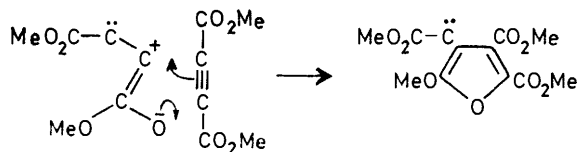


Generation and Reactions of a 3-Furylcarbene and of an Isoxazol-4-ylcarbene

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2,5-Diphenylfuran-3-carbaldehyde reacted with 1-amino-*trans*-2,3-diphenylaziridine to give the hydrazone (6), which on photolysis or pyrolysis gave products derived from the 3-furylcarbene (5). In contrast to reactions reported for 2-furylcarbenes there is no evidence of ring-opening in the 3-furylcarbene, and the reactions observed (insertion and cycloaddition) are those of a normal arylcarbene. A similar investigation of the corresponding hydrazone (8) from an isoxazole-4-carbaldehyde shows that ring cleavage does occur on pyrolysis. The relevance of these observations to a possible mechanism for the thermal decomposition of 3-phenylprop-2-ynal is discussed.

THE thermal tetramerisation of dimethyl acetylenedicarboxylate is thought to involve a step in which one molecule of the ester adds to another in 1,3-dipolar fashion, giving a 3-furylcarbene (Scheme 1).¹ In view of



SCHEME 1

the unusually mild conditions under which some five-membered heteroaromatic azides and diazoalkanes are cleaved,^{2,3} it seemed possible that a more general interconversion of acetylenes and 3-furylcarbenes might occur. Hoffman and Shechter have shown that certain 2-furylcarbenes are readily cleaved to give open-chain isomers (Scheme 2), this reaction occurring in preference to the more usual carbene reactions such as insertion and cycloaddition.³ However, reactions of 3-furylcarbenes have not been reported hitherto.

¹ E. LeGoff and R. B. LaCount, *Tetrahedron Letters*, 1967, 2333; E. Winterfeldt and G. Giesler, *Chem. Ber.*, 1968, **101**, 4022; R. Gericke and E. Winterfeldt, *Tetrahedron*, 1971, **27**, 4109.

² P. A. S. Smith, L. O. Krbecek, and W. Resemann, *J. Amer. Chem. Soc.*, 1964, **86**, 2025; P. A. S. Smith and J. G. Wirth, *J. Org. Chem.*, 1968, **33**, 1145; P. A. S. Smith, G. J. W. Breen, M. K. Hajek, and D. V. C. Awang, *ibid.*, 1970, **35**, 2215; P. A. S. Smith and H. Dounchis, *ibid.*, 1973, **38**, 2958; P. A. S. Smith and E. M. Bruckmann, *ibid.*, 1974, **39**, 1047.

One reaction for which an extension of the mechanism shown in Scheme 1 could provide an explanation is the thermal decarbonylation of 3-phenylprop-2-ynal. When the aldehyde is heated above *ca.* 100 °C, carbon monoxide is evolved and the dimeric aldehydes (1) and (2) are produced.⁴ By invoking an initial cycloaddition step analogous to that of Scheme 1, a sequence can be considered (Scheme 3) which leads to the observed products.

In order to test the feasibility of such a process we have explored the chemistry of a simple 3-furylcarbene and



SCHEME 2

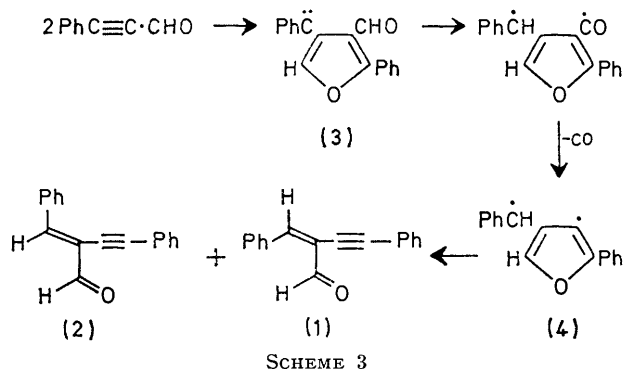
have also attempted to generate a 3-furylcarbene with a formyl group at the 4-position, as a model for the carbene (3). We have also explored a route to diradicals analogous to (4) to determine whether they can undergo the proposed ring opening.

2,5-Diphenylfuran-3-carbaldehyde was used as starting material for generation of the 3-furylcarbene (5).

³ R. V. Hoffman and H. Shechter, *J. Amer. Chem. Soc.*, 1971, **93**, 5940; *J. Org. Chem.*, 1974, **39**, 2939.

