Conjugated Schiff Bases; 17[1]. Direct Synthesis of Mono-*N*-oxides of Some 1,4-Diazabutadienes

Janusz MOSKAL*

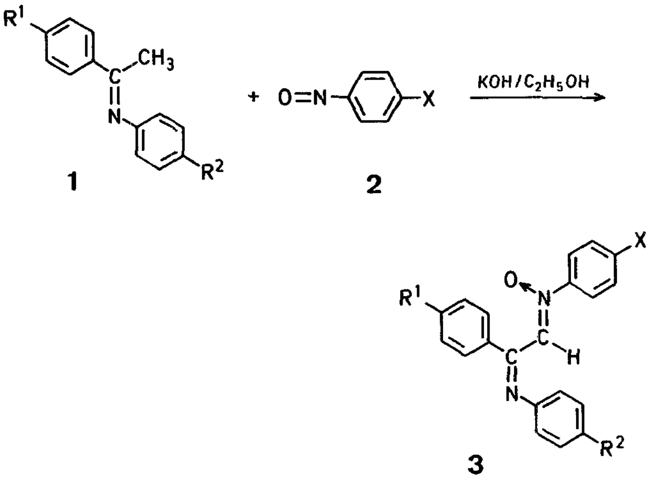
Department of Organic Chemistry, University School of Kielce, Pl-25020 Kielce, Poland

Piotr MILART

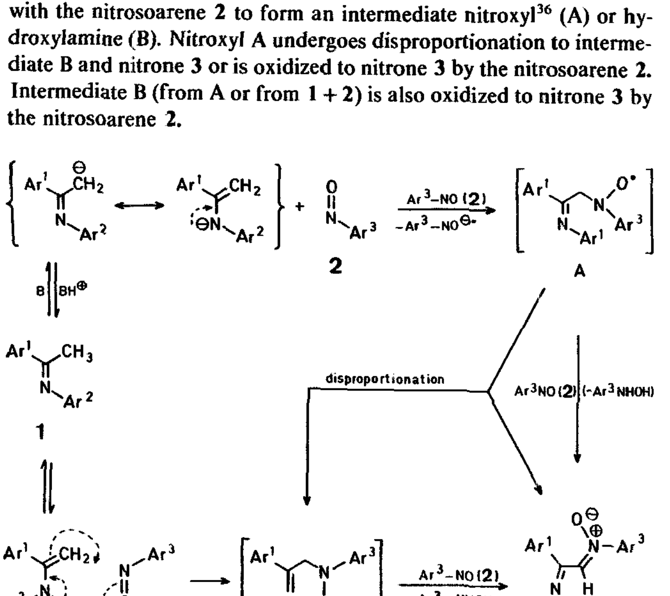
Department of Organic Chemistry, Jagiellonian University, Pl-30060 Cracow, Poland

The base-promoted condensation of *CH*-acids with nitrosoarenes proceeds in different ways depending on factors such as strength of the *CH*-acid, type of nitrosoarene, efficiency of catalyst, reaction time, concentration of reactants, etc.[2-6], yielding either azomethines or/and nitrones. The use of strongly *CH*-acidic compounds such as β-dicarbonyl compounds or some of their nitrogen analogs[7,8] renders possible the synthesis of a series of 1,3-heterodienes containing a C=N double bond which can be employed in heterodiene synthesis[9-12]. Nitrones derived from 1,3-heterodienes (1,3-heterodiene *N*-oxides) have only rarely been described[13,14,16,17,18]; this applies in particular to 1,4-diazabutadiene *mono-N-oxides*[15].

We report here a facile direct synthesis of some 1,4-diazabutadiene 4-oxides (**3**) from 1,*N*-diphenylethanimines (**1**, acetophenone anils) and nitrosobenzenes (**2**).



