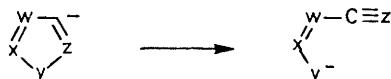


Ring-opening of 2,5-Diaryl-3-lithiofurans

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The 2,5-diaryl-3-bromofurans (1) react with butyl-lithium to give the corresponding 2,5-diarylfurans and the allenes (4) or the acetylenes (6): by carrying out the reaction in hexane at 65–70 °C the allenes and acetylenes can be obtained in good yields. Enolate intermediates (5) are proposed: these can also be intercepted by acetic anhydride, to give the acetylenic enol acetates (7), and by aromatic aldehydes, to give the pentenediones (8). 3-Bromo-1-methyl-2,4,5-triphenylpyrrole (2) does not give products of ring-opening with butyl-lithium, but from 4-bromo-2,5-diphenyloxazole (3) an open-chain intermediate (9) is formed which reacts with benzaldehyde to give the amide (10).

CARBANIONS derived from aromatic five-membered heterocycles undergo two general types of ring-opening



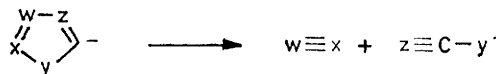
SCHEME 1

(Schemes 1 and 2). Ring-cleavage involving the breaking of just one bond (Scheme 1) is the more common;

¹ A. Quilico, 'The Chemistry of Heterocyclic Compounds, Five- and Six-membered Compounds with Nitrogen and Oxygen,' ed. R. H. Wiley, Interscience, New York, 1962, p. 44; R. B. Woodward and R. A. Olofson, *J. Amer. Chem. Soc.*, 1961, **83**, 1007; S. Cabiddu and V. Solinas, *Gazzetta*, 1969, **99**, 1107.

² R. G. Micetich, *Canad. J. Chem.*, 1970, **48**, 2006; see V. Bertini, A. De Munno, A. Menconi, and A. Fissi, *J. Org. Chem.*, 1974, **39**, 2294.

such reactions are especially favourable when a nitrile function is generated ($z = \text{N}$). Examples have been reported with isoxazoles,¹ isothiazoles,² pyrazoles,³



SCHEME 2

1,2,3-triazoles,⁴ 1,2,4-oxadiazoles,⁵ and 1,2,5-oxadiazoles.⁶ In the potentially more useful cases where an acetylene

³ R. Fusco and M. Bianchi, *Gazzetta*, 1967, **97**, 410.

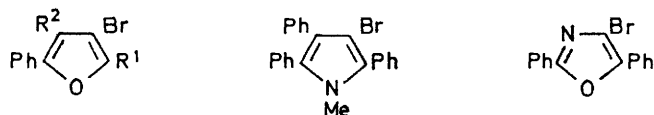
⁴ D. J. Brecknell, R. M. Carman, H. C. Deeth, and J. J. Kibby, *Austral. J. Chem.*, 1969, **22**, 1915.

⁵ D. M. Zimmerman and R. A. Olofson, *Tetrahedron Letters* 1970, 3453.

⁶ A. Russanow, *Ber.*, 1891, **24**, 3497.

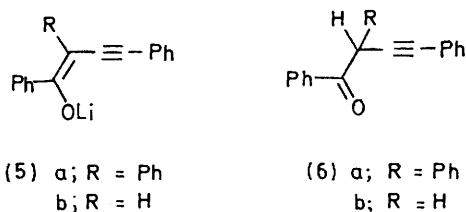
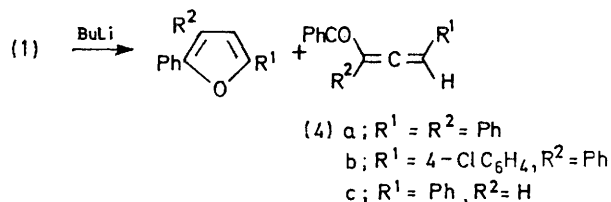
would be generated by ring-opening ($z = CR$) this type of reaction can still occur, although with an appreciable activation energy. Several 3-lithiothiophenes have been found to give products of ring-opening;⁷⁻⁹ the reaction has also been observed with selenophenes⁸⁻¹⁰ and, in one case, with a furan.⁹ The ring-opening occurs readily in some benzo-derivatives: examples have been reported both with benzothiophenes¹¹ and with benzofurans.¹²

