Extended Dipolar Cycloadditions [1]

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Whilst the simple azomethine imine (5) undergoes the expected 1,3-dipolar cycloaddition to acetylenic esters, the extended azomethine imines (1) undergo 1,5- rather than 1,3-dipolar cycloaddition to give benzo[*c*][1,2,5]-triazepino[1,2-*a*]cinnolines (2), possibly by a stepwise mechanism 2-Alkyl-2$\lambda^5\sigma^3$-naphtho[1,8-*de*]triazines (12) and 2$\lambda^4\sigma^2$-naphtho[1,8-*cd*]thiadiazine (18) undergo 1,11-dipolar [12π + 2π] cycloaddition to acetylenic esters to give the *peri*-bridged acenaphthylenes (14) and (19), after spontaneous dehydrogenation. It is suggested that these and other reactions in the literature illustrate the potential generality of extended dipolar cycloadditions.

THE recent theoretical work of Woodward and Hoffmann,[2] Dewar,[3] Fukui,[4] and others has done much to rationalise and stimulate further investigation into pericyclic reactions of all-carbon polyenes. Such processes should have their counterparts in isoelectronic dipolar systems containing heteroatoms. This is indeed the case for 1,3-dipolar cycloadditions [5] (*cf.* Diels–Alder reactions), 2,3-sigmatropic reactions [6] (*cf.* Cope and related rearrangements), 1,4 [7] and 1,6 H-shifts [8] (*cf.* 1,5 and 1,7 H-shifts), and electrocyclic reactions involving 1,3-,[9] 1,5-,[10] and 1,7-dipoles.[11]

1,3-Dipolar cycloaddition has proved extremely useful in the synthesis of five-membered heterocyclic compounds. The potential of extended 1,3-dipoles, with six or more π-electrons, in cycloaddition has however not been explored despite the considerable synthetic and theoretical interest associated with such processes. In order to illustrate the potential of such systems we report our work with the azomethine imines (1), which act as 1,5-dipoles, and with 2-substituted 2$\lambda^5\sigma^3$-naphtho[1,8-*de*]triazines (12),† which act as 1,11-dipoles and so provide rare examples of [12π + 2π] cycloaddition.

1,3-Dipolar cycloaddition of azomethine imines is well established. Formation of the adduct (6) from the benzocinnolinium ylide (5) [12] and dimethyl acetylenedicarboxylate within 30 min in dimethylformamide was therefore as expected. Confirmation of structure (6) comes from its n.m.r. spectrum, which shows two different methyl ester groups and two identical ethyl ester groups, and from its u.v. spectrum [$\lambda_{max.}$ 262 (ε 30,000) and 394 nm (12,000)], which is consistent with an almost planar biphenyl chromophore.

The azomethine imines (1) [12] are more interesting

† Structures of types (12) and (18) are named on the basis of IUPAC Nomenclature of Organic Chemistry, Section D, Tentative Rules, IUPAC, Oxford, 1973, pp. 3, 12.

[1] Preliminary communications, S. F. Gait, M. J. Rance, C. W. Rees, and R. C. Storr, *J.C.S. Chem. Comm.*, 1972, 806; C. W. Rees, R. W. Stephenson, and R. C. Storr, *ibid.*, p. 1281.

[2] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[3] M. J. S. Dewar, *Angew. Chem. Internat. Edn.*, 1971, **10**, 761.

[4] K. Fukui, *Accounts Chem. Res.*, 1971, **4**, 57.

[5] R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565, 633.

[6] T. L. Gilchrist and R. C. Storr, 'Organic Reactions and Orbital Symmetry,' Cambridge University Press, 1972, p. 234.

[7] M. G. Pleiss and J. A. Moore, *J. Amer. Chem. Soc.*, 1968, **90**, 4738; S. R. Tanny and F. W. Fowler, *ibid.*, 1973, **95**, 7320.

[8] J. J. Barr, J. Rimmer, and R. C. Storr, *J.C.S. Chem. Comm.*, 1974, 657.

[9] R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, 1967, **89**, 1753; H. Hamberger and R. Huisgen, *Chem. Comm.*, 1971, 1190; A. Dahman, H. Hamberger, R. Huisgen, and V. Markowski, *ibid.*, p. 1192.