The reaction is assumed to proceed *via* base-catalyzed isomerization of the imine **1** to its enamine (or the anion thereof) which then reacts with the nitrosoarene **2** to form an intermediate nitroxyl[36] (A) or hydroxylamine (B). Nitroxyl A undergoes disproportionation to intermediate B and nitrone **3** or is oxidized to nitrone **3** by the nitrosoarene **2**. Intermediate B (from A or from **1** + **2**) is also oxidized to nitrone **3** by the nitrosoarene **2**.



The structure of the 1,2,4-triaryl-1,4-diazabutadiene 4-*N*-oxides was established on the basis of microanalyses and spectral data. Thus, there is a characteristic I.R. absorption of the C=N double bond of the nitrone moiety at $\nu \approx 1540$ cm^{-1}[19,20]. The absorption of the azomethine C=N stretching vibrations is found to be shifted towards longer waves due to conjugation with the nitrone group and appears at $\nu \approx 1600$ cm^{-1}[21]. The =N—O stretching vibrations are observable by the strong absorption bands in the region $\nu \approx 1050$ cm^{-1}[22]. The ^{1}H-N.M.R. spectra exhibit complex multiplets in the aromatic proton region ($\delta = 6.7$-7.8 ppm) which also cover the vinyl nitrone proton signals appearing usually at $\delta = 7.6$ to 7.9 ppm[23]. However, use of DMSO-d_6 permits to see these signals as singlets shifted downfield to $\delta \approx 8.05$ ppm. The presence of the single signals suggests the existence of only one geometric isomer. Proton-containing substituents [CH_3, OCH_3, $N(CH_3)_2$] on the aryl rings also produce single signals which reveals the fixed coplanar *Z,Z* arrangement of the substituents attached to the 1,4-diazabutadiene moiety[21,24] and partly hindered rotation around C-2 and C-3 which causes preferentially the *Z,Z,s-trans*

Table 1. New 1,*N*-Diphenylethanimines (**1**) prepared

R^1	R^2	Yield [%]	m.p. [°C]	Molecular Formula[a]	M.S.[b] *m/e*	I.R. (Nujol)[c] ν [cm^{-1}]	U.V. (methanol)[d] λ_{max} [nm] (ε)	^{1}H-N.M.R. (CCl_4/TMS_{int})[e] δ [ppm]
OCH_3	$N(CH_3)_2$	83	132–133°	$C_{17}H_{20}N_2O$ (268.3)	268 (M^+, 95%); 269 (M+1, 18.7); 253 (M−15, 100)	1620 s (C=N); 2416, 1408; 1364 s (CH_{3def}); 815, 770, 695 s (ring subst.)	270 (26100); 328 (6300); 346 (6300)	7.50 (q_{AB}, 4H, $J_{H,H}$ = 10 Hz); 6.85 (m, 4H); 3.92 (s, 3H); 3.00 (s, 6H); 2.28 (s, 3H)
CH_3	$N(CH_3)_3$	84	104–106°	$C_{17}H_{20}N_2$ (252.3)	252 (M^+, 100%); 253 (M+1, 13.9); 237 (M−15, 99)	1615 s (C=N); 1425, 1406; 1360 s (CH_{3def}); 810, 768, 690 s (ring subst.)	262 (24300); 332 (4700); 348 (4700)	7.61 (q_{AB}, 4H, $J_{H,H}$ = 8 Hz); 6.86 (m, 4H); 3.03 (s, 6H); 2.46 (s, 3H); 2.32 (s, 3H)
Cl	$N(CH_3)_2$	86	142–143°	$C_{16}H_{17}ClN_2$ (272.8)	272 (M^+, 100%); 273 (M+1, 19.2); 274 (M+2, 31.6); 257 (M−15, 86.8); 259 (29.5)	1620 s (C=N); 1420, 1406; 1365 s (CH_{3def}); 812, 772, 700 s (ring subst.)	260 (33300); 333 (6000); 362 (6200)	7.71 (q_{AB}, 4H, $J_{H,H}$ = 9 Hz); 6.85 (m, 4H); 3.02 (s, 6H); 2.31 (s, 3H)
Br	$N(CH_3)_2$	80	149–150°	$C_{16}H_{17}BrN_2$ (317.3)	317 (M^+, 100%); 318 (M+1, 18.2); 319 (M+2, 96); 302 (M−15, 36.2); 304 (36)	1620 s (C=N); 1418, 1402; 1358 s (CH_{3def}); 808, 775, 700 s (ring subst.)	263 (16000); 357 (37000)	7.70 (q_{AB}, 4H, $J_{H,H}$ = 10 Hz); 6.82 (m, 4H); 3.00 (s, 6H); 2.27 (s, 3H)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.36; H, ±0.20; N, ±0.17; Hal, ±0.16.

