The Reaction of 1,3-Disubstituted Triazenes with Phenyl Isocyanide. N^1-Aryldiazoformamidines

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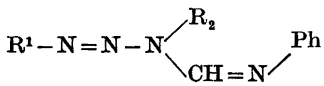
Triazenes attract some interest in the literature, especially with regard to tautomerism [1,2] and *Z/E* isomerism.[3] Recently the thermal [4] and photochemical [5] decomposition of triazenes have been studied. As a result of our interest in this field [5] we now report a new reaction for 1,3-disubstituted triazenes, namely the reaction with phenyl isocyanide with formation of the hitherto unknown N^1-aryldiazoformamidines (*2*).

$$R^1-N=N-NH-R^2 + PhNC \rightarrow$$



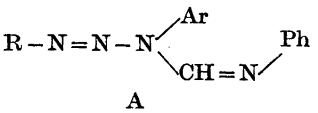
1a–e *2a–e*

Compound	R^1	R^2
a	Ph	Ph
b	*p*-$CH_3C_6H_4$	Me
c	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$
d	Ph	$PhCH_2$
e	*p*-$CH_3C_6H_4$	$PhCH_2$

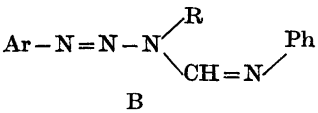
The reactions were carried out at room temperature with equivalent amounts of phenyl isocyanide and triazene, catalyzed with copper(I) chloride. After 1 – 12 h the isocyanide had disappeared. Light petroleum was added and the products separated as yellow crystals in good yields after cooling at – 20 °C overnight. The products could be recrystallized from benzene/light petroleum.

The N^1-aryldiazoformamidines (*2*) are stable compounds at room temperature and in neutral solution at elevated temperature up to 80 °C. On treatment with catalytic amounts of acid the N^1-aryldiazo-N^1,N^2-diarylformamidines (*2a,2c*) decomposed very fast. Decomposing *2a* in benzene solution with a few drops of acetic acid gave an almost quantitative yield of *N,N'*-diphenylformamidine. Acid catalysed decomposition of *2b* resulted in tarry materials and *2d* was quite stable upon this treatment.

The structure of the N^1-diazoformamidines (*2*) could be settled by ^1H and ^{13}C NMR spectroscopy. For *2b*, *2d* and *2e* there are two possibilities, namely N^1-alkyldiazo-N^1-arylformamidine (A) or the N^1-alkyl-N^1-aryldiazoformamidine (B).



A



B

The presence of only one set of signals in the ^1H and ^{13}C NMR spectra indicated that only one isomer was formed. To distinguish between the possibilities A and B we used the "*p*-tolyl method".[6] By means of this method the ^1H NMR chemical shift values for the *p*-tolylamino and the *p*-tolyldiazo group were established as δ 2.41 and 2.32 respectively for *2c*. For *2b* and *2e* the methyl signals are found at δ 2.33 and 2.35 indicating that the structure must be a B type.

From the ^{13}C NMR spectra the same structure could be established by observing the quarternary carbons atoms. From the ^{13}C NMR data of *2c* and of 3,3-dimethyl-1-*p*-totyl-triazene [1] the chemical shifts for the two types of *p*-tolyl groups could be established. The *p*-tolyldiazo group is found at δ 146.5 and 138.5 and the *p*-tolylamino group at δ 138.7 and 133.7. For *2b* the two quarternary carbon atoms corresponding to the *p*-totyl group are found at δ 146.7 and 138.3 and for *2e* at δ 146.3 and 138.3. The amino type *p*-tolyl group is not seen in the spectra of *2b* and *2e* which is also why the ^{13}C NMR spectra indicate that the structure is a B type.

Experimental. The instrumental equipment is reported earlier.[7] ^{13}C NMR spectra were recorded on a Bruker WH 90 apparatus. Melting points are uncorrected. All the triazenes have been prepared in accordance with a previously published procedure.[8] Attempted preparation of 3-methyl-1-phenyltriazene gave a 1:1 mixture of the triazene and 3-methyl-1,5-diphenylpentaazadiene. This compound was therefore omitted and instead 3-methyl-1-*p*-tolyltriazene (*1b*), which was formed without contamination of pentaazadiene was used.