[10] H. Reimlinger, *Chem. Ber.*, 1970, **103**, 1900 *et seq.*

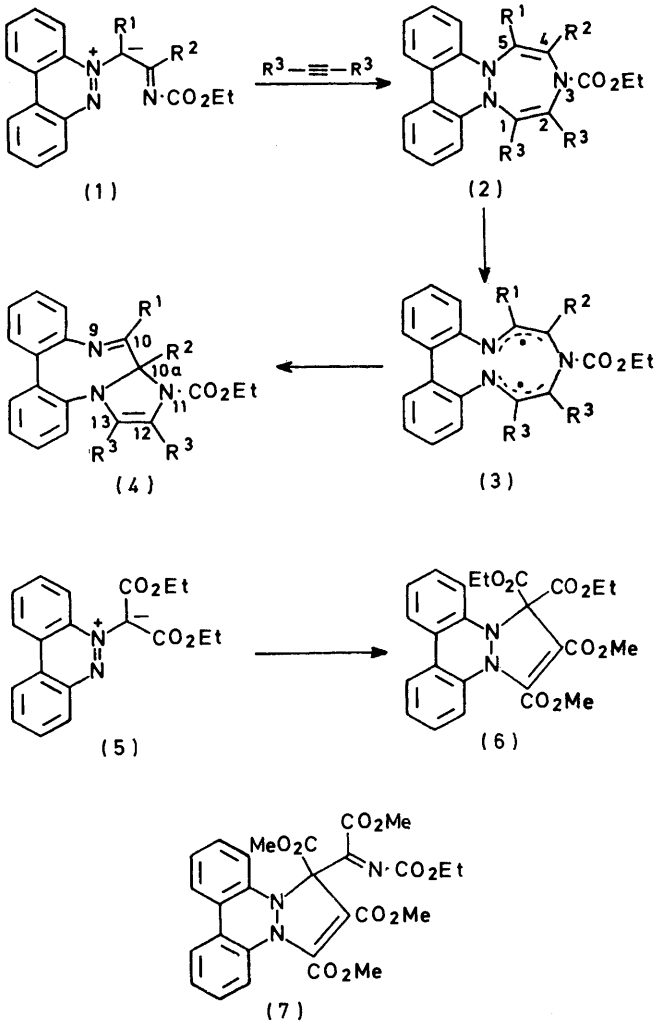
[11] See for example J. T. Sharp and P. B. Thorogood, *Chem. Comm.*, 1970, 1197; R. H. Findley, J. T. Sharp, and P. B. Thorogood, *ibid.*, p. 909.

[12] S. R. Challand, S. F. Gait, M. J. Rance, C. W. Rees, and R. C. Storr, *J.C.S. Perkin I*, 1975, 26.

since, because of their extended side chain, they could act as 6 π-electron 1,5-dipoles as well as 4 π-electron 1,3-dipoles in cycloaddition. Indeed, it transpires that 1,5-dipolar cycloaddition is their preferred mode of reaction with acetylenic esters. Thus the reaction of compound (1; $R^1 = R^2 = CO_2Me$) with dimethyl acetylenedicarboxylate in dimethylformamide at room temperature over 24 h gave the yellow 1,2,5-triazepine (2; $R^1 = R^2 = R^3 = CO_2Me$) together with a colourless isomeric adduct, tentatively assigned the structure (4; $R^1 = R^2 = R^3 = CO_2Me$). The colourless adduct (4) is a secondary product formed by rearrangement of the initially formed triazepine. This rearrangement occurs only slowly at room temperature but is complete within 15 min in dimethylformamide at 70°, and therefore only the colourless adduct is isolated when the reaction is carried out at 70° over 0·5 h. The reactions of compound (1; $R^1 = R^2 = CO_2Et$) with dimethyl acetylenedicarboxylate and of (1; $R^1 = R^2 = CO_2Me$) with diethyl acetylenedicarboxylate gave identical mixtures of the same two products [(4; $R^1 = R^2 = CO_2Et$, $R^3 = CO_2Me$) and (4; $R^1 = R^2 = CO_2Me$, $R^3 = CO_2Et$)]. This was shown by isolation of the same major pure isomer and by identical n.m.r. spectra for the total mixture of crude adducts in each case. The separate isomers (4) are stable under the reaction conditions; thus all, or substantially all the product (4) is formed *via* the symmetrical triazepine adduct.

