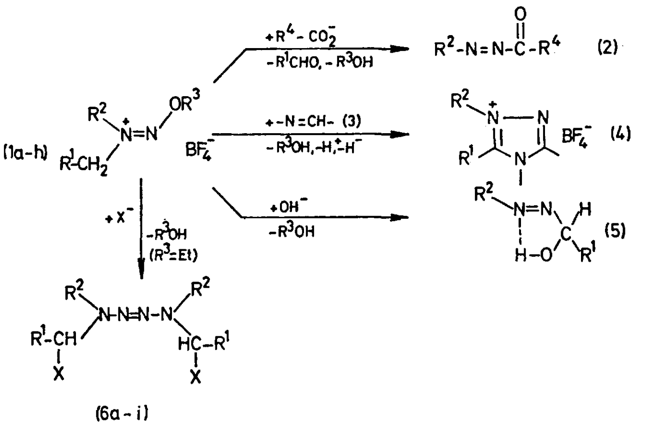
αα′-Dialkoxy- and αα′-Diazido-tetrazenes from Alkoxydiazenium Salts†

By JÜRGEN CRAMER, HANSPETER HANSEN, and SIEGFRIED HÜNIG*
(*Institut für Organische Chemie, Würzburg, Am Hubland, Deutschland*)

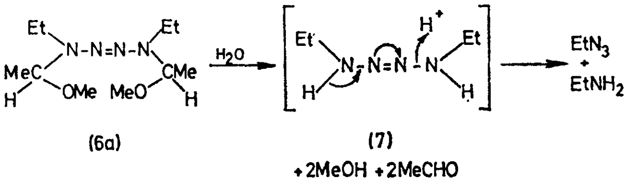
Summary Reaction of the alkoxydiazenium salts(**1**) with alkoxide or azide ions yields αα′-disubstituted tetrazenes (**6**) the structures of which are confirmed by their spectral data and easily obtainable hydrolysis products.

ALKOXYDIAZENIUM salts (**1**), easily accessible from nitrosamines by alkylation with trialkyloxonium salts,[1] react with different nucleophiles in rather unexpected ways.



	R^1	R^2	X		R^1	R^2	X
a	Me	Et	OMe	**f**	H	Ph	N_3
b	$CH_2O[CH_2]_2$		OMe	**g**	H	*p*-MeC_6H_4	N_3
c	$[CH_2]_4$		OEt	**h**	H	*p*-$MeOC_6H_4$	N_3
d	$[CH_2]_5$		OMe	**i**	H	*p*-MeC_6H_4	OEt
e	$[CH_2]_4$		OMe				

The salts (**1**) are rapidly attacked under very mild conditions by carboxylate ions, bases of type (**3**) (Schiff bases, pyridine, *etc.*), and hydroxide ions. Thereby the acylazocompounds (**2**),[2] triazolium salts (**4**),[3] and α-hydroxyazocompounds (**5**)[4] are formed. We now report that the reactions of (**1**) with alkoxide or azide ions take another surprising course and yield the previously unknown[5] αα′-dialkoxy- (**6a**—**e**) and αα′-diazido-tetrazenes (**6f**—**h**) respectively.



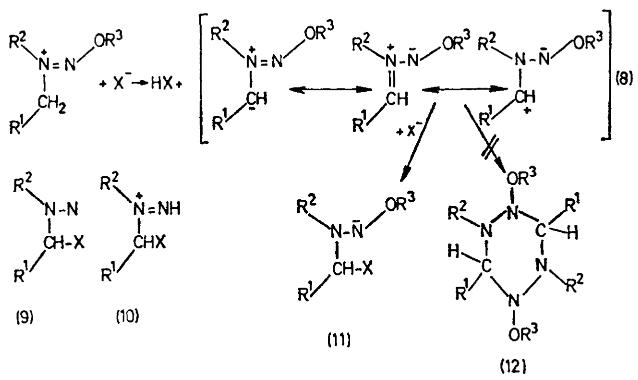
The αα′-dialkoxytetrazenes (**6a**—**e**) (34—72% yield by u.v.) are easily obtained within 2—4 h by addition of compounds (**1**; R^1, R^2 = alkyl) to R^5OH-K_2CO_3 or better R^5OH-R^5OK at −40°. They form colourless crystals‡ (15—32%)§¶ from EtOAc. The u.v. absorption of (**6a**—**e**) [271—286 (ε 10,100—15,600) and 245—250sh nm in MeOH] is typical of tetrazenes and nearly identical with that of the parent compounds.[6] The n.m.r. spectra are consistent with structures (**6a**—**e**) but do not exclude the dimeric structures (**12**). The experiments demonstrate incorporation of the solvent (anion) and explusion of R^3O^- behaviour which is typical of half-aminals,[7] to which compounds (**6a**—**e**) are related. Accordingly, *e.g.*, (**6d**) is transformed into (**6c**) if recrystallized from ethanol. For the same reasons, the αα′-alkoxytetrazenes (**6a**—**e**) are hydrolysed even by water whereas the parent compounds are attacked by hot strong acids only.[6b] Acetaldehyde (95%) was obtained from hydrolysis of (**6a**), as well as ethyl azide (ν_{max} 2100 cm^{-1}) and ethylamine (95%) which presumably result from the decomposition of the tetrazene (**7**). Compounds (**1f**—**h**) decompose to various products in basic alcoholic solution but form crystalline αα′-diazido-tetrazenes (**6f**—**h**)‡ (31—45%)§ when treated with sodium azide

† Dissertations: J. Cramer, University of Würzburg, 1968, and H. Hansen, University of Würzburg, 1967.