In an attempt to develop the reaction into a more general route to conjugated acetylenes, we have investigated the properties of some 2,5-diaryl-3-lithiofurans, generated by the reaction of the 3-bromofurans



- (1) a; $R^1 = R^2 = Ph$
 b; $R^1 = 4-ClC_6H_4, R^2 = Ph$
 c; $R^1 = Ph, R^2 = H$

(1) with butyl-lithium. Corresponding reactions of 3-bromo-1-methyl-2,4,5-triphenylpyrrole (2) and of 4-bromo-2,5-diphenyloxazole (3) have also been explored.



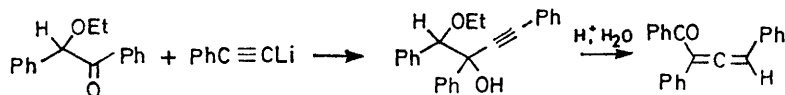
3-Lithio-2,4,5-triphenylfuran was first generated by Gilman and Melstrom from the 3-bromofuran (1a) and butyl-lithium in ether at room temperature.¹³ They

of the reaction between the bromofuran (1a) and butyl-lithium are dependent upon both the solvent and the temperature. A reaction carried out at room temperature in benzene, and followed by the addition of water, gave two products which were isolated and identified as 2,3,5-triphenylfuran (30%) and 1,2,4-triphenylbuta-2,3-dien-1-one (4a) (60%). The allene (4a) showed i.r. absorption at 1910 cm^{-1} , and was identical with material synthesised independently (Scheme 3).

When a similar reaction was performed in ether at room temperature, the allene was isolated in only 5% yield, the major product being 2,3,5-triphenylfuran (60%). In hexane, the 3-lithiofuran was precipitated. When this was filtered off and hydrolysed it gave 2,3,5-triphenylfuran (81%). When the suspension of the lithiofuran in hexane was heated at $65-70^\circ$, however, the precipitate dissolved, and a second precipitate appeared. After 1 h the precipitate was filtered off; its i.r. spectrum showed $\nu_{\text{max.}} 2180\text{ cm}^{-1}$, and when it was hydrolysed it gave the allene (4a) in 77% yield, with only a trace of triphenylfuran.

The lithium enolate (5a) thus appears to be formed in some solvents and particularly at higher temperatures. Protonation of the enolate at C-4 then gives the allene (4a). A reaction mixture which was quenched with acetic acid instead of water gave a mixture consisting of the allene (4a) and the isomeric acetylene (6a) in approximately equal amounts, but when attempts were made to separate the mixture, the acetylene isomerised to the allene.

Analogous reactions were carried out with 3-bromo-2-(4-chlorophenyl)-4,5-diphenylfuran (1b) and with 3-bromo-2,5-diphenylfuran (1c). The bromofuran (1b) gave, with butyl-lithium in benzene at room temperature, a mixture of 5-(4-chlorophenyl)-2,3-diphenylfuran (40%) and the allene (4b) (40%). An authentic specimen of the furan was prepared by a standard route. Reaction of the bromofuran (1c) in benzene gave 2,5-diphenylfuran (40%) and a mixture of the allene (4c) and the isomeric acetylene (6b) (54%). This mixture was not separated, but in a subsequent reaction carried out at $65-70^\circ$ in which the mixture was quenched by the addition of acetic acid, the acetylene (6b) was isolated



SCHEME 3

used the derivative to prepare the 3-furoic acid in good yield, and they later commented on the apparent stability of the ring system compared with that of 3-lithiobenzofuran.^{12b} We have found that the products

⁷ H. J. Jakobsen, *Acta Chem. Scand.*, 1970, **24**, 2663.

⁸ S. Gronowitz and T. Frejd, *Acta Chem. Scand.*, 1970, **24**, 2656; 1973, **27**, 2242.

⁹ S. Gronowitz and T. Frejd, *Internat. J. Sulphur Chem. (A)*, 1972, **2**, 165.

