[20] *R. C. Courtney, R. L. Gustafson, S. Chaberek jr & A. E. Martell*, J. Amer. chem. Soc. *81*, 519 (1959); *R. L. Gustafson & A. E. Martell*, J. Amer. chem. Soc. *81*, 525 (1959).
[21] *Th. Kaden & A. Zuberbühler*, Helv. *54*, 1361 (1971).
[22] *R. M. Smith & A. E. Martell*, Critical Stability Constants, Plenum Press New York and London 1971.
[23] *H. B. Jonassen, R. E. Reeves & L. Segal*, J. Amer. chem. Soc. *77*, 2748 (1955).
[24] *G. Schwarzenbach, G. Anderegg, W. Schneider & H. Senn*, Helv. *38*, 1147 (1955).
[25] *P. Souchay, N. Israily & P. Gouzerh*, Bull. Soc. chim. France *1966*, 3917.
[26] *T. F. Dorigatti & E. J. Billo*, J. inorg. nucl. Chemistry *37*, 1515 (1975).
[27] *A. Kaneda & A. E. Martell*, J. coord. Chemistry *4*, 137 (1975).
[28] *W. Schneider*, Dissertation, Universität Zürich 1955.
[29] *C. K. Jørgensen*, Acta chem. scand. *10*, 887 (1956).
[30] *F. J. C. Rossotti & H. Rossotti*, The Determination of Stability Constants, McGraw-Hill Inc. London 1961.
[31] *H. Ackermann & G. Schwarzenbach*, Helv. *32*, 1543 (1949).
[32] *E. J. Billo*, Inorg. nucl. Chemistry Letters *10*, 613 (1974).
[33] *W. Schneider*, private communication.
[34] *I. Poulsen & J. Bjerrum*, Acta chem. scand. *9*, 1407 (1955).
[35] *A. Albert & E. P. Serjeant*, Ionisation Constants of Acids and Bases, Methuen/Wiley, London New York 1962.
[36] *Y. Fuji & M. Kodama*, Bull. chem. Soc. Japan *42*, 3172 (1969).
[37] *J. E. Prue & G. Schwarzenbach*, Helv. *33*, 985 (1950).
[38] *J. Clark & D. D. Perrin*, Quart. Rev. *18*, 295 (1964).
[39] *R. Lloyd*, Thesis, Temple univ. Philadelphia, Penn. 1954.
[40] *G. Anderegg*, Helv. *44*, 1673 (1961).
[41] *G. Anderegg*, Helv. *45*, 901 (1962).
[42] *H. Stünzi & G. Anderegg*, Helv. *56*, 1698 (1973).
[43] *P. Fournari, M. Farnier & C. Fournier*, Bull. Soc. chim. France *1972*, 283.

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170. Thermolysis of 1,3,4-Oxadiazole-5-ones, a New Precursor of Nitrilimines. A Novel Synthesis of Indazoles

Preliminary communication

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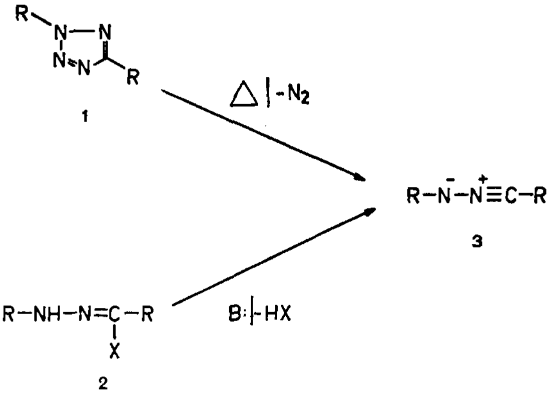
(1. VI. 76)

Summary. Thermolyses of the title compounds at various temperatures have been investigated. At the lower end of the temperature range studied indazoles **5a, b** are formed in nearly quantitative yields, while at the upper end formal carbene-type reaction-products **6**, **7**, **8** have been isolated in just as high yields.

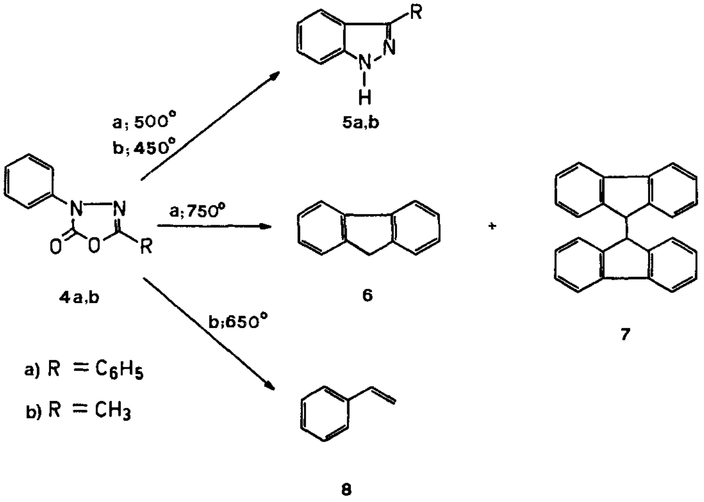
The most commonly used method of preparation of the highly reactive transient 1,3-disubstituted nitrilimines **3** is based on the facile thermal elimination of nitrogen from the corresponding 1,3-disubstituted tetrazoles **1** [1]. Some of these precursors (**1**) are fairly easily available; however, they all involve preparation and handling of somewhat hazardous azides [2]. An alternative method involves base-induced 1,3-elimination of hydrogen halide from hydrazonoyl halides **2** [2] [3].