N¹,N²-Diphenyl-N¹-phenyldiazoformamidine 2a. A solution of phenyl isocyanide (50 mmol) and copper(I) chloride (1 mmol) in benzene (100 ml) was stirred at room temperature with 1,3-diphenyltriazene (50 mmol) for 2 h, *i.e.* until the phenyl isocyanide was consumed. Light petroleum (150 ml) was added and the mixture left at – 20 °C overnight. The precipitate was filtered off giving 91 % of a yellow powder. The product could be recrystallized from a mixture of benzene and light petroleum

giving yellow needles, m.p. 120 °C (dec.). Anal. $C_{19}H_{16}N_8$: C, H, N. ^{1}H NMR ($CDCl_3$): δ 6.80–7.55 (15 H, m), 8.83 (1 H, S).

N^1-*Methyl*-*N*^{2}-*phenyl*-*N*^{1}-p-*tolyldiazoformamidine* 2b. This compound was prepared analogously to *2a*, m.p. 90 °C, yield 63 %. Anal. $C_{15}H_{10}N_4$: C, H, N. ^{1}H NMR ($CDCl_3$): δ 2.33 (3 H, s), 3.54 (3 H, s), 6.57–7.62 (9 H, m), 8.54 (1 H, s).

N^2-*Phenyl*-*N*^{1}-p-*tolyl*-*N*^{1}-p-*tolyldiazoformamidine* 2c. This compound was prepared analogously to *2a*, m.p. 135 °C (dec.), yield 100 %. Anal. $C_{21}H_{20}N_4$: C, H, N. ^{1}H NMR ($CDCl_3$): δ 2.32 (3 H, s), 2.41 (3 H, s), 6.67–7.38 (13 H, m), 8.70 (1 H, s).

N^1-*Benzyl*-*N*^{2}-*phenyl*-*N*^{1}-*phenyldiazoformamidine* 2d. The reaction did not take place in benzene solution analogously to *2a* even at reflux temperature. Without solvent the reaction proceeded for 3 h with a yield of 79 % of a yellow mass which could be recrystallized from ethanol, m.p. 100 °C. Anal. $C_{20}H_{18}N_4$: C, H, N. ^{1}H NMR ($CDCl_3$): δ 5.50 (2H, s), 6.95–7.56 (15 H, m), 8.60 (1 H, s).

N^1-*Benzyl*-*N*^{2}-*phenyl*-*N*^{1}-*p-tolyldiazoformamidine* 2e. This compound was prepared analogously to *2a*, m.p. 106 °C, yield 85 %. Anal. $C_{21}H_{20}N_4$: C, H, N. ^{1}H NMR ($CDCl_3$): δ 2.35 (3 H, s), 5.53 (2 H, s), 7.00–7.63 (14 H, m), 8.75 (1 H, s).

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Preparaton of *N*-Acylformimidates. Reaction of Carboxamides with Triethyl Orthoformate

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Several reports on the synthesis of *N*-acylformimidates by reaction between triethyl orthoformate and amides have appeared in the literature.[1–6] For the carboxamides [1,2] more extensive work has shown the structural assignment to be wrong.[5–7] The compounds formed were trisacylaminomethanes and not *N*-acylformimidates. For the reaction of sulfonylamides [3] and phosphorylamides [4] with triethyl orthoformate the corresponding formimidates were actually formed.

N-Acylimidates have previously been synthesized by alkylation of the silver salts of diacylamines [8] and by acylation [9,10] of the corresponding imidates; no formimidate has been reported. We have reinvestigated the reaction between carboxamides and triethyl orthoformate in order to prepare the hitherto unknown *N*-acylformimidates and report here the preparation of the formimidates listed in Scheme 1. Attempts to prepare ethyl *N*-benzoylformimidate *2d* by benzoylation of *O*-ethyl formimidate [11,12] were unsuccessful.

$$RCONH_2 + HC(OC_2H_5)_3 \rightarrow RCON{=}C(H)(OC_2H_5) + 2C_2H_5OH$$

1a–k	R	*2a–k*	R
a	$ClCH_2$	*f*	*o*-ClC_6H_4
b	Cl_2CH	*g*	*m*-ClC_6H_4
c	Cl_3C	*h*	*p*-ClC_6H_4
d	C_6H_5	*i*	*o*-BrC_6H_4
e	*o*-FC_6H_4	*j*	*o*-$CH_3C_6H_4$
		k	2,6-$Cl_2C_6H_3$

Scheme 1.

Results. The reactions were carried out by refluxing the amide with excess orthoester and a few drops of concentrated sulfuric acid distilling off ethanol while it was formed. Evaporation of excess orthoester and subsequent distillation gave the acylformimidates in yields ranging from 11 to 90 %. It turned out that the electronegativity of the substituent in *1* strongly influenced the reaction pathway and the yield of formimidate. Thus benzamide gave a yield of 33 % and *o*-fluorobenzamide a yield of 73 %. The same was observed with