¹⁰ S. Gronowitz and T. Frejd, *Acta Chem. Scand.*, 1969, **23**, 2540.

in 75% yield. The acetylene has been prepared previously by a different route.¹⁴

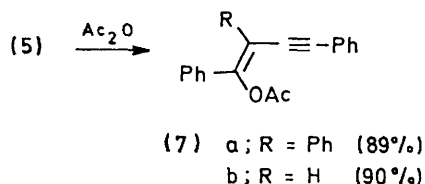
¹¹ R. P. Dickinson and B. Iddon, *Tetrahedron Letters*, 1970, 975; *J. Chem. Soc. (C)*, 1968, 2733; 1970, 2592; 1971, 2504, 3447; *Internat. J. Sulphur Chem. (C)*, 1971, **6**, 59.

¹² (a) T. Reichstein and J. Baud, *Helv. Chim. Acta*, 1937, **20**, 892; (b) H. Gilman and D. S. Melstrom, *J. Amer. Chem. Soc.*, 1948, **70**, 1655.

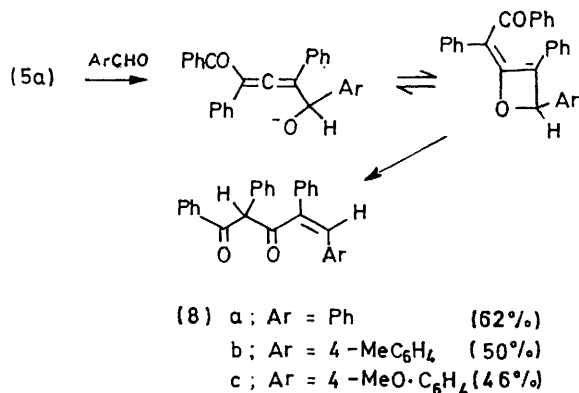
¹³ H. Gilman and D. S. Melstrom, *J. Amer. Chem. Soc.*, 1946, **68**, 103.

¹⁴ A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *J. Amer. Chem. Soc.*, 1967, **89**, 4435.

Reactions of the open-chain lithium enolates with other electrophiles were then investigated. When the suspensions containing the enolates (5a and b) were quenched by the addition of acetic anhydride, the enol acetates (7) were isolated in high yields. The enolate (5a) reacted with aromatic aldehydes in the presence of



hexamethylphosphoramide to give 1:1 adducts. These were assigned the pent-4-ene-1,3-dione structures (8) on the basis of their spectral properties: thus, the n.m.r. spectrum of (8a) showed one-proton singlets at δ 6.00 and 7.77, and carbonyl i.r. absorptions at 1705 and 1664 cm^{-1} . A mechanism for the formation of these diketones is shown in Scheme 4; a similar reaction of lithium



SCHEME 4

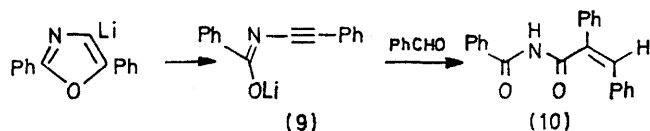
ketenimides with aromatic aldehydes has recently been described,¹⁵ and a similar rationale put forward. By analogy with the products reported,¹⁵ the pentenediones (8) are probably the *Z*-isomers.

These reactions thus provide a useful route to the lithium enolates (5), and to products derived from them. Unfortunately the reaction appears to be limited in scope, since both Gronowitz and Frejd⁹ and ourselves have found that 3-bromofuran and 2,5-dialkyl-3-bromofurans give lithium enolates which are unstable and liable to polymerise.

In order to determine whether the analogous ring-opening of a simple pyrrole could be observed, we prepared 3-bromo-1-methyl-2,5-diphenylpyrrole (2) and subjected it to the same reaction conditions as the furans. The bromopyrrole reacted readily with butyllithium in hexane and the solution of the lithiopyrrole was heated at 65–70 °C for 1 h. The i.r. spectrum of the

solid at this stage showed no absorption in the region 2500–2000 cm^{-1} , and when water was added 1-methyl-2,3,5-triphenylpyrrole was isolated in nearly quantitative yield. The activation energy for opening of the 3-pyrrolyl-lithium derivative is, not surprisingly, higher than for the corresponding furans. An electron-withdrawing group on the nitrogen atom might make the ring-opening easier.

