

## 281. Flash Pyrolysis of 4-Arylmethylidene-oxazolones and -isoxazolones. A Versatile Synthesis of Arylacetylenes

Preliminary communication

by **Curt Wentrup**<sup>1)</sup> and **Werner Reichen**

Institut de Chimie Organique de l'Université, CH-1005 Lausanne, Switzerland

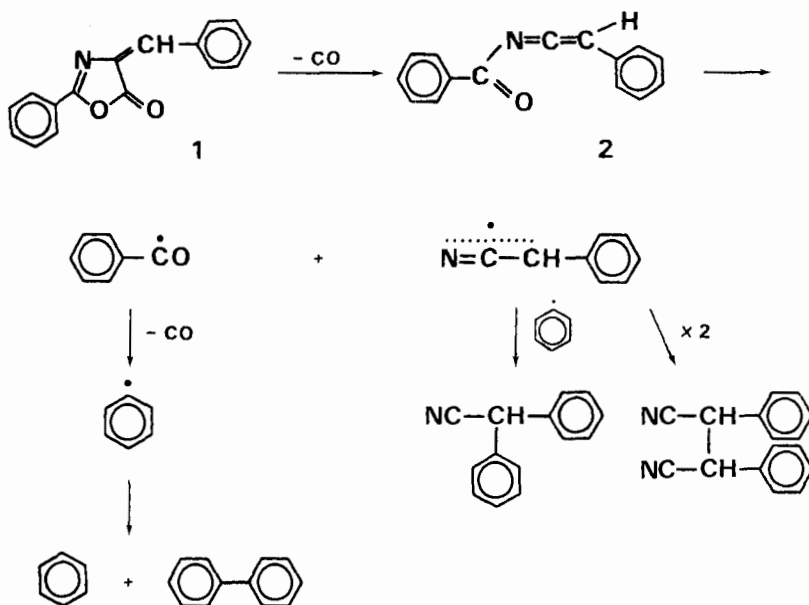
(21. IX. 76)

*Summary.* Flash pyrolysis of 4-benzylidene-2-phenyl-5(4*H*)-oxazolone (**1**) yields carbon monoxide, benzene, biphenyl, diphenylacetonitrile, and 2,3-diphenylsuccinonitrile; N-benzoyl-phenylketenimine is implicated as the primary intermediate. The flash pyrolysis of 4-arylmethylidene-3-methyl-5(4*H*)-isoxazolones (**3**) yields carbon dioxide, acetonitrile, and phenylacetylenes substituted by alkoxy, chloro, dimethylamino, and hydroxy groups, in yields of 45–95%. Arylmethylidenecarbenes are implicated as intermediates.

The technique of flash pyrolysis offers considerable scope for the study of reactive intermediates as well as the synthesis of novel compounds [1]. In continuation of our studies on differential CO and CO<sub>2</sub> extrusion from heterocyclic molecules [2] we now report the pyrolysis of the title compounds, which has led to a new synthesis of arylacetylenes.

The pyrolysis of 4-benzylidene-2-phenyl-5(4*H*)-oxazolone (**1**) between 600°–900°/10<sup>-2</sup>–10<sup>-4</sup> Torr resulted in a clean elimination of carbon monoxide with only traces

Scheme 1



<sup>1)</sup> Present address: Fachbereich Chemie der Universität, D-3550 Marburg/Lahn, Lahnberge.

of carbon dioxide, as shown by IR. spectroscopy. The main products (with isolated yields from a pyrolysis at  $650^{\circ}/10^{-3}$  Torr) were benzene (30%), biphenyl (4%), diphenylacetonitrile (7%), and 2,3-diphenylsuccinonitrile (32%). The formation of these products is rationalized in *Scheme 1*. A trace of benzonitrile was detectable by GC. and IR. spectroscopy of the pyrolysate.

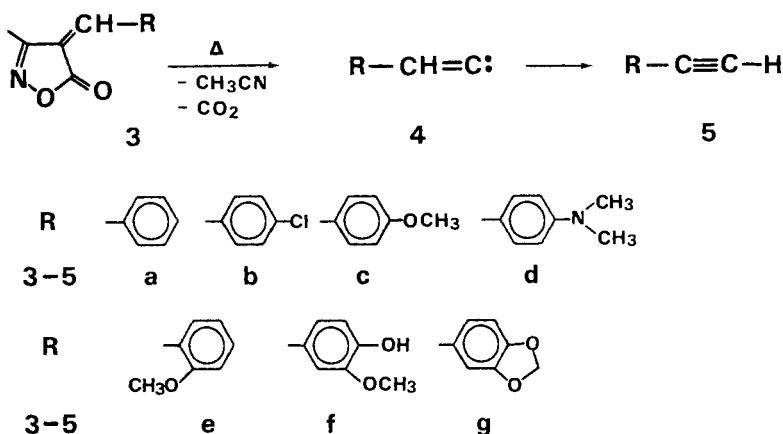
The chelotropic extrusion of CO leads to N-benzoyl-phenylketenimine (**2**) which under the reaction conditions fragments into benzoyl and ketenimine radicals. Other examples of radical fragmentation of ketenimines have been reported [3]. The final products are derived from hydrogen abstraction or recombination of the ensuing radicals.

