# Elimination of Nitriles in Retro-diene Reactions

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The Diels–Alder reactions of the oxazoles (II; R = H or Me) and (III) with diphenylcyclopropenone and acetylenic dienophiles have been studied. In no case were the bicyclic adducts isolable, but ready elision of hydrogen cyanide or a nitrile occurred, giving a γ-pyrone (V) and furans as the major heterocyclic products.

COMBINATION of the azabutadiene system (I) [1,2] with a 3-carbon dienophile [3-6] in a Diels–Alder reaction would provide a synthesis of 7-membered nitrogen heterocycles.[7] We investigated this possibility, using the azabutadiene system in oxazoles with diphenylcyclopropenone [8] as the dienophile. The latter has been shown to function formally as a dienophile but distinction between a concerted and a two-step cycloaddition is lacking.

Heating the oxazoles (II; R = H or Me) with diphenylcyclopropenone in toluene for 16 hr. gave none of the adduct, (IV); instead both oxazoles gave the γ-pyrone (V), identified on the basis of spectral data. Acetonitrile was detected as a product of the reaction of (II; R = Me) by g.l.c. analysis. In an attempt to isolate the intermediate adduct (IV; R = Me) the oxazole (II; R = Me) was treated with diphenylcyclopropenone in boiling benzene, but although the reaction was slower the tricyclic adduct (IV) could not be detected. The less reactive oxazole (III) did not react with diphenylcyclopropenone in boiling xylene.

These reactions, and others described later, appear to be the first examples of retro-diene reactions [9] involving elimination of hydrogen cyanide or a nitrile (IV; arrows). Nitriles are known to be poor dienophiles,[10] and only

[1] (*a*) G. Ya. Kondrat'eva and C.-H. Huang, *Doklady Akad. Nauk S.S.S.R.*, 1962, 142 (*Chem. Abs.*, 1962, **57**, 2204h); (*b*) R. A. Firestone, E. E. Harris, and W. Reuter, *Tetrahedron*, 1967, **23**, 943; (*c*) M. Murakami, K. Takahshi, J. Matsumoto, K. Tamazawa, K. Murase, H. Iwamoto, and M. Iwanami, *Bull. Chem. Soc. Japan*, 1968, **41**, 628; M. Murakami and M. Iwanami, *ibid.*, p. 726.

[2] J. Hamer in '1,4-Cycloaddition Reactions,' Academic Press, New York, 1967, ch. 1.

[3] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 2046.

[4] H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, *J. Chem. Soc.* (*B*), 1968, 57; H. M. R. Hoffmann and D. R. Joy, *ibid.*, p. 1182.

[5] A. W. Fort, *J. Amer. Chem. Soc.*, 1962, **84**, 4979; R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *J. Chem. Soc.* (*C*), 1967, 473; N. J. Turro, S. E. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *J. Amer. Chem. Soc.*, 1969, **91**, 2283.

[6] M. A. Battiste, *J. Amer. Chem. Soc.*, 1963, **85**, 2175.

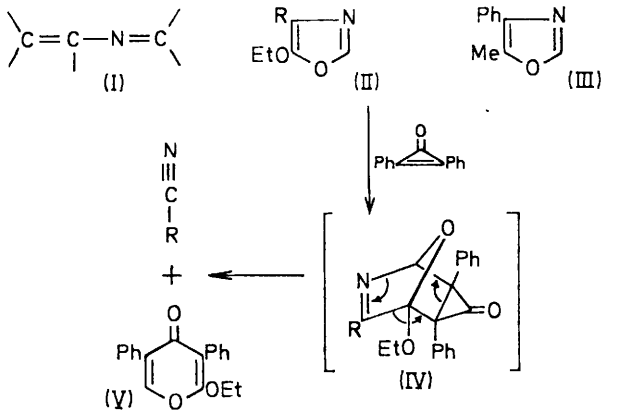
[7] R. F. Childs, R. Grigg, and A. W. Johnson, *J. Chem. Soc.* (*C*), 1967, 201.

[8] J. Ciabattoni and G. A. Berchtold, *J. Amer. Chem. Soc.*, 1965, **87**, 1404.