The reaction of a related oxazole, 4-bromo-2,5-diphenyl-oxazole (3), with butyllithium, was also investigated. Although no ring-opening reactions of oxazol-4-yl salts have been reported, there has been considerable recent interest in the mechanism of the Cornforth rearrangement, a thermal reaction involving cleavage of the oxazole ring in which the nitrogen lone pair acts in much the same way as the carbanion lone pair in Scheme 1.¹⁶ The bromo-oxazole (3) reacted with butyllithium in hexane and, at 65–70°, gave a precipitate which was stable in air and which showed i.r. absorption at 2200 cm^{-1} . Attempts to intercept the open-chain intermediate with a variety of electrophiles were unsuccessful, however, and complex mixtures were obtained from which diphenyloxazole could be isolated in low yields. The intermediate (9), analogous to those formed from the furans, is probably generated, but the products derived from it by protonation or acylation are



clearly much less stable than the allenes and acetylenes, (4) and (6). Only in one case was an open-chain product isolated: reaction of the enolate (9) with benzaldehyde in the presence of hexamethylphosphoramide gave a 1:1 adduct, ν_{max} 3410, 1740, and 1610 cm^{-1} , to which structure (10) is assigned by analogy with the reactions described earlier.

EXPERIMENTAL

I.r. spectra were obtained using a Perkin-Elmer 125 spectrometer (KBr discs) or a Pye-Unicam SP 200 spectrometer (chloroform solutions and Nujol mulls). U.v. spectra were measured using a Pye-Unicam SP 800 spectrophotometer and mass spectra were obtained with an A.E.I. MS 12 machine at 70 eV by using a direct insertion probe. ¹H N.m.r. spectra were obtained at 100 MHz with a Varian HA100 instrument. Preparative layer chromatography was carried out with silica gel PF₂₅₄ (Merck) as the stationary phase. Benzene, ether, hexane, and tetrahydrofuran were dried and distilled from lithium aluminium hydride before use.

2,3,5-Triphenylfuran,¹⁷ 3-bromo-2,4,5-triphenylfuran,¹⁸ 3-bromo-2-(4-chlorophenyl)-4,5-diphenylfuran,¹⁸ and 3-bromo-2,5-diphenylfuran¹⁹ were prepared by the literature

¹⁷ H. M. Taylor and C. R. Hauser, *J. Amer. Chem. Soc.*, **1960**, **82**, 1790.

¹⁸ C. F. H. Allen and H. B. Rosener, *J. Amer. Chem. Soc.*, **1927**, **49**, 2110.

¹⁹ P. M. G. Bavin, *J. Pharm. Pharmacol.*, **1965**, **17**, 236.

¹⁵ U. Schöllkopf and I. Hoppe, *Annalen*, **1974**, 1655.

¹⁶ M. J. S. Dewar and I. J. Turchi, *J. Amer. Chem. Soc.*, **1974**, **96**, 6148; I. J. Turchi and M. J. S. Dewar, *Chem. Rev.*, **1975**, **75**, 389.

procedures indicated. Butyl-lithium in hexane (Fluka) was titrated before use. Reactions with butyl-lithium were performed under nitrogen in flasks fitted with rubber septums.

Reactions of 3-Bromo-2,4,5-triphenylfuran (1a) with Butyl-lithium.—(a) *In benzene.* The furan (250 mg, 0.67 mmol) was dissolved in benzene (10 ml) at room temperature under nitrogen. Butyl-lithium in hexane (0.68 mmol) was added. The solution was left at room temperature for 1 h and quenched with water. Layer chromatography (ether-hexane, 3:20) gave 2,3,5-triphenylfuran (60 mg, 30%), m.p. 90–91° (lit.,¹⁷ 90.5–91.5°), $\delta(\text{CDCl}_3)$ 6.70 (1 H) and 7.1–7.8 (15 H, m); and 1,2,4-triphenylbuta-2,3-dien-1-one (4a) (121 mg, 60%), m.p. 98–99.5° (from ether-hexane) (Found: C, 88.9; H, 5.3. $\text{C}_{22}\text{H}_{16}\text{O}$ requires C, 89.2; H, 5.4%); ν_{max} (KBr) 1 910 and 1 650 cm^{-1} ; $\delta(\text{CCl}_4)$ 6.54 (1 H), 7.0–7.4 (13 H, m), and 7.75–7.88 (2 H, m); m/e 296 (M^+), 268, 191, and 105 (base). The spectra were identical with those obtained from a specimen synthesised from phenylacetylene, as detailed below.