The symmetrical structures for the adducts (2; $R^1 = R^2 = R^3 = CO_2Me$) and (2; $R^1 = R^2 = R^3 = CO_2Et$) were confirmed by their n.m.r. spectra, which showed three different types of ester group in the ratio 2 : 2 : 1, and a symmetrical distribution of aromatic protons. The more tentative assignment of structure (4) is based on the availability of a reasonable mechanistic route from (2) *via* the stabilised diradical (3) and on the fact that the n.m.r. spectrum of (4; $R^1 = R^2 = R^3 = CO_2Me$) shows four different methyl ester groups and one ethyl ester group. The alternative structure (7), which could have been formed by rearrangement of (2; $R^1 = R^2 = R^3 = CO_2Me$), and is the [3 + 2] cycloadduct analogous to (6), is eliminated by the fact that the u.v. spectrum [$\lambda_{max.}$ 231, 254sh, and 290 nm (ε 26,000, 19,500 and 9500)] of the thermal rearrangement product differs significantly from that of (6) and is consistent with a twisted biphenyl structure. Dreiding models indicate an angle of *ca.* 75° between the planes of the aromatic rings in structure (4).

The azomethine imine (1; $R^1 = CO_2Me$, $R^2 = H$) obtained by cycloaddition of benzocinnoline *N*-ethoxycarbonylimide to methyl propiolate [12] also gave adducts (2; $R^1 = R^3 = CO_2Me$, $R^2 = H$) and (2; $R^1 = CO_2Me$, $R^2 = H$, $R^3 = CO_2Et$) with dimethyl and diethyl acetylenedicarboxylate. The triazepine structure for (2; $R^1 = R^2 = CO_2Me$, $R^2 = H$) has been confirmed by *X*-ray crystallography.[13] This unambiguous location of the unsubstituted carbon atom demonstrates that the expected regioisomer (1; $R^1 = CO_2Me$, $R^2 = H$) is formed from benzocinnoline *N*-ethoxycarbonylimide and methyl propiolate.[12] Methyl propiolate was not sufficiently reactive to give an adduct with compounds (1; $R^1 = R^2 = CO_2Me$ or CO_2Et). The triazepines (2; $R^2 = H$) were significantly more stable than those with



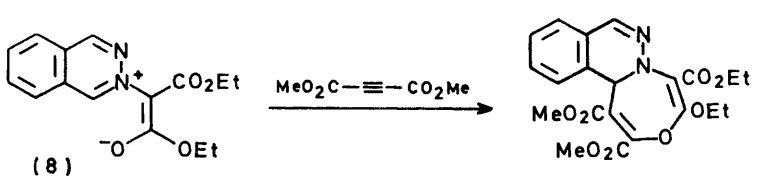
$R^2 = CO_2Me$ or CO_2Et and did not rearrange to imidazodiazocines (4). It appears that removal of one of the stabilising ester groups in the intermediate diradical (3) is critical.

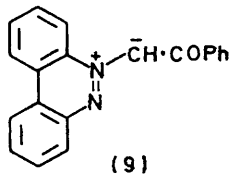
It is surprising that the azomethine imines (1) function as 6 π-electron 1,5-dipoles rather than 4 π-electron 1,3-dipoles. An analogous 1,5-dipolar cycloaddition has been reported for the phthalazinium ylide (8) with dimethyl acetylenedicarboxylate.[14] This is in contrast to the normal 1,3-dipolar additions which occur with the related benzocinnolinium ylides (5) and (9).[15] The tentative suggestion has also been made that such an addition may be involved in the formation of a trace of methyl cyclopent-2-enecarboxylate from methyl acrylate

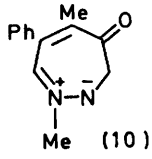
[13] A. F. Cameron and A. A. Freer, *Acta Cryst.*, 1974, **30B**, 2696.
[14] M. Petrovanu, A. Sauciuc, and I. Zugrăvescu, *Anal. sti. Univ. 'Al. I. Cusa' Iasi, Sect. Ic*, 1970 **16**, 65.
[15] S. H. Alsop, University of Liverpool, unpublished data; see also M. Dorneanu, E. Carp, and I. Zugrăvescu, *Anal. Sti. Univ. 'Al. I. Cuza' Iasi, Sect. Ic*, 1973, **19**(2), 223 (*Chem. Abs.*, 1974, **80**, 133,371).