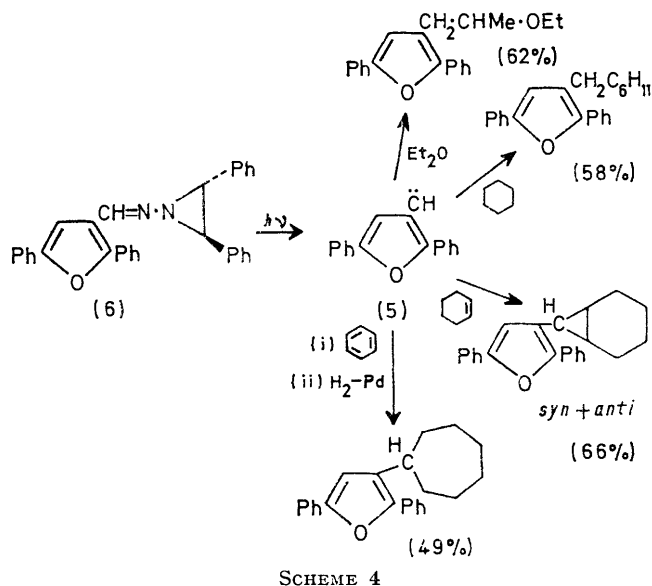
⁴ L. Claisen, *Ber.*, 1898, **31**, 1021; R. K. Bentley, U. Graf, E. R. H. Jones, R. A. M. Moss, V. Thaller, and R. A. Vere Hodge, *J. Chem. Soc. (C)*, 1969, 683.

Eschenmoser and his co-workers⁵ have used aziridinylimines as masked diazo-compounds; these have the advantage over other diazoalkane precursors, such as tosylhydrazones, that they are cleaved thermally without the introduction of an external base, and, being soluble in organic solvents, they allow homogeneous reactions to



occur. The disadvantage of the reagents is that mild conditions are required to form the hydrazones from the corresponding amino-aziridines, and less reactive carbonyl compounds (such as diaryl ketones) do not react in these conditions.

Photolysis of the aziridinylimine (6) provided a good route to the carbene (5). In a variety of solvents, products were obtained which were consistent with the intermediacy of this carbene, as shown in Scheme 4. In

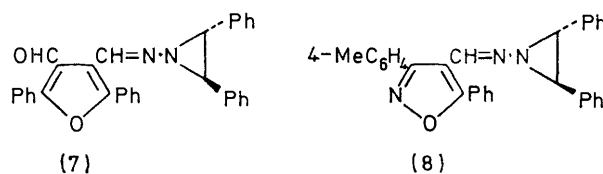


none of these reactions was there any evidence for fragmentation of the carbene into phenylacetylene and

⁵ D. Felix, R. K. Müller, U. Horn, R. Joos, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, 1972, **55**, 1276.

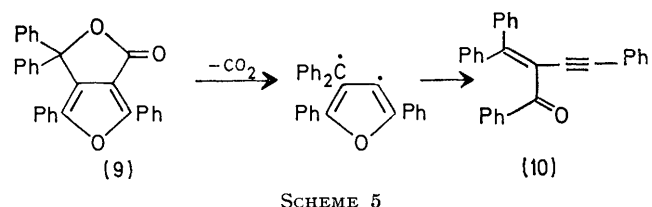
⁶ C. D. Gutsche, G. L. Bachman, and R. S. Coffey, *Tetrahedron*, 1962, **18**, 617; G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, 1964, **86**, 4042.

benzoylacetylene; the reactions are similar to those of phenylcarbene.⁶

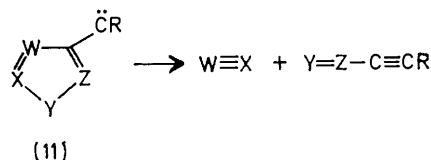


The aziridinylimine (7), prepared from 2,5-diphenylfuran-3,4-dicarbaldehyde and 1-amino-2,3-diphenylaziridine, was readily decomposed thermally and photochemically, but gave a mixture of products from which only 2,5-diphenylfuran-3,4-dicarbaldehyde was isolated. The carbene was not intercepted by sulphur, by alkanes, or by olefins, and appears to be an efficient oxygen scavenger. Again, no evidence for ring cleavage was obtained. In contrast, melt pyrolysis of the isoxazol-4-yl aziridinylimine (8) gave a mixture of the expected ring-cleavage products, benzoylacetylene and 4-toluenitrile.