(b) *In hexane.* Addition of butyl-lithium (0.68 mmol) to a solution of the bromofuran (250 mg, 0.67 mmol) in hexane produced a cream-coloured precipitate showing no i.r. absorption in the region of 2 200–2 000 cm^{-1} (in Nujol). Quenching with water gave 2,3,5-triphenylfuran (163 mg, 81%).

In other experiments, the mixture containing the precipitate was heated at 65–70° for 1 h. The solid dissolved and another precipitate appeared; this had ν_{max} (Nujol) 2 180 cm^{-1} . Addition of water gave 1,2,4-triphenylbuta-2,3-dien-1-one (155 mg, 77%).

Addition of acetic acid to the reaction mixture instead of water gave a mixture containing the allene (4a) (40%) and 1,2,4-triphenylbut-3-yn-1-one (6a) (40%) (by n.m.r.); $\delta(\text{CDCl}_3)$ 5.42 and 6.54. Layer chromatography gave the allene (4a) (132 mg, 66%).

(c) *In ether.* Reaction of the 3-bromofuran (0.67 mmol) with butyl-lithium in ether at 20 °C for 1 h gave, after layer chromatography, 2,3,5-triphenylfuran (60%) and the allene (4a) (5%).

1,2,4-Triphenylbuta-2,3-dien-1-one (4a).—(a) *1-Ethoxy-1,2,4-triphenylbut-3-yn-2-ol.* Phenylacetylene (0.82 g, 8 mmol) in benzene (20 ml) was treated with butyl-lithium (8 mmol) at 20 °C. After 10 min, benzoin ethyl ether²⁰ (1.92 g, 8 mmol) in benzene (5 ml) was added. The solution was stirred for 10 min then quenched with water, and the organic solution was diluted with ether, dried, and evaporated to give 1-ethoxy-1,2,4-triphenylbut-3-yn-2-ol (2.0 g, 73%), m.p. 51–54° (from ether-hexane) (Found: C, 84.3; H, 6.6. $\text{C}_{24}\text{H}_{22}\text{O}_2$ requires C, 84.2; H, 6.5%); ν_{max} (KBr) 3 550 and 2 220 cm^{-1} ; $\delta(\text{CDCl}_3)$ 0.91 (3 H, t, J 7 Hz), 3.00 (1 H), 3.23 (2 H, q, J 7 Hz), 4.29 (1 H), and 6.9–7.3 (15 H, m); m/e 342 (M^+).

(b) A solution of 1-ethoxy-1,2,4-triphenylbut-3-yn-2-ol (0.17 g) in benzene containing a crystal of toluene-*p*-sulphonic acid was heated under reflux for 18 h. Layer chromatography gave 1,2,4-triphenylbuta-2,3-dien-1-one (0.097 g, 56%), m.p. and mixed m.p. 98–99°, identical (i.r.) with the specimen isolated from the reaction of 3-bromo-2,4,5-triphenylfuran with butyl-lithium.

Reaction of 3-Bromo-2-(4-chlorophenyl)-4,5-diphenylfuran with Butyl-lithium.—The bromofuran (1b) (205 mg, 0.50 mmol) was dissolved in benzene (10 ml) and the solution treated with butyl-lithium (0.52 mmol) in hexane at 20 °C. After 1 h the mixture was quenched with water and the

products were separated by layer chromatography (ether-hexane, 1:5). This gave 5-(4-chlorophenyl)-2,3-diphenylfuran (133 mg, 40%), m.p. 100–102° (from chloroform-methanol) (Found: C, 79.8; H, 4.6; Cl, 10.9. $\text{C}_{22}\text{H}_{15}\text{ClO}$ requires C, 79.9; H, 4.6; Cl, 10.7%); $\delta(\text{CCl}_4)$ 6.64 (1 H) and 7.1–7.7 (14 H, m); m/e 332 and 330 (M^+). A second band gave 4-(4-chlorophenyl)-1,2-diphenylbuta-2,3-dien-1-one (4b) (137 mg, 41%), m.p. 81.5–83° (from ether-hexane) (Found: C, 79.6; H, 4.4; Cl, 10.9. $\text{C}_{22}\text{H}_{15}\text{ClO}$ requires C, 79.9; H, 4.6; Cl, 10.7%); ν_{max} (KBr) 1 918 and 1 650 cm^{-1} ; $\delta(\text{CCl}_4)$ 6.52 (1 H), 7.1–7.4 (12 H, m), and 7.74–7.87 (2 H, m); m/e 332 and 330 (M^+), and 227 and 225 ($M^+ - \text{PhCO}$).