[9] H. Kwart and K. King, *Chem. Rev.*, 1968, 415.

[10] G. J. Janz in '1,4-Cycloaddition Reactions,' Academic Press, New York, 1967, ch. 4.

function as such in favourable cases, *e.g.* the reaction of benzonitrile with tetraphenylcyclopentadienone to give pentaphenylpyridine and carbon monoxide.[11] This



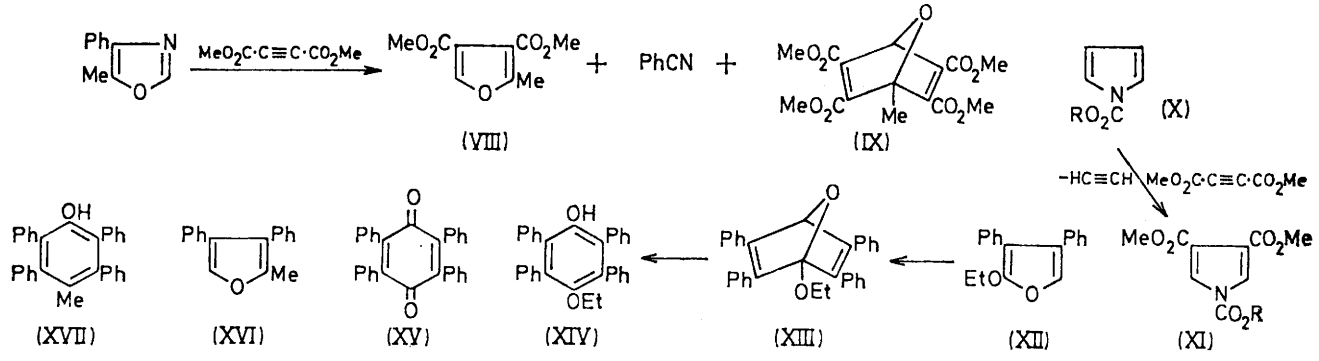
fact, coupled with the lack of diene properties in the γ-pyrone * make the fragmentation process (IV) → (V) essentially irreversible.

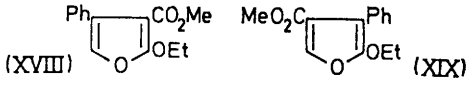
The ready elimination of hydrogen cyanide and acetonitrile led us to examine the Diels–Alder reactions of acetylenes with oxazoles, to ascertain the effect of replacing the strained three-membered ring bond in the proposed intermediate (IV) by a double bond. Dimethyl acetylenedicarboxylate reacted readily at room temperature with the oxazoles (II; R = H or Me), and again the intermediate adducts (VI) could not be isolated. The products in both cases were the furan (VII) and the appropriate nitrile. The oxazole (III) required more vigorous conditions (boiling toluene) for reaction with the acetylenic ester; the expected furan (VIII) (69%) was then obtained together with 10% of its Diels–Alder adduct (IX) and benzonitrile was isolated. A related exchange reaction involving loss of acetylene [(X) → (XI)] occurs when *N*-alkoxycarbonyl pyrroles are heated with dimethyl acetylenedicarboxylate.[12]

Diels–Alder reactions between the oxazoles and diphenylacetylene, a less reactive dienophile, required more vigorous conditions (sealed tube; 220—255°). The oxazole (II; R = Me) gave no heterocyclic products, but a phenol (XIV) was isolated in low yield (6%). Presumably formation of the furan (XII) is followed by addition of diphenylacetylene and thermal rearrangement of the adduct (XIII). The structure of (XIV) was confirmed by its conversion (75%) into the known quinone (XV). Similar treatment of the oxazole (II; R = H) with diphenylacetylene gave starting material at low temperatures and tarry mixtures at higher temperatures. These results must be attributed largely to the thermal instability of the oxazoles (II; R = H or Me). The thermally more stable oxazole (III) gave the expected furan (XVI) (38%) together with a small amount (6·9%) of a phenol (XVII).

The Diels–Alder reaction with an unsymmetrical acetylenic dienophile was briefly investigated. The oxazole (II; R = Me) reacted only slowly with methyl phenylpropiolate in boiling toluene, but the rate of reaction increased when boron trifluoride was added as a catalyst.