‡ Correct elemental analyses and molecular weights (osmom; m.s.) were obtained for all compounds.

§ Conditions have not been optimized.

¶ Compound (**6a**) can be recrystallized from acetone at −70°.



in methanol at *ca.* −20°. Again typical u.v. spectra of compounds (**6f**—**h**) correspond to those of the parent compounds.¶ By heating (**6g**) with EtOH-EtOK even N_3^- can be removed and (**6i**) is isolated in 30% yield. Compounds (**6g**) and (**6i**) afford *p*-tolyl azide on hydrolysis with dilute acid. Thus, all the tetrazenes (**6a**—**i**) break down in a similar way.

The mechanism of reactions (**1**) → (**6**) has not yet been elucidated. However, the route to (**2**),[2] (**4**),[3] and (**5**)[4] starts with formation of the dipole (**8**) by rapid, irreversible[4] deprotonation. In all subsequent steps (**8**) acts as a C-electrophile.[2–4] Attack of R^5O^- or N_3^- on compound (**1**) therefore should produce the crucial intermediate (**8**). The isolated material cannot be (**12**), a dimer of (**8**), because (**12**) would not allow ready exchange of R^3O for R^5O and cannot display u.v. absorption in the observed range.[8] Compounds (**10**) and (**9**) may be further intermediates formed from (**11**). Compound (**6**) could be formed by the reactions (**1**) + (**11**), (**10**) + (**11**), (**9**) + (**10**),[9] (**9**) + (**11**), or (**9**) + (**9**).[10]

Financial support of this work by Fonds der Chemischen Industrie and Badische Anilin- & Sodafabrik, Ludwigshafen (Rhein), is acknowledged.

(*Received*, 10*th December* 1973; *Com.* 1675.)

---

[1] (a) S. Hünig, L. Geldern, and E. Lücke, *Revue de Chimie VII*, 1962, 935. (b) S. Hünig, L. Geldern, and E. Lücke, *Angew. Chem.*, 1963, **75**, 476; *Angew. Chem. Internat. Edn.*, 1963, **2**, 327; (c) S. Hünig, G. Büttner, J. Cramer, L. Geldern, H. Hansen, and E. Lücke, *Chem. Ber.*, 1969, **102**, 2093.

[2] (a) Th. Eicher, S. Hünig, and H. Hansen, *Angew. Chem.*, 1967, **79**, 681; *Angew. Chem. Internat. Edn.*, 1967, **6**, 699; (b) S.Hünig, Th. Eicher, and H. Hansen, *Chem. Ber.*, 1969, **102**, 2889.

[3] (a) Th. Eicher, S. Hünig and P. Nikolaus, *Angew. Chem.*, 1967, **79**, 682; *Angew. Chem. Internat. Edn.*, 1967, **6**, 700; (b) S. Hünig, Th. Eicher, H. Hansen, and P. Nikolaus, *Chem. Ber.*, 1969, **102**, 3159.

[4] (a) S. Hünig and J. Cramer, *Angew. Chem.*, 1968, **80**, 1000; *Angew. Chem. Internat. Edn.*, 1968, **7**, 943; (b) S. Hünig and G. Büttner, *Angew. Chem.*, 1969, **81**, 465; *Angew. Chem. Internat. Edn.*, 1969, **8**, 451; (c) G. Büttner and S. Hünig, *Chem. Ber.*, 1971, **104**, 1088; (d) G. Büttner and S. Hünig, *ibid.*, p. 1117; (e) S. Hünig, G. Büttner, J. Cramer, and L. Geldern, *ibid.*, p. 1118.

[5] Since the completion of this work tetrazenes of type (**6**) have been obtained from α-alkoxyhydrazines by oxidation (K. F. Hebenbrock and K. Eiter, *Annalen*, 1972, **765**, 78.

[6] (a) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **64**, 149; (b) H. Wieland, *Ber. deut. chem. Ges.*, 1908, **41**, 3498.

[7] *Cf.* P. A. Smith, 'The Chemistry of Open-Chain Nitrogen Compounds,' Benjamin, New York, 1965.

[8] Products with the skeleton of (**12**) which may be derived from (**8**) or a similar dipole (D. L. Lemal 'Aminonitrenes' p. 385 in W. Lwowski, 'Nitrenes,' Interscience, New York, 1970) can be obtained under different conditions.†

[9] Compare dialkyldiazenium ions, W. H. Urry, P. Szeczi, C. Ikoku, and D. W. Moore, *J. Amer. Chem. Soc.*, 1964, **86**, 2224; W. McBride and H. W. Kruse, *ibid*, 1951, **79**, 572; W. R. McBride and E. M. Bens, *ibid.*, 1959, **81**, 5546.

[10] The comparison with alkoxynitrenes (S. J. Brois, *J. Amer. Chem. Soc.*, 1970, **92**, 1079) seems to be more relevant than with the less basic acylaminonitrenes (T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J.C.S. Perkin I*, 1973, 555 and preceding papers. Review: S. Hünig, *Helv. Chim. Acta*, 1971, **54**, 1721.)