5-(4-Chlorophenyl)-2,3-diphenylfuran.—This was prepared according to the general method of Lutz and Rowlett.²¹ 4-(4-Chlorophenyl)-1,2-diphenylbut-2-ene-1,4-dione¹⁸ (5 g) was added in portions to a heated solution of tin(II) chloride (5 g) in acetic acid (5 ml) and concentrated hydrochloric acid (5 ml). The mixture was heated under reflux for 0.5 h, cooled, and diluted with water, and the solid was extracted with ether to give 5-(4-chlorophenyl)-2,3-diphenylfuran (1.6 g, 35%), m.p. 100–102° (from chloroform-methanol).

Reactions of 3-Bromo-2,5-diphenylfuran (1c) with Butyl-lithium.—(a) Butyl-lithium (0.68 mmol) in hexane was added to a solution of the bromofuran (200 mg, 0.67 mmol) in benzene (10 ml) at 20 °C. After 1 h, water (10 ml) was added and the products were subjected to layer chromatography (ether-petroleum, 1:5). This gave 2,5-diphenylfuran (60 mg, 40%), m.p. 88–90° (lit.,²¹ 89.5–90°), and a mixture (*ca.* 1:1, by n.m.r.) of 1,4-diphenylbuta-2,3-dien-1-one (4c) and 1,4-diphenylbut-3-yn-1-one (6b) (80 mg, 54%); ν_{max} (liq.) 1 935, 1 683, and 1 647 cm^{-1} ; $\delta(\text{CCl}_4)$ 3.88 (CH₂ of alkynone), and 6.29 (d, J 6.5 Hz) and 6.41 (d, J 6.5 Hz) (CH of allene).

(b) A reaction mixture prepared as in (a) was heated at 65–70 °C for 1 h; it was then cooled and hydrolysed with acetic acid (2 ml). The mixture was diluted with water and the organic product was extracted with ether. Crystallisation gave 1,4-diphenylbut-3-yn-1-one (110 mg, 75%), m.p. 71–73° (from dichloromethane-hexane) (lit.,¹⁴ 75–76°); ν_{max} (KBr) 1 688 cm^{-1} ; $\delta(\text{CCl}_4)$ 3.86 (2 H), 7.1–7.4 (8 H, m), and 7.9–8.0 (2 H, m); m/e 220 and 192.

1,2,4-Triphenylbut-1-en-3-ynyl Acetate (7a).—3-Bromo-2,4,5-triphenylfuran (250 mg, 0.67 mmol) and butyl-lithium (0.68 ml) in hexane were heated at 65–70 °C for 1.5 h and acetic anhydride (0.4 ml) was then added. The mixture was maintained at 65 °C for 10 min, and was then cooled and diluted with water and ether. The organic product was crystallised to give 1,2,4-triphenylbut-1-en-3-ynyl acetate (7a) (217 mg, 89%), m.p. 95–96.5° (from ether-hexane) (Found: C, 85.0; H, 5.6. $\text{C}_{24}\text{H}_{18}\text{O}_2$ requires C, 85.2; H, 5.4%); ν_{max} (KBr) 2 190w and 1 750 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.30 (3 H) and 7.15–7.50 (15 H, m); m/e 338 (M^+), 296, 191, and 105 (base).

1,4-Diphenylbut-1-en-3-ynyl Acetate (7b).—Reaction of 3-bromo-2,5-diphenylfuran with butyl-lithium and hexane as in the preceding experiment gave 1,4-diphenylbut-1-en-3-ynyl acetate (7b) (154 mg, 90%), m.p. 107–108° (from ether-hexane) (Found: C, 82.5; H, 5.5. $\text{C}_{18}\text{H}_{14}\text{O}_2$ requires C, 82.4; H, 5.4%); ν_{max} (KBr) 2 200w and 1 756 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.35 (3 H), 6.11 (1 H), and 7.2–7.5 (10 H, m); m/e 262 (M^+), 220, 191, and 105.