N.m.r. monitoring of the reaction indicated that both possible isomers, (XVIII) and (XIX) were being formed, and that the isomer distribution (3 : 2) was unchanged throughout the reaction. The α-proton signals of the isomers occurred at τ 2·41 and 3·15, the lower value being tentatively assigned to (XIX).





When cycloaddition reactions between furan, 2-methylfuran, and *N*-ethoxycarbonylpyrrole with diphenylcyclopropenone were attempted in boiling toluene the sole products were two new dimers of diphenylcyclopropenone. The same dimer, m.p. 159—161°, was

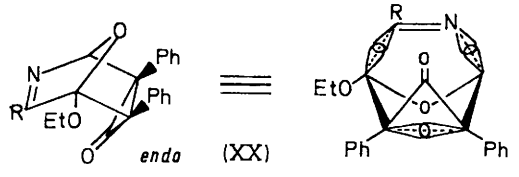
* No reaction was observed when an equimolar solution of the pyrone (V) and dimethyl acetylenedicarboxylate was boiled under reflux in toluene for 14 hr.

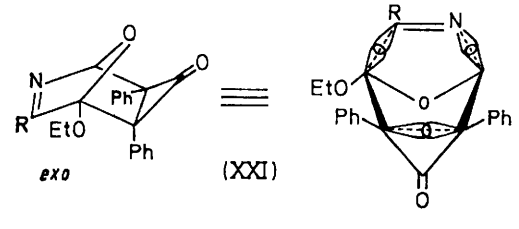
[11] W. Dilthey, W. Schommer, W. Hoschen, and H. Dierichs, *Ber.*, 1935, **68**, 1159.

[12] R. M. Acheson and J. M. Vernon, *J. Chem. Soc.*, 1961, 457; N. W. Gabel, *J. Org. Chem.*, 1962, **27**, 301.

obtained from reactions with both furan and 2-methylfuran, whereas the reaction involving the pyrrole gave a different dimer, m.p. 275—276°. Pyrolysis of diphenylcyclopropenone at 145—150° has been reported [13] to give a dimer, m.p. 181—182°. The new dimers both exhibited i.r. absorption between 1810—1860 cm.$^{-1}$, suggesting that both still contained a cyclopropene or cyclopropanone fragment, but apart from spectral data no structural investigation was attempted.*

The formation of the γ-pyrone (V) from the reaction of the oxazoles (II; R = H or Me) with diphenylcyclopropenone constitutes an example of a retro-homo-Diels–Alder reaction; several related examples [14-16] have been reported recently. In particular, evidence for a preferred transition-state geometry, in which the cyclopropane ring and the departing molecule are *trans*, was obtained.[14,16] This geometry allows maximum orbital overlap of bonds undergoing fission. In our examples the expected adduct [17,18] is the *endo*-isomer (XX), in which the cyclopropanone ring and the departing fragment are *cis*, whereas the *exo*-isomer (XXI) in




which the cyclopropanone ring and the departing fragment are *trans* should undergo a more readily retro-homo-Diels–Alder reaction. Whether the transient nature of the adduct (IV) is due to formation of the *exo*-adduct or whether the presence of the more strained cyclopropanone ring accelerates fragmentation of the *endo*-isomer is not known.

## EXPERIMENTAL

Except where otherwise stated u.v. spectra were determined for solutions in ethanol, i.r. spectra for potassium bromide discs, and n.m.r. spectra for solutions in deuteriochloroform with a Perkin-Elmer R10 (60 MHz).

*5-Ethoxyoxazole* (II; R = H).—Prepared (17·7%) by adaptation of an oxazole synthesis,[19] the product was a colourless oil, b.p. 52°/15 mm. (Found: C, 53·05; H, 6·0; N, 12·45. $C_5H_7NO_2$ requires C, 53·1; H, 6·25; N, 12·4%), $\lambda_{max.}$ 225 nm. (ε 5560), $\nu_{max.}$ (film) 983, 1042, 1257, 1341, 1524, 1617, 2989, and 3144 cm.$^{-1}$, τ ($CCl_4$) 2·66 and 3·95 (2H, s, ring protons), 5·91 (2H, q, $MeCH_2$), and 8·63 (3H, t, $MeCH_2$).