[b] Measured on an LKB-9000S spectrometer using a D.I. system (electron voltage 70 eV, acc. voltage 3.5 kV, I.S. temperature 250 °C).

[c] Determined on a Specord IR-71, Zeiss.

[d] Determined on a Specord UV Zeiss using 0.1 cm silica transmission cells.

[e] Recorded on a Varian-100 spectrometer.

Table 2. 1,2,4-Triaryl-1,4-diazabutadiene 4-*N*-Oxides (**3**)

3	R^1	R^2	X	Yield [%]	m.p. [°C]	Molecular Formula[a]	M.S.[b] m/e	I.R. (Nujol or KBr)[c] ν [cm^{-1}]	U.V. (methanol)[d] λ_{max} [nm] (ε)	^{1}H-N.M.R. (DMSO-d_6/TMS$_{int}$)[e] δ [ppm]
a	H	H	H	66	168–169°	$C_{20}H_{16}N_2O$ (300.4)	300 (M^+, 2.4%); 301 (M+1, 0.6); 284 (M−16, 20.5); 180 (100)	1580 s (C=N); 1520 s (C=NO); 1060 s (NO); 770, 700 s (ring subst.)	262 (19600)	8.00 (s, 1H); 7.7–6.7 (m, 15H)
b	CH_3	H	H	58	179–180°	$C_{21}H_{18}N_2O$ (314.4)	314 (M^+, 2.7%); 315 (M+1, 0.9); 298 (M−16, 21.7); 194 (100)	1582 s (C=N); 1528 s (C=NO); 1062 s (NO); 815, 765, 695 s (ring subst.)	268 (19000)	8.03 (s, 1H); 7.75–6.85 (m, 14H); 2.45 (s, 3H)
c	OCH_3	H	H	53	121–122°	$C_{21}H_{18}N_2O_2$ (330.4)	330 (M^+, 3.1%); 331 (M^+, 1.1); 210 (M−16, 100)	1595 s (C=N); 1565 s (C=NO); 1045 s (NO); 810, 768, 700 s (ring subst.)	282 (23900)	8.00 (s, 1H); 7.75–6.75 (m, 14H); 3.92 (s, 3H)
d	Cl	H	H	62	157–158°	$C_{20}H_{15}ClN_2O$ (334.8)	334 (M^+, 2.7%); 335 (M+1, 0.7); 336 (M+2, 0.9); 318 (M−16, 22.4); 320 (8.1); 214 (95); 216 (32.2)	1605 s (C=N); 1515 s (C=NO); 1055 s (NO); 812, 772, 700 s (ring subst.)	267 (21900)	8.05 (s, 1H); 7.7–7.0 (m, 14H)
e	H	CH_3	H	60	170–171°	$C_{21}H_{18}N_2O$ (314.4)	314 (M^+, 2.9%); 315 (M+1, 0.7); 336 (M+2, 0.9); 298 (M−16, 23.6); 194 (98.9); 77 ($C_6H_5^+$, 100)	1605 s (C=N); 1505 s (C=NO); 1030 s (NO); 815, 752, 695 s (ring subst.)	222 (18400); 263 (18600)	8.05 (s, 1H); 7.75–6.8 (m, 14H); 2.40 (s, 3H)
f	H	OCH_3	H	72	161–162°	$C_{21}H_{18}N_2O_2$ (330.4)	330 (M^+, 2.9%); 331 (M+1, 1.0); 314 (M−16, 23.8); 210 (100)	1605 s (C=N); 1540 s (C=NO); 1055 s (NO); 812, 770, 695 s (ring subst.)	237 (18600); 263 (18800); 366 (5200)	8.03 (s, 1H); 7.80–6.85 (m, 14H); 3.81 (s, 3H)