1,2,4,5-Tetraphenylpent-4-ene-1,3-dione (8a).—To 3-

²⁰ R. Quelet and E. Frainnet, *Compt. rend.*, 1953, **236C**, 492.
²¹ R. E. Lutz and R. J. Rowlett, *J. Amer. Chem. Soc.*, 1948, **70**, 1359.

bromo-2,4,5-triphenylfuran (0.75 g, 2 mmol) and hexamethylphosphoramide (0.75 g) in hexane (30 ml) at 70 °C was added butyl-lithium in hexane (2 mmol). The mixture was heated at 70 °C for 20 min and benzaldehyde (0.23 g, 2.2 mmol) was added. After 1 h at 70 °C, the mixture was cooled and diluted with water and chloroform. The organic layer yielded 1,2,4,5-tetraphenylpent-4-ene-1,3-dione (8a) (0.50 g, 62%), m.p. 145–147° (from ethanol) (Found: C, 86.4; H, 5.6. $C_{29}H_{22}O_2$ requires C, 86.6; H, 5.5%); ν_{\max} (KBr) 1705, 1664, and 1619 cm^{-1} ; $\delta(CDCl_3)$ 6.00 (1 H), 6.9–7.4 (18 H, m), 7.6–7.75 (2 H, m), and 7.77 (1 H); m/e 402 (M^+), 384, 325, and 105 (base).

1,2,4-Triphenyl-5-(4-tolyl)pent-4-ene-1,3-dione (8b).—By the foregoing procedure 3-bromo-2,4,5-triphenylfuran (0.75 g, 2 mmol) and *p*-tolualdehyde (0.26 g, 2.2 mmol) gave an oil which was subjected to layer chromatography (ether–pentane, 3:10). This gave 1,2,4-triphenyl-5-(4-tolyl)pent-4-ene-1,3-dione (8b) (0.42 g, 50%), m.p. 155–157° (from ethanol) (Found: C, 86.5; H, 5.9. $C_{30}H_{24}O_2$ requires C, 86.5; H, 6.0%); ν_{\max} (KBr) 1698, 1660, and 1616 cm^{-1} ; $\delta(CDCl_3)$ 2.19 (3 H), 6.00 (1 H), 6.84 (4 H), 7.0–7.4 (13 H, m), 7.63–7.75 (2 H, m), and 7.78 (1 H); m/e 416 (M^+), 398, 325, and 221 (base).

5-(4-Methoxyphenyl)-1,2,4-triphenylpent-4-ene-1,3-dione (8c).—By the procedure for the preparation of compound (8a), 3-bromo-2,4,5-triphenylfuran (0.75 g, 2 mmol) and *p*-methoxybenzaldehyde (0.30 g, 2.2 mmol) gave, after layer chromatography of the crude product, 5-(4-methoxyphenyl)-1,2,4-triphenylpent-4-ene-1,3-dione (8c) (0.40 g, 46%), m.p. 125–127° (from ethanol) (Found: C, 83.1; H, 5.7. $C_{30}H_{24}O_3$ requires C, 83.3; H, 5.6%); ν_{\max} (KBr) 1700, 1662, 1618, and 1600 cm^{-1} ; $\delta(CDCl_3)$ 3.66 (3 H), 5.98 (1 H), 6.59 (2 H, d, *J* 9 Hz), 6.91 (2 H, d, *J* 9 Hz), 7.04–7.24 (13 H, m), 7.64–7.76 (2 H, m), and 7.75 (1 H); m/e 432 (M^+), 414, 325, and 237 (base).