*Cycloaddition of Diphenylcyclopropenone to 5-Ethoxy-4-methyloxazole.*—Diphenylcyclopropenone (2·06 g., 0·01 mole) and 5-ethoxy-4-methyloxazole (1·90 g., 0·015 mole) were boiled under reflux in toluene (25 ml.) for 16 hr. The cooled mixture deposited crystals, which were washed with a little cold ether and dried. A second crop was obtained by concentration of the mother liquors to give *2-ethoxy-3,5-diphenyl-4-pyrone* (V) (total yield 2·08 g., 71%). The product gave colourless needles from benzene, m.p. 158—159° [Found: C, 78·2; H, 5·6%; *M* (mass spectrum), 292. $C_{19}H_{16}O_3$ requires C, 78·05; H, 5·52%; *M*, 292], $\lambda_{max.}$ 234 nm. (ε 23,400), $\lambda_{infl.}$ 261 nm. (ε 11,600), $\nu_{max.}$ ($CHCl_3$) 1647, 1567, 1416, 1348, and 1309 cm.$^{-1}$, τ 2·35 (s, 6-H), 2·55 (10H, m, aromatic), 5·7 (q, $MeCH_2$), and 8·71 (t, $MeCH_2$).

G.l.c. of the reaction mixture (6 ft. Carbowax 20M column at 190°) demonstrated the presence of acetonitrile (r.t. 6 min.).

*Cycloaddition of Diphenylcyclopropenone to 5-Ethoxyoxazole.*—Diphenylcyclopropenone (1·03 g., 0·005 mole) and 5-ethoxyoxazole (0·57 g., 0·005 mole) were refluxed in toluene (10 ml.) for 16 hr. The resulting dark solution was evaporated to a black viscous oil (1·57 g.) smelling of hydrogen cyanide. The i.r. spectrum indicated that this contained some unchanged diphenylcyclopropenone. The oil was dissolved in ether and chromatographed on alumina (Spence type H). Elution with ether gave a small amount (0·23 g.) of diphenylacetylene produced by breakdown of the diphenylcyclopropenone. Further elution with ether gave a red oil (0·21 g.) which when rechromatographed on alumina with 40% ether in light petroleum (b.p. 40—60°) as eluant gave *2-ethoxy-3,5-diphenyl-4-pyrone* (V) (151 mg., 10·4%) as cream needles, m.p. 157—158°, identical with the product from the previous reaction. Elution of the main chromatography column with benzene gave some unchanged diphenylcyclopropenone (0·10 g.), m.p. 119—120°. Further elution, with chloroform, yielded intractable tars.

*Cycloaddition of Dimethyl Acetylenedicarboxylate to 5-Ethoxyoxazole.*—Dimethyl acetylenedicarboxylate (0·71 g., 0·005 mole) and 5-ethoxyoxazole (0·85 g., 0·0075 mole) were dissolved in dry ether (5 ml.) and kept at room temperature overnight. The ether was then removed *in vacuo* to give a brown viscous oil (1·09 g.), which was distilled in a short path still (100°/2 mm.) to give *dimethyl 2-ethoxyfuran-3,4-dicarboxylate* (VII) (0·58 g., 51%) as a pale yellow oil, identical with the product described later. The residue remaining after distillation (0·51 g.) could not be purified further.

* Diphenylcyclopropenone causes dermatitis; over a period of time sensitisation occurs so that even stringent precautions fail to eliminate this unpleasant effect. The two dimers were much worse than diphenylcyclopropenone in this respect and therefore work on them was abandoned. We cannot rule out the possibility that traces of dimer in diphenylcyclopropenone are responsible for its dermatitic properties.