g	H	Cl	H	35	165–166°	$C_{20}H_{15}ClN_2O$ (334.8)	334 (M^+, 2.9%); 335 (M+1, 0.9); 336 (M+2, 1.0); 318 (M−16, 24.7); 320 (6.6); 214 (100); 216 (34.2)	1605 s (C=N); 1540 s (C=NO); 1050 s (NO); 810, 775, 700 s (ring subst.)	229 (18700); 262 (20300)	8.05 (s, 1H); 7.8–7.0 (m, 14H)
h	H	$N(CH_3)_2$	H	81	177–178°	$C_{22}H_{21}N_3O$ (343.4)	343 (M^+, 3.3%); 344 (M+1, 0.7); 327 (M−16, 26.1); 223 (100)	1605 s (C=N); 1525 s (C=NO); 1058 s (NO); 8.18, 772, 700 s (ring subst.)	260 (24700); 435 (8500)	8.10 (s, 1H); 7.76–6.62 (m, 14H); 3.00 (s, 6H)
i	OCH_3	$N(CH_3)_2$	H	89	170–171°	$C_{23}H_{23}N_3O_2$ (373.4)	373 (M^+, 3.2%); 374 (M+1, 1.2); 357 (M−16, 27.4); 253 (100)	1605 s (C=N); 1510 s (C=NO); 1035 s (NO); 820, 805, 775, 692 s (ring subst.)	253 (25100); 294 (22000); 425 (8500)	8.05 (s, 1H); 7.80–6.65 (m, 13H); 3.90 (s, 3H); 3.03 (s, 6H)
j	CH_3	$N(CH_3)_2$	H	84	161–162°	$C_{23}H_{23}N_3O$ (357.4)	357 (M^+, 2.8%); 358 (M+1, 0.9); 341 (M−16, 25.5); 237 (100)	1605 s (C=N); 1515 s (C=NO); 1050 s (NO); 818, 810, 770, 700 s (ring subst.)	253 (19600); 430 (6100)	8.05 (s, 1H); 7.85–6.70 (m, 13H); 3.05 (s, 6H); 2.45 (s, 3H)
k	Cl	$N(CH_3)_2$	H	58	173–174°	$C_{22}H_{20}ClN_3O$ (377.9)	377 (M^+, 3.8%); 378 (M+1, 1.6); 379 (M+2, 1.3); 361 (M−16, 22.8); 363 (6.1); 256 (100); 258 (33.8)	1605 s (C=N); 1515 s (C=NO); 1035 s (NO); 815, 778, 690 s (ring subst.)	260 (21100); 442 (7900)	8.03 (s, 1H); 7.65–6.65 (m, 13H); 2.85 (s, 6H)
l	Br	$N(CH_3)_2$	H	50	155–156° (dec)	$C_{22}H_{20}BrN_3O$ (422.4)	422 (M^+, 3.1%); 423 (M+1, 1.6); 424 (M+2, 3.1); 406 (M−16, 21.3); 408 (22.0); 301 (100); 303 (99.6)	1605 s (C=N); 1515 s (C=NO); 1060 s (NO); 815, 771, 700 s (ring subst.)	261 (21300); 434 (5400)	8.05 (s, 1H); 7.61 (q_{AB}, $J_{H,H}=8$ Hz, 4H); 7.35–6.78 (m, 5H); 2.90 (s, 6H)
m	H	$N(CH_3)_2$	Cl	52	166–167° (dec)	$C_{22}H_{20}ClN_3O$ (377.9)	377 (M^+, 3.0%); 378 (M+1, 1.2); 379 (M+2, 1.1); 361 (M−16, 24.4); 363 (6.3); 223 (100)	1600 s (C=N); 1520 s (C=NO); 1055 s (NO); 815, 775, 700 s (ring subst.)	253 (20700); 444 (5200)	8.05 (s, 1H); 7.78–6.70 (m, 13H); 2.98 (s, 6H)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.39; H, ±0.13; N, ±0.32; Hal, ±0.21. Exception: **3a**, C, −0.53.