3-Bromo-1-methyl-2,4,5-triphenylpyrrole (2).—1-Methyl-2,3,5-triphenylpyrrole²² (1.0 g, 3.3 mmol) and *N*-bromosuccinimide (0.7 g, 4 mmol) were heated in carbon tetrachloride (15 ml) under reflux for 1 h. The mixture was cooled and filtered. The filtrate, after treatment with charcoal, gave 3-bromo-1-methyl-2,4,5-triphenylpyrrole (2) (1.1 g, 88%), m.p. 133–134° (from ether–hexane) (Found: C, 70.9; H, 4.9; N, 3.4. $C_{23}H_{18}BrN$ requires C, 71.1; H, 4.7; N, 3.6%); ν_{\max} 1600 and 1349 cm^{-1} ; $\delta(CCl_4)$ 3.29 (3 H) and 7.0–7.5 (15 H, m); m/e 389 and 387 (M^+).

Reaction of 3-Bromo-1-methyl-2,4,5-triphenylpyrrole with

²² A. Lespagnol, J. M. Dumont, J. Mercier, and Mme. Etzensperger, *Bull. Soc. pharm. Lille*, 1955, No. 1, 87 (*Chem. Abs.*, 1956, 50, 3399b).

Butyl-lithium.—The bromopyrrole (130 mg, 0.33 mmol) in cyclohexane (10 ml) was treated with butyl-lithium (0.34 mmol) in hexane, and the solution was heated at 65–70 °C for 1 h. The i.r. spectrum of the solution then showed no absorption in the region 2500–2000 cm^{-1} . It was treated with water (10 ml) and diluted with ether (10 ml); the organic solution gave 2,3,5-triphenylpyrrole (100 mg, 97%), m.p. 175–177° (lit.,²² 177–178°).

4-Bromo-2,5-diphenyloxazole (3).—2,5-Diphenyloxazole (1.0 g, 4.5 mmol) and *N*-bromosuccinimide (1.0 g, 5.7 mmol) were heated in carbon tetrachloride (10 ml) containing a few drops of hydrobromic acid. After 3 h the mixture was cooled and filtered; the filtrate gave 4-bromo-2,5-diphenyloxazole (1.2 g, 88%), m.p. 70–72° (from methanol) (lit.,²³ 66°).

Reaction of 4-Bromo-2,5-diphenyloxazole with *Butyl-lithium*.—The oxazole (200 mg, 0.67 mmol) in hexane (10 ml) and butyl-lithium (0.68 mmol) in hexane were mixed and heated at 65–70 °C for 1 h. A precipitate appeared; this was filtered off and had ν_{\max} (KBr) 2220 cm^{-1} . The solid was treated with water (10 ml) and ether (10 ml); the organic solution was evaporated and the residual mixture was subjected to layer chromatography (ether–hexane, 1:1). This gave 2,5-diphenyloxazole (15 mg, 10%) as the only identified product.

N-Benzoyl-2,3-diphenylacrylamide (10).—4-Bromo-2,5-diphenyloxazole (200 mg, 0.67 mmol) and butyl-lithium (0.68 mmol) were heated in hexane (15 ml) containing hexamethylphosphoramide (0.2 ml) at 65–70 °C for 20 min. Benzaldehyde (106 mg, 1 mmol) in hexane was then added, and the solution was again heated at 65–70 °C. After 1 h water (10 ml) was added; the organic layer was diluted with ether, washed, dried, and evaporated. Trituration of the residual oil with ether gave *N*-benzoyl-2,3-diphenylacrylamide (10) (108 mg, 50%), m.p. 199–201° (from chloroform–ethanol) (Found: C, 80.8; H, 5.3; N, 4.4. $C_{22}H_{17}NO_2$ requires C, 80.7; H, 5.2; N, 4.3%); ν_{\max} (KBr) 3410, 1740, 1610, and 1570 cm^{-1} ; λ_{\max} (EtOH) 228 (ϵ 17 700) and 300 nm (16 000); $\delta(CDCl_3)$ 6.9–7.5 (15 H, m), 8.00 (1 H), and 8.58 (1 H; disappears with D_2O); m/e 327 (M^+), 299, and 105 (base).

We thank Professor C. W. Rees and Dr. C. Thomas for discussion, and the S.R.C. for a Research Studentship (to D. P. J. P.).

[5/2108 Received, 28th October, 1975]

²³ O. P. Shvaika and G. P. Klimisha, *Dopovidi Akad. Nauk Ukrain. R.S.R.*, 1965, 1479 (*Chem. Abs.*, 1966, 65, 7159h).