily residue was subjected to column chromatography on silica gel. Elution with benzene afforded 0.29 g of chlorobiphenyl (69%), consisting of the *ortho* (55%) and a mixture (45%) of the *meta* and *para* isomers, as revealed by vpc analysis.

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