[b] Recorded in part on an LKB-9000S and in part on a Micromass 3D8 (electron voltage, 70 eV).

[c] Recorded on a Specord IR-71 and on a Perkin-Elmer 257 spectrophotometer.

[d] see Footnote d of Table 1.

[e] Recorded on a Hitachi-Perkin-Elmer R-24B spectrometer.

Table 3. 1,2,4-Triaryl-1,4-diazabutadienes (**4**, X = H)

4	R^1	R^2	Yield [%]	m.p. [°C]	Molecular Formula[a]	M.S.[b] m/e	I.R. (Nujol or KBr)[c] ν [cm^{-1}]	U.V. (methanol)[d] λ_{max} [nm] (ε)	^{1}H-N.M.R. (DMSO-d_6/TMS$_{int}$)[e] δ [ppm]
a	H	H	91[f], 95[g]	105-107°	$C_{20}H_{16}N_2$ (284.4)	284 (M$^+$, 7.5%); 285 (M+1, 2); 180 (100)	1590 s (C=N); 1575 s (CH=N); 772, 700 s (ring subst.)	230 (19500); 267 (14100)	8.59, 8.30 (2s, 1H); 8.15 (d, 2H, $J_{H,H}$ = 10 Hz); 7.6-7.0 (m, 13H)
b	CH$_3$	H	88[f]	119-121°	$C_{21}H_{18}N_2$ (298.4)	298 (M$^+$, 18.9%); 299 (M+1, 4.3); 194 (100)	1585 s (C=N); 1565 s (CH=N); 810, 773, 695 s (ring subst.)	238 (21900); 265 (13300)	8.57, 8.32 (2s, 1H); 8.04 (d, 2H, $J_{H,H}$ = 10 Hz); 7.62-6.80 (m, 12H); 2.45 (s, 3H)
c	OCH$_3$	H	82[f]	98-100°	$C_{21}H_{18}N_2O$ (314.4)	314 (M$^+$, 21.5%); 315 (M+1, 5.1); 210 (100)	1590 s (C=N); 1575 s (CH=N); 810, 770, 690 s (ring subst.)	234 (24300); 282 (13000)	8.55, 8.26 (2s, 1H); 8.14 (d, 2H, $J_{H,H}$ = 10 Hz); 7.42-6.70 (m, 12H); 3.81, 3.92 (2s, 3H)
d	Cl	H	94[f], 96[g]	94-95°	$C_{20}H_{15}ClN_2$ (318.8)	318 (M$^+$, 20.2%); 319 (M+1, 4.7); 320 (M+2, 6.8); 214 (100); 216 (33.9)	1585 s (C=N); 1565 s (CH=N); 812, 778, 702 s (ring subst.)	223 (22700); 263 (14700)	8.57, 8.30 (2s, 1H); 8.12 (d, 2H, $J_{H,H}$ = 10 Hz); 7.55-6.75 (m, 12H)
e	H	CH$_3$	96[g]	107-109°	$C_{21}H_{18}N_2$ (298.4)	298 (M$^+$, 35.8%); 299 (M+1, 7.4); 194 (100)	1582 s (C=N); 1563 s (CH=N); 813, 770, 700 s (ring subst.)	232 (20700); 270 (13900)	8.41, 8.02 (2s, 1H); 7.81 (d, 2H, $J_{H,H}$ = 8 Hz); 7.25-6.70 (m, 12H); 2.38, 2.26 (s, 3H)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.32; H, ±0.09; N, ±0.10; Cl, −0.06. Exception: **4a**, C, −0.61.