[13] R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, 1965, **87**, 1320.
[14] B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Amer. Chem. Soc.*, 1967, **89**, 5964.
[15] W. L. Mock, Abstracts of 155th National Meeting of Amer. Chem. Soc., 1968, Abstracts, P20.
[16] J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, 1969, **91**, 777.
[17] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 15; *J. Amer. Chem. Soc.*, 1965, **87**, 4388.
[18] K. Alder and G. Stein, *Angew. Chem.*, 1937, **50**, 510.
[19] Belg.P. 666,285.

*Cycloaddition of Dimethyl Acetylenedicarboxylate to 5-Ethoxy-4-methyloxazole.*—5-Ethoxy-4-methyloxazole (2·54 g., 0·02 mole) and dimethyl acetylenedicarboxylate (2·84 g., 0·02 mole.) were dissolved in dry ether (30 ml.) and stored at room temperature overnight. Evaporation then gave a black viscous oil (4·6 g.) which gave two fractions on distillation, b.p. 145—150°/2 mm. (0·43 g., 9·4%) and b.p. 151—155°/2 mm. (2·41 g., 52·7%). Spectroscopic investigation showed a slight trace of impurity in the lower-boiling fraction but indicated that the higher-boiling fraction was pure *dimethyl 2-ethoxyfuran-3,4-dicarboxylate* (VII). An analytical sample had b.p. 152—154°/2 mm. [Found: C, 52·8; H, 5·3%; *M* (mass spectrum), 228. $C_{10}H_{12}O_6$ requires C, 52·65; H, 5·3%; *M*, 228], $\lambda_{max.}$ 250 nm. (ε 7060), $\nu_{max.}$ ($CHCl_3$) 1743, 1720, 1607, 1459, and 1331 cm.$^{-1}$, τ 2·55 (s, 5-H), 5·56 (q, MeC$H_2$), 6·16 (6H, s, 2 × $CO_2$Me), and 8·57 (t, *Me*$CH_2$).

*Cycloaddition of Dimethyl Acetylenedicarboxylate to 5-Methyl-4-phenyloxazole.*—Dimethyl acetylenedicarboxylate (3·42 g., 0·024 mole) and 5-methyl-4-phenyloxazole (3·83 g., 0·024 mole) were boiled under reflux in toluene (20 ml.) for 13 hr., during which time the solution darkened. Removal of the solvent and distillation of the residual oil (6·77 g.) afforded three fractions: (i), b.p. 30—81°/1 mm. (1·31 g.), mainly benzonitrile; (ii) slightly impure *dimethyl 2-methylfuran-3,4-dicarboxylate* (VIII), b.p. 82—86°/1 mm. (0·48 g., 10·2%); and (iii), b.p. 86—93°/1 mm. (2·82 g., 59%), pure *furan ester*. An analytical sample had b.p. 88—90°/1 mm. (Found: C, 54·95; H, 5·1; $C_9H_{10}O_5$ requires C, 54·55; H, 5·1%), $\lambda_{max.}$ 242 nm. (ε 5610), $\nu_{max.}$ (film) 1737 and 1731 cm.$^{-1}$, τ 2·35 (1H, s, ring proton), 6·25 (6H, d, 2 × $CO_2$Me), and 7·53 (s, ring Me).

The black residue remaining after distillation was triturated with ether and filtered to give a light brown powder. Crystallisation from light petroleum (b.p. 60—80°) gave *tetramethyl 1-methyl-7-oxabicyclo*[2,2,1]*hepta-2,5-diene-2,3,5,6-tetracarboxylate* (IX) as colourless, light-sensitive needles (0·4 g., 9·8% based on acetylene ester), m.p. 85—87° (analytical sample, m.p. 88—89°) (Found: C, 52·95; H, 4·8. $C_{15}H_{16}O_9$ requires C, 52·95; H, 4·75%), $\lambda_{max.}$ 222 nm. (ε 11,630), $\nu_{max.}$ 1749 and 1737infl. cm.$^{-1}$, τ 4·13 (1H, s, bridgehead proton), 6·15 (12H, d, 4 × $CO_2$Me), and 8·14 (s, bridgehead Me).