Pyrolysis of the lactone (9) in the vapour phase at 675 °C and 0.02 mmHg gave the acetylene (10) in good yield: a mechanism (Scheme 5) involving a diradical



similar to the diradical (4) in Scheme 3 can account for the formation of this product, and provides a possible model for the fragmentation of Scheme 3. However, we conclude that the energy barrier to ring cleavage of 3-furylcarbenes is higher than for 2-furylcarbenes, and that there is no evidence for a general equilibration of conjugated acetylenic carbonyl compounds and 3-furylcarbenes. The known² examples of cleavage of carbenes of the general formula (11), and that of the isoxazol-4-yl imine (8), all involve the production of the fragment W≡X, either as molecular nitrogen or as a nitrile; fragmentation to give an acetylene W≡X has not been



observed. A similar difference in the stabilities of 2- and 3-azidofurans has been noted recently.⁷

⁷ S. Gronowitz, C. Westerlund, and A.-B. Hörnfeldt, *Acta Chem. Scand.*, 1975, **B29**, 224.

EXPERIMENTAL

3-(trans-2,3-Diphenylaziridin-1-yliminomethyl)-2,5-diphenylfuran (6).—To a solution of 2,5-diphenylfuran-3-carbaldehyde⁸ (0.400 g, 1.61 mmol) in ether (5 ml) was added 1-amino-trans-2,3-diphenylaziridine⁵ (0.400 g, 1.90 mmol) in ether (5 ml). After the mixture had been kept at 5 °C for 16 h the crystalline precipitate was filtered off. Recrystallisation gave the aziridinylimine (6) (0.460 g, 65%), m.p. 115.5–117.5° (decomp.) (from ether–hexane) (Found: C, 84.5; H, 5.4; N, 6.4. C₃₁H₂₄N₂O requires C, 84.5; H, 5.45; N, 6.4%); λ_{max.} (cyclohexane) 314 nm (ε 33 400); δ(CDCl₃) 3.70–3.85 (2 H, m), 7.00 (1 H), 7.1–7.6 (18 H, m), 7.64–7.75 (2 H, m), and 8.07 (1 H); m/e 464 (C₃₄H₂₄O₂⁺), 412 (M⁺ – 28), and 180 (C₁₄H₁₂⁺, base).

Photolysis of the Aziridinylimine (6).—(a) *In ether*. The imine (0.20 g, 0.45 mmol) dissolved in dry degassed ether (110 ml) was irradiated (500 W medium-pressure lamp, Pyrex filter) for 1 h. Layer chromatography (ether–pentane, 2 : 3) and distillation gave 3-(2-ethoxypropyl)-2,5-diphenylfuran (0.086 g, 62%), b.p. 140–150° at 3 × 10⁻² mmHg (Found: C, 82.2; H, 7.0. C₂₁H₂₂O₂ requires C, 82.3; H, 7.2%); δ(CCl₄) 1.19 (3 H, t, J 7 Hz), 1.23 (3 H, d, J 6.5 Hz), 2.85 (2 H, dq, AB of ABX, J_{AB} 15, J_{AX} 6.5 Hz), 3.58 (3 H, m, OCH and OCH₂), 6.68 (1 H), 7.16–7.50 (6 H, m), and 7.63–7.80 (4 H, m); m/e 306 (M⁺), 262, and 233 (base).

(b) *In cyclohexane*. The imine (0.20 g, 0.45 mmol) was irradiated in cyclohexane (110 ml) as described in the preceding experiment, and gave 3-cyclohexylmethyl-2,5-diphenylfuran (0.082 g, 58%), m.p. 64–67° (Found: C, 87.0; H, 7.4. C₂₃H₂₄O requires C, 87.3; H, 7.6%); δ(CCl₄) 1.0–2.0 (11 H, m), 2.53 (2 H, d, J 6.5 Hz), 6.47 (1 H), 7.05–7.45 (6 H, m), and 7.52–7.70 (4 H, m); m/e 316 (M⁺), 233, and 77 (base).

(c) *In cyclohexene*. Irradiation of the imine (0.20 g, 0.45 mmol) in cyclohexene gave a mixture of exo- and endo-3-bicyclo[4.1.0]heptan-7-yl-2,5-diphenylfuran (0.094 g, 66%), b.p. 210° at 4 × 10⁻² mmHg (Found: C, 87.7; H, 7.0. C₂₃H₂₀O requires C, 87.9; H, 7.0%); δ(CCl₄) 1.0–2.2 (11 H, m), 6.32 and 6.77 (together 1 H), and 7.0–8.0 (10 H, m); m/e 314 (M⁺), 233, and 105 (base). G.l.c. (5% OV1 on Celite; 250 °C) showed two isomers in the ratio 1 : 1.8, but the isomers were not separated by preparative chromatography.