[b-e] see Footnotes b-e of Table 2.

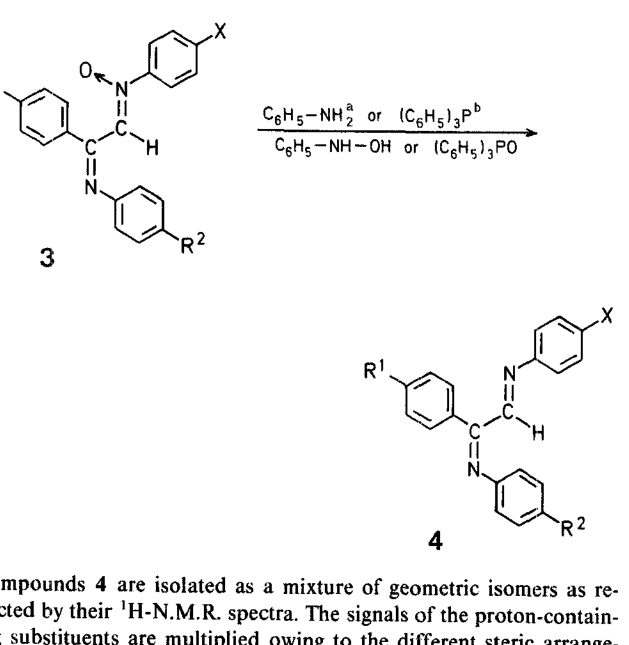
[f] Reaction with aniline.

[g] Reaction with triphenylphosphine.

configuration[25] (as depicted in formulas **3**). The ^{13}C-N.M.R. spectra (Nicolet-200; CDCl$_3$/TMS$_{int}$) of nitrones **3c** and **3f** (as selected compounds) *support the existence of only one geometric isomer of* **3** showing the azomethine and nitrone carbons at δ = 158.77 and 157.99, and 130.12 and 130.13 ppm, respectively, as single signals. Nitrone sp^2 carbons were found to be at unusually high field which indicates partial double-bond character of the N—O function[26,27]. Also the $J_{C,H}$ coupling constants are higher than those reported for unsaturated aldehydes and their aldimine-type derivatives[28]; they are 183.32 and 181.90 Hz, respectively.

The U.V. spectra of compounds **3** show an intense absorption in the range λ = 250–310 nm which can be ascribed to the E2 band according to the classification of Wheeler and Gore[29]. The other bands, i.e., E1 and K are observable in a few cases only[25,30]. The E2 absorption proves to be affected by substituents located on the aryl ring Ar^1 at C-2 and is shifted bathochromically by electron-releasing groups[31]. Substituents on the aryl ring Ar^2 at N-1 do not affect the E2 but give rise to an E1 absorption band, thus suggesting mixed $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions in the anil moiety[24]. The mass spectra exhibit characteristic M − 16 peaks[32] resulting from loss of oxygen from the well recognizable molecular ion. The main fragmentation pathway is then based on C-2,C-3 bond cleavage.

Nitrones **3** can be deoxygenated by reaction with anilines[14] or triphenylphosphine[33] to give the 1,2,4-triaryl-1,4-diazabutadienes **4**.