*Cycloaddition of Diphenylacetylene to 5-Ethoxy-4-methyloxazole.*—Diphenylacetylene (3·56 g., 0·020 mole) and 5-ethoxy-4-methyloxazole (3·18 g., 0·025 mole) were heated in a sealed Carius tube, which had been flushed with nitrogen, for 14 hr. at 220°. The black, viscous oil produced (6·51 g.) was triturated with ether and filtered to give a brown solid (0·27 g.), which was slurried in ethanol to give the white product (163 mg.). More product (67 mg.), together with some unchanged diphenylacetylene (260 mg.), was obtained by chromatography of the residue on alumina [light petroleum (b.p. 40—60°)]. The two crops of *4-ethoxy-2,3,5,6-tetraphenylphenol* (XIV) (5·6%) yielded colourless needles from ethanol–chloroform; sublimation gave an analytical sample, m.p. 246—247° (Found: C, 87·15; H, 6·05. $C_{32}H_{26}O_2$ requires C, 86·85; H, 5·9%), $\lambda_{max.}$ 243 and 305 nm. (ε 30,140 and 5230), $\lambda_{infl.}$ 265 nm. (ε 13,520), $\nu_{max.}$ 3540, 3059, 1600, 1406, 1088, 753, and 704 cm.$^{-1}$, τ 2·2br (s, OH), 2·84 (m, 20H, aromatic), 6·88 (q, MeC$H_2$), and 9·48 (t, *Me*$CH_2$).

*2,3,5,6-Tetraphenylbenzoquinone* (XV).—A solution of 4-ethoxy-2,3,5,6-tetraphenylphenol (68 mg.) in methanol (4 ml.) and conc. hydrochloric acid (3 ml.) containing anhydrous iron(III) chloride (5·0 g.) was boiled for 15 min. Water (2 ml.) was then added, and the solution was boiled for a further 5 min. then poured into water (100 ml.). The precipitate was filtered off, washed with a little ice-cold methanol, and dried (64·6 mg.). Sublimation at 250°/0·05 mm. gave orange *needles* (47·4 mg., 75%), m.p. 308—314° (lit.,[20] 311—315°). Crystallisation from chloroform–methanol gave a hemihydrate which on resublimation gave a sample, m.p. 315—316° (Found: C, 87·0; H, 4·9. $C_{30}H_{20}O_2$ requires C, 87·35; H, 4·9%), $\lambda_{max.}$ 234, 302, and 334 nm. (ε 30,680, 8890, and 6690), $\lambda_{infl.}$ 384 nm. (ε 2520), $\nu_{max.}$ 1651, 1603, 1443, 1286, 1140, 729, and 700 cm.$^{-1}$.

*Cycloaddition of Diphenylacetylene to 5-Methyl-4-phenyloxazole.*—5-Methyl-4-phenyloxazole (3·07 g., 0·0193 mole) and diphenylacetylene (3·44 g., 0·0193 mole) were heated together under nitrogen at 255° in a Carius tube for 42 hr. The resulting amber liquid was fractionally distilled. Five fractions were collected: (i), b.p. 40—55°/0·2 mm., (1·78 g., 89%), benzonitrile; (ii) b.p. 56—125°/0·2 mm. (0·15 g.), unchanged 5-methyl-4-phenyloxazole; (iii), b.p 138—142°/0·2 mm. (482 mg.); (iv), b.p. 143—150°/0·2 mm. (645 mg.); and (v), b.p. 151—155°/0·2 mm. (579 mg.). Spectroscopy showed fractions 3—5 to be *2-methyl-3,4-diphenylfuran* (XVI) (1·706 g., 37·6%), and indicated slight impurities in fractions 3 and 5 [Found (for fraction 4): C, 86·8; H, 6·0. $C_{17}H_{14}O$ requires C, 87·15; H, 6·0%], $\lambda_{max.}$ 225 nm. (ε 19,830), $\lambda_{infl.}$ 247 nm. (ε 8400), $\nu_{max.}$ (film) 3081, 1607, 1561, 1498, 1144, 777, and 753 cm.$^{-1}$, τ ($CCl_4$) 2·73 (s, 5-H), 2·95 (10H, m, aromatic), and 7·83 (s, Me).