(d) *In benzene*. Irradiation of the imine (0.20 g, 0.45 mmol) in benzene gave a mixture of isomers of 3-cycloheptatrienyl-2,5-diphenylfuran (0.084 g, 60%), which by catalytic reduction gave 3-cycloheptyl-2,5-diphenylfuran (0.070 g, 49%), b.p. 180–190° at 10⁻¹ mmHg (Found: C, 87.2; H, 7.6. C₂₃H₂₄O requires C, 87.3; H, 7.6%); δ(CCl₄) 1.5–2.2 (12 H, m), 2.8–3.1 (1 H, m), 6.58 (1 H), and 7.0–7.7 (10 H, m); m/e 316 (M⁺) and 105 (base).

Thermolysis of the Imine (6).—The imine (0.15 g, 0.34 mmol) in cyclohexane (30 ml) was heated under nitrogen at 80 °C for 8 h; no starting material then remained. Layer chromatography gave 3-(cyclohexylmethyl)-2,5-diphenylfuran (0.055 g, 51%), m.p. 64–67°.

2,5-Diphenylfuran-3,4-dicarbaldehyde.—A suspension of 3,4-bishydroxymethyl-2,5-diphenylfuran⁹ (1.28 g, 0.46 mmol) in dry dichloromethane (50 ml) was added to a solution of chromium trioxide (6 g) in pyridine (9.5 g) and dichloromethane (150 ml) at 20 °C. After 0.5 h the super-

natant liquid was decanted and the dark residue was dissolved by shaking with dichloromethane (150 ml) and aqueous sodium hydroxide (5%; 150 ml). The organic solutions were combined and washed with aqueous sodium hydroxide (5%; 3 × 200 ml), hydrochloric acid (5%; 150 ml), aqueous sodium hydrogen carbonate (150 ml), and saturated aqueous sodium chloride (100 ml). Column chromatography (silica; chloroform) of the residue gave the dialdehyde (0.73 g, 57%), m.p. 134–136° (from dichloromethane–hexane) (lit.,¹⁰ 140°), ν_{max.} (KBr) 1 682 and 1 668 cm⁻¹; δ(CDCl₃) 7.40–7.60 (6 H, m), 7.85–8.02 (4 H, m), and 10.46 (2 H); m/e 276 (M⁺), 248, and 220.

Reaction of 2,5-Diphenylfuran-3,4-dicarbaldehyde with 1-Amino-trans-2,3-diphenylaziridine.—The aldehyde (50 mg, 0.18 mmol) was suspended in ether (5 ml) and the aziridine (38 mg, 0.18 mmol) was added. After 1 h at room temperature the mixture was subjected to column chromatography giving the crude imine (7) as an oil; ν_{max.} 1 675 (C=O) and 1 600 cm⁻¹ (C=N); δ(60 MHz; CCl₄) 3.60–3.80 (2 H, m), 7.0–7.9 (20 H, m), 8.50 (1 H, CH=N), and 10.35 (1 H, CH=O).

Reactions of the Imine (7).—(a) *Photolysis*. The imine (78 mg, 0.17 mmol) in benzene (110 ml) was irradiated under N₂ for 2 h (100 W medium-pressure immersion lamp, Pyrex filter). Layer chromatography gave a mixture of *cis*- and *trans*-stilbene (16 mg, 53%) and 2,5-diphenylfuran-3,4-dicarbaldehyde (13 mg, 28%).

(b) *Pyrolysis*. The imine (75 mg, 0.16 mmol) was heated under reflux in toluene (25 ml) under N₂ for 0.5 h. Layer chromatography gave *trans*-stilbene (18 mg, 63%) and 2,5-diphenylfuran-3,4-dicarbaldehyde (10 mg, 23%).

Pyrolysis of 3,3,4,6-Tetraphenyl-3H-furo[3,4-c]furan-1-one (9).—Pyrolysis of the lactone (9)¹¹ (150 mg, 0.35 mmol) at 675 °C and 0.02 mmHg gave 2-diphenylmethylene-1,4-diphenylbut-3-yn-1-one (10) (107 mg, 80%), m.p. 142.5–143.5° (from dichloromethane–hexane) (Found: C, 90.3; H, 5.4. C₂₆H₂₀O requires C, 90.6; H, 5.2%); ν_{max.} (KBr) 2 180w (C≡C), 1 660s (C=O), 1 230, and 970 cm⁻¹; λ_{max.} (cyclohexane) 251 (ε 31 000) and 318 nm (19 000); δ(CCl₄) 7.05 (5 H), 7.14 (5 H), 7.26–7.43 (6 H, m), 7.55–7.70 (2 H, m), and 7.90–8.02 (2 H, m); m/e 384 (M⁺), 307, 279 (M⁺ – PhCO), and 105 (base).