3

4

Compounds **4** are isolated as a mixture of geometric isomers as reflected by their ^{1}H-N.M.R. spectra. The signals of the proton-containing substituents are multiplied owing to the different steric arrangement of the aryl groups in the stereoisomers [there are probably four isomers (*E,E*, *E,Z*, *Z,E*, and *Z,Z*) if free rotation around the C-3,C-3 bond is assumed]. The aldimine proton at C-3 appears as two signals at $\delta \approx$ 8.3 and 8.5 ppm suggesting the existence of at least two isomers[7]. The I.R. spectra show two strong absorption bands at $\nu \approx$ 1580 and 1570 cm^{-1} originating from stretching vibrations of the C=N double bonds and supporting a conjugated coplanar skeletal structure of compounds **4**. The mass spectra exhibit base fragmentation connected with C-2,C-3 bond cleavage[34]. The ^{13}C-N.M.R. spectrum of compound **4c** proves the presence of isomers showing C-2 as two singlets at δ = 162.55 and 161.71 ppm and C-3 as two doublets at δ = 156.94 and 155.79 ppm with coupling constants of 172.66 and 151.73 Hz which can be attributed to isomers in which the aldimine moiety (C-3,N-4) has the *E* or *Z* geometry, respectively[35]. The aromatic C-atoms give very complex signals in the region δ = 150.3–113.0 ppm. The methoxy C-atom gives three closely neighboured singlets at δ = 54.85, 55.00, and 55.10 ppm (ratio 1 : 2 : 2.7) which can be ascribed to the (*E,E*)- and (*E,Z*)-isomers, to the (*Z,Z*)-isomer, and to the (*Z,E*)-isomer, respectively, assuming that the methoxy signal of the corresponding nitrone **3c** which probably has the (*Z,Z,s*)-*trans* configuration appears at δ = 55.14 ppm. The coupling constant of the signal

$\delta = 55.10$ ppm of **4c** is 149.11 Hz whereas that of the signal $\delta = 55.14$ ppm of **3c** is 148.65 Hz.

1,*N*-Diphenylethanimines (1, Acetophenone Anils); General Procedure (cf. Ref.[31]):

A mixture of an acetophenone (15 mmol) and an aniline (10 mmol) is heated up to 160-180°C and an aniline/zinc chloride mixture $ArNH_2 \cdot ZnCl_2$ (0.1 g) is added in small portions within 1h. Evolution of water is observed. The mixture is then cooled to 60°C and filtered. The unchanged rectants are distilled off under low pressure (10 torr) and then a corresponding acetophenone anil is distilled and purified by crystallization from *n*-pentane if necessary; yield: 40 to 65%.

1,2,4-Triaryl-1,4-diazabutadiene 4-*N*-Oxides (3); General Procedure:

A solution of an 1,*N*-diphenylethanimine[17] (**1**; 3 g) in 96% ethanol (20 ml) is combined with a solution of a nitrosobenzene (**2**; 3 mol equiv with respect to **1**) in 96% ethanol (20 ml). The mixture is briefly heated to boiling. Then, aqueous 25% potassium hydroxide (0.2 ml) is added whereupon an exothermic reaction ensues and the mixture turns from deep green to deep red. On cooling, a crystalline yellow product precipitates. It is isolated by suction, washed with ice-cold ethanol, and purified by column chromatography on alumina (Brockmann 90, activity II/III) using dichloromethane/hexane (2/1) as eluent. Recrystallization from ethanol gives the analytically pure product **3**.

In the case of the dimethylamino compound **1h**, the use of potassium hydroxide is not necessary because of an autocatalytic effect of the anil **1h**.

1,2,4-Triaryl-1,4-diazabutadienes (4); General Procedure:

Equimolecular amounts of the nitrone **3** and aniline or triphenylphosphine (e.g., 10 mmol) are refluxed in absolute ethanol (10 ml) for 2 h. Then, ethanol is distilled off, the oily residue is dissolved in dichloromethane (2 ml), and this solution column-chromatographed on silica gel 60 (70 g) using dichloromethane as eluent. Recrystallization from methanol gives the analytically pure product **4**.

Received: June 20, 1983

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* Address for correspondence.
Dept. of Organic Chemistry, University of Groningen, 9747 AG Groningen, The Netherlands

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