The search for new precursors of **3** led us to examine the thermal behaviour of 1,3,4-oxadiazole-5-ones **4**. In spite of being easily accessible and for providing a number of rearrangement possibilities their chemistry has so far been neglected.



Flash vacuum pyrolysis of **4a** at 400°1) gave a mixture of starting material and 3-phenylindazole (**5a**) (ratio 4:6, total yield: 95%). At 500° the yield of **5a** was nearly quantitative and only traces of unidentified products were present. At temperatures above 750° **5a** was no longer detected but a mixture of two new compounds appeared: fluorene (**6**) and 9,9'-bifluorenyl (**7**)2) (ratio 8,5:1; total yield: 95%) along with some coloured compounds. The yield of **7** increased slightly at still higher temperatures.

Thermolysis of **4b** at 450° resulted in a 95% yield of 3-methylindazole (**5b**), while at temperatures above 650° only styrene (**8**) could be isolated.



Initial elimination of carbon dioxide from **4a, b** leads to the nitrilimines **3a, b** which have been known to undergo bimolecular condensation reactions [1–3]. Under our conditions (0,01 Torr,) an intramolecular electrophilic substitution leading to **5a, b** is the preferred reaction path. Analogous reactions of related compounds are

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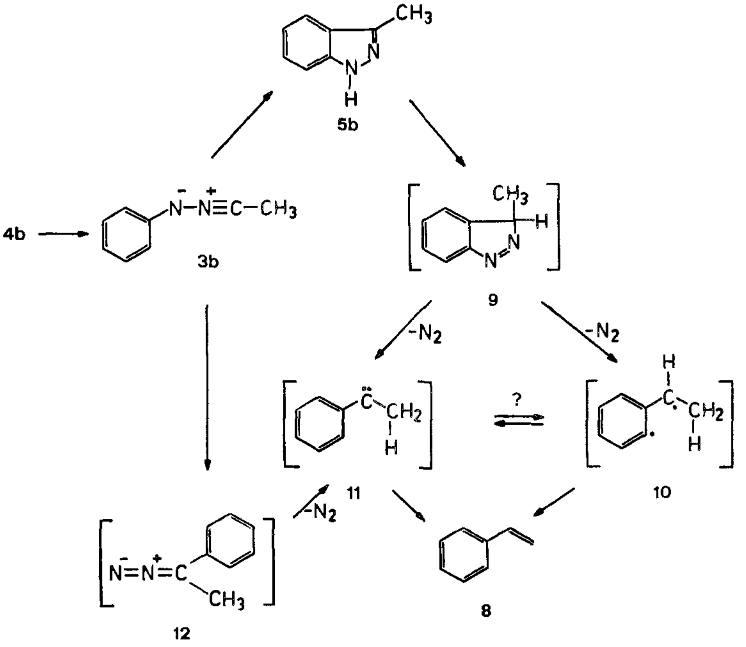
[1] Compounds **4** are reported to be fairly stable at high temperatures (**4a** can even be distilled under atmospheric pressure at 310° [4]).

[2] A similar result has been obtained by *C. Wentrup* in this Institute by gas-phase pyrolysis of 2,5-diphenyltetrazole. *C. Wentrup*, personal communication.

well known in the *Fischer* indole synthesis [5] and the conversion of diarylaminoisocyanates to indazolones [6] [7].

It has been proposed [8] that 3-methylindazole (**5b**) undergoes (at least to a certain extent) 1,3-hydrogen shift at elevated temperatures to form (3*H*)-3-methylindazole (**9**) which then extrudes nitrogen leading to the 1,3-diradical intermediate **10**; a 1,4-hydrogen shift might then take place to give styrene (**8**). Labeling experiments have shown, however, that a reaction path passing through phenyl-methylcarbene (**11**) competes[8]. An alternative explanation for the formation of formal carbene products **6**, **7**, **8** would be that at higher temperatures the intermediate nitrilimine **3a, b** does not cyclise to an indazole derivative. A direct 1,3-phenyl migration followed by nitrogen elimination also leads to the phenyl-methyl- (**11**) or diphenylcarbene.



Experiments to distinguish the possibilities mentioned are being carried out.

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REFERENCES

[1] *R. Huisgen*, Angew. Chem. *75*, 604 (1963).
[2] *R. Huisgen, M. Seidel, G. Wallbillich & H. Knupfer*, Tetrahedron *17*, 3 (1962).
[3] *R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland & G. Wallbillich*, J. org. Chemistry *24*, 892 (1959).
[4] *H. Rupe*, Ber. deutsch. chem. Ges. *32*, 10 (1900).
[5] *E. Fischer*, Liebigs Ann. Chem. *236*, 116, 126 (1886).
[6] *R. Stollé*, Ber. deutsch. chem. Ges. *57*, 1063 (1924).
[7] *N. Koga, G. Koga & J.-P. Anselme*, Tetrahedron *28*, 4515 (1972).
[8] *W. D. Crow & M. N. Paddon-Row*, Tetrahedron Letters *1972*, 3207.