5-Phenyl-3-(4-tolyl)isoxazole-4-carbaldehyde. 3-Phenylprop-2-ynal (1.3 g, 10 mmol) and 4-methylbenzohydroximidoyl chloride¹² (1.69 g, 10 mmol) were dissolved in dichloromethane (20 ml), and triethylamine (1.1 g, 11 mmol) in dichloromethane (10 ml) was added dropwise. After 1 h the mixture was evaporated to dryness and the residue was partitioned between water and ether. The organic phase was dried and evaporated; crystallisation of the residue gave 5-phenyl-3-(4-tolyl)isoxazole-4-carbaldehyde (0.80 g, 30%), m.p. 115–116° (from ether–hexane) (Found: C, 77.7; H, 5.3; N, 5.35. C₁₇H₁₃NO₂ requires C, 77.5; H, 5.0; N, 5.3%); ν_{max.} (KBr) 1 688s cm⁻¹ (C=O); δ(CDCl₃) 2.43 (3 H), 7.30 (2 H, J 8 Hz), 8.40–8.60 (3 H, m), 8.65 (2 H, d, J 8 Hz), 7.98–8.12 (2 H, m), and 10.00 (1 H); m/e 263 (M⁺) and 234 (M⁺ – CHO).

4-(trans-2,3-Diphenylaziridin-1-yliminomethyl)-5-phenyl-3-(4-tolyl)isoxazole (8).—A solution of the foregoing aldehyde (0.30 g, 1.14 mmol) and 1-amino-trans-2,3-diphenylaziridine

¹⁰ Y. Lepage and A. Verine, *Compt. rend.*, 1972, **274C**, 1534.

¹¹ D. V. Nightingale and B. Sukornick, *J. Org. Chem.*, 1959, **24**, 497.

¹² H. Rheinboldt, M. Dewald, F. Jansen, and O. Schmitz-Dumont, *Annalen*, 1926, **451**, 161.

⁸ V. J. Traynelis, J. J. Miskel, and J. R. Sowa, *J. Org. Chem.*, 1957, **22**, 1269.

⁹ S. Adjangba, D. Billet, and C. Mentzer, *Bull. Soc. chim. France*, 1962, 132.

(0.30 g, 1.4 mmol) in ether (10 ml) was kept at 5 °C for 16 h. A crystalline solid was formed; this was filtered off and recrystallised to give the *aziridinylimine* (8) (0.35 g, 67%), m.p. 138.5–140° (from ether–hexane) (Found: C, 81.5; H, 5.6; N, 9.1. $C_{31}H_{25}N_3O$ requires C, 81.7; H, 5.5; N, 9.2%); ν_{\max} (KBr) 1 620 and 1 598 cm^{-1} ; $\delta(CDCl_3)$ 2.40 (3 H), 3.2–3.4 (2 H, m), 6.7–7.6 (19 H, m), and 7.95 (1 H).

Photolysis of the Imine (8) in Ether.—A solution of the imine (205 mg, 0.45 mmol) in ether (125 ml) was irradiated (500 W medium-pressure lamp, Pyrex filter) for 1 h. Chromatography of the products gave *cis*- and *trans*-stilbene (67 mg, 94%) and an oil, identified as 4-(2-ethoxypropyl)-5-phenyl-3-(4-tolyl)isoxazole (70 mg, 48%), b.p. 160–170° at 0.06 mmHg (Found: C, 78.2; H, 7.0; N, 4.5. $C_{21}H_{23}NO_2$ requires C, 78.5; H, 7.2; N, 4.4%); $\delta(CDCl_3)$ 0.98 (3 H, t,

J 7 Hz), 1.00 (3 H, d, J 7 Hz), 2.41 (3 H), 2.88 (2 H, dq, J 10 and 7 Hz), 3.25 (1 H, m), 3.40 (2 H, q, J 7 Hz), 7.26 (2 H, d, J 8 Hz), 7.35–7.48 (3 H, m), 7.56 (2 H, d, J 8 Hz), and 7.77–7.92 (2 H, m); m/e 321 (M^+).

Pyrolysis of the Imine (8).—The imine (280 mg, 0.61 mmol) was heated at 200 °C for 5 min and the residue was subjected to layer chromatography. 4-Toluenitrile and benzoylacetylene were obtained as a 1 : 1 mixture, the i.r. spectrum of which was identical with that of a mixture of authentic specimens: ν_{\max} 3 290 (C≡C–H), 2 220 (C≡N), 2 090 (C=CH), and 1 650 cm^{-1} (C=O).

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