Since only traces of carbon dioxide and benzonitrile were formed, the fragmentation of **1** to phenylmethylidenecarbene is not competitive. This carbene would rearrange to phenylacetylene [4] which was, however, not detectable<sup>2)</sup>.

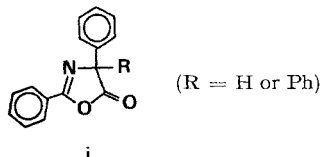
In contrast, the isomeric 4-arylmethylidene-isoxazol-5(4*H*)-ones (**3**) upon flash pyrolysis at  $520\text{--}650^{\circ}/0.01\text{--}0.05$  Torr gave high yields of the desired acetylenes **5** (*Scheme 2* and Table).

Even quite reactive acetylenes carrying sensitive substituents can be prepared in this way. The volatile reaction products are easily removed by distillation on the

*Scheme 2*



<sup>2)</sup> Exclusive CO elimination was also observed in the flash pyrolysis of 2,4-diphenyl- and



2,4,4-triphenyl-2-oxazolin-5-ones (**i**), leading to N-benzoylbenzaldimine and benzophenone N-benzoylimine, respectively; these undergo further fragmentation into benzaldehyde and benzophenone, respectively, and benzonitrile [5]. The reaction is all the more remarkable since variously substituted 2-oxazolin-5-ones are reported [6] to extrude  $\text{CO}_2$  thermally in solution, leading to nitrile ylide intermediates.

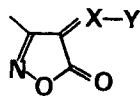
Synthesis of arylacetylenes (5) by pyrolysis of 4-arylmethylidene-isoxazolones (3)<sup>a)</sup>

Starting material <b>3</b>	Temp. °C	yield of <b>5</b> (%)
<b>a</b>	620	85
<b>b</b>	600	60
<b>c</b>	600	75
<b>d</b>	620	85
<b>e</b>	580	95
<b>f</b>	520	45
<b>g</b>	650	50

a) All pyrolyses were carried out using a 40×3.5 cm quartz tube at 0.01–0.05 Torr. Starting materials were sublimed in below their melting points. The yields indicated are those of isolated, pure materials.

vacuum line, and they were shown by IR. spectroscopy to consist of CO<sub>2</sub> and acetonitrile.

The clean and facile fragmentation of **3** to intermediate methylenecarbenes **4** opens the possibility of generating a variety of reactive and/or hitherto unknown classes of compounds by flash pyrolysis of isoxazolones of the general type **6**, e.g. aminoacetylenes (X–Y = HC–N<sub>2</sub>), isocyanides (X–Y = N–R), isocyano-amines



**6**

(X–Y = N–NRR'), and fulminates (X–Y = N–OR). One of these reactions is described in the accompanying communication [7].

The financial support of this work by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* (Project No. 2.258.074) and this Institute (Prof. H. Dahn) is gratefully acknowledged. C. W. thanks Mr. E. Evkohen for some initial experiments.

#### REFERENCES

- [1] H. J. Hageman & U. E. Wiersum, *Chem. in Britain* **9**, 206 (1973); *Chem. Eng. News*, Sept. 23, p. 25; C. Wentrup, *Top. Curr. Chemistry* **62**, 173 (1976).
- [2] W. Reichen, *Helv.* **59**, 1636 (1976); C. Wentrup & P. Müller, *Tetrahedron Letters* **1973**, 2915; C. Wentrup, *ibid.* **1973**, 2919.
- [3] T. L. Gilchrist, G. E. Gymer & C. W. Rees, *J. C. S. Perkin Trans. I*, **1975**, 1, and literature cited therein.
- [4] R. F. C. Brown, F. W. Eastwood, K. J. Harrington & G. L. McMullen, *Austral. J. Chemistry* **27**, 2393 (1974); H. D. Hartzler, in 'Carbenes', Vol. 2, p. 43, R. A. Moos & M. Jones, Editors, John Wiley & Sons, New York, N.Y. 1974.
- [5] R. Harder & C. Wentrup, unpublished work; R. Harder, Dissertation, Université de Lausanne, 1976.
- [6] W. Steglich, P. Gruber, H.-J. Heininger & F. Kneidl, *Chem. Ber.* **104**, 3816 (1971).
- [7] W. Reichen & C. Wentrup, *Helv.* **59**, 2618 (1976).