The residue in the distillation flask was triturated with chloroform (*ca.* 10 ml.), set aside for several hr., and then filtered to give colourless needles of *4-methyl-2,3,5,6-tetraphenylphenol* (XVII) (274 mg., 6·9%), m.p. 324—328° (m.p. after sublimation 326—328°) (Found: C, 90·15; H, 5·85. $C_{31}H_{24}O$ requires C, 90·25; H, 5·85%), $\lambda_{max.}$ 237 nm. (ε 28,180), $\lambda_{infl.}$ 264 nm. (ε 8960), $\nu_{max.}$ 3535, 3056, 1600, 1411, 1284, 1143, 751, and 705 cm.$^{-1}$, τ ($CDCl_3$–$CF_3$·$CO_2H$) 2·81 (m, aromatic) and 8·16 (s, Me).

*Cycloaddition of Methyl Phenylpropiolate to 5-Ethoxy-4-methyloxazole.*—Methyl phenylpropiolate (2·40 g., 0·015 mole) and 5-ethoxy-4-methyloxazole (2·54 g., 0·02 mole) were boiled under reflux in toluene (25 ml.) containing boron trifluoride–ether complex (4 drops) for 60 hr. Toluene was removed under reduced pressure leaving a dark viscous oil (3·96 g.), which was distilled to give fractions (*a*), b.p. 138—142°/0·5 mm. (0·414 g.); (*b*), b.p. 143—145°/0·5 mm. (0·988 g.); and (*c*), b.p. 146—148°/0·5 mm. (0·994 g.). Fraction (*a*) contained a little methyl phenylpropiolate; fractions (*b*) and (*c*) (1·982 g., 53·5%) contained the mixed isomers *methyl 2-ethoxy-4-phenylfuran-3-carboxylate* (XVIII) and *methyl 2-ethoxy-3-phenylfuran-4-carboxylate* (XIX) (Found: C, 67·95; H, 5·65. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·75%). The n.m.r. spectrum clearly indicated the presence of two isomers; the more predominant isomer [probably (XVIII)] exhibited resonances at τ 3·22 (1H, s, ring proton), 5·63 (2H, q, MeC$H_2$), 6·39 (3H, s, $CO_2$Me), and 8·55 (3H, t, *Me*$CH_2$). The less abundant isomer showed peaks at τ 2·50, 5·92, 6·39, and 8·74. Both isomers gave aromatic resonances centred at τ 2·78.

*Diphenylcyclopropenone Dimers.*—(*a*) Diphenylcyclopropenone (2·06 g.) and furan (2 ml.) were boiled under reflux in toluene (20 ml.) for 48 hr. The cooled solution deposited

[20] D. E. Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56**, 2478.

large colourless crystals (740 mg.) of a dimer, which were filtered off. Evaporation of the filtrate and trituration of the residue with light petroleum afforded more dimer (450 mg., total yield 1·19 g., 58%), which gave colourless needles, m.p. 159—161° (from methanol) [Found: C, 87·35; H, 4·8%; *M*(Rast), 396. $C_{30}H_{20}O_2$ requires C, 87·35; H, 4·9%; *M*, 412], $\lambda_{max.}$ 221, 228, 288, 298, and 313 nm. (ε 37,400, 37,600, 41,900, 46,100, and 32,200), $\nu_{max.}$ ($CHCl_3$) 982, 1366, 1544, 1626, 1735, and 1851 cm.$^{-1}$, τ 1·85—2·80 (complex m). In a similar experiment in which 2-methylfuran was used in place of furan an identical dimer was obtained (60%).

(*b*) Diphenylcyclopropenone (0·51 g., 0·0025 mole) and *N*-ethoxycarbonylpyrrole (0·34 g., 0·0025 mole) were boiled under reflux in toluene (10 ml.) for 16 hr. The dark solution when cooled deposited colourless *plates* (171 mg., 33·6%), which yielded material m.p. 275—276° (from chloroform) [Found: C, 87·2; H, 5·05%; *M* (mass spectrum) 412], $\nu_{max.}$ 695, 944, 990, 1053, 1112, 1368, 1496, and 1810 cm.$^{-1}$, τ ($CDCl_3$–$CF_3$·$CO_2H$) 2·6 (m).

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