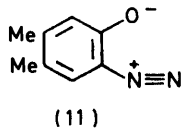
and vinyldiazomethane.[16] Formally similar [2 + 5] additions of cumulenes to the diazepinone (10)[17] and of diphenylketen to benzenediazonium-2-olate (11)[18] are also known. However the known propensity of ketens, and therefore possibly other cumulenes with low lying π^* orbitals, to undergo concerted $[_\pi 2_s + _\pi 2_a]$ cycloadditions raises the possibility that these reactions may be allowed $[_\pi 6_s + _\pi 2_a]$ processes.

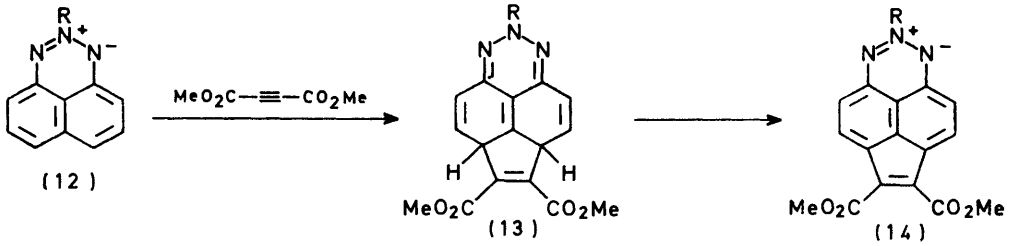
Concerted thermal $[_\pi 6_s + _\pi 2_s]$ cycloaddition is disallowed for polyenes and, if we assume that the symmetry ordering of the π-orbitals in (1) parallels that in the isoelectronic pentadienide anion, a concerted 1,5-dipolar cycloaddition is also disallowed, whereas the 1,3-dipolar cycloaddition mode is allowed. Introduction of three nitrogen atoms and substituents into the pentadienide anion system must considerably perturb the orbitals however, perhaps even to the extent of changing the expected symmetry ordering. Formation of the adduct (2) can most reasonably be accommodated by a stepwise mechanism initiated by nucleophilic attack by the ylide side chain through nitrogen on the electrophilic acetylene. Such a stepwise reaction through a stabilised zwitterion could well be more favourable than the alternative concerted [3 + 2] cycloaddition mode in such a highly polarised structure. Formation of the expected [3 + 2] adduct from the simpler ylide (5) may be the result of a concerted 1,3-dipolar cycloaddition since the side-chain oxygen atom in (5) is less nucleophilic than the nitrogen atom in (1). Epiotis [19] has recently suggested that many disallowed cycloadditions which have generally been considered to be stepwise, for example $[_\pi 2_s + _\pi 2_s]$ cyclo-











cycloaddition is also disallowed, whereas the 1,3-dipolar cycloaddition mode is allowed. Introduction of three nitrogen atoms and substituents into the pentadienide anion system must considerably perturb the orbitals however, perhaps even to the extent of changing the expected symmetry ordering. Formation of the adduct (2) can most reasonably be accommodated by a stepwise mechanism initiated by nucleophilic attack by the ylide side chain through nitrogen on the electrophilic acetylene. Such a stepwise reaction through a stabilised zwitterion could well be more favourable than the alternative concerted [3 + 2] cycloaddition mode in such a highly polarised structure. Formation of the expected [3 + 2] adduct from the simpler ylide (5) may be the result of a concerted 1,3-dipolar cycloaddition since the side-chain oxygen atom in (5) is less nucleophilic than the nitrogen atom in (1). Epiotis [19] has recently suggested that many disallowed cycloadditions which have generally been considered to be stepwise, for example $[_\pi 2_s + _\pi 2_s]$ cyclo-

additions between polar reactants, are actually concerted. This is a consequence of configuration interaction between the reactants which lowers the orbital-symmetry-imposed energy barrier for the formally disallowed process. Such consideration may also apply to this $[_\pi 6_s + _\pi 2_s]$ cycloaddition, but further discussion must await a full mechanistic investigation. Since we have so far been unable to observe additions of (1) to olefinic dipolarophiles, stereospecificity is not a readily available criterion here.

2-Substituted $2\lambda^5\sigma^3$-naphtho[1,8-*de*]triazines (12) are of interest in cycloadditions since they incorporate the three-nitrogen azimine 1,3-dipolar unit for which the first examples of 1,3-dipolar cycloaddition have only recently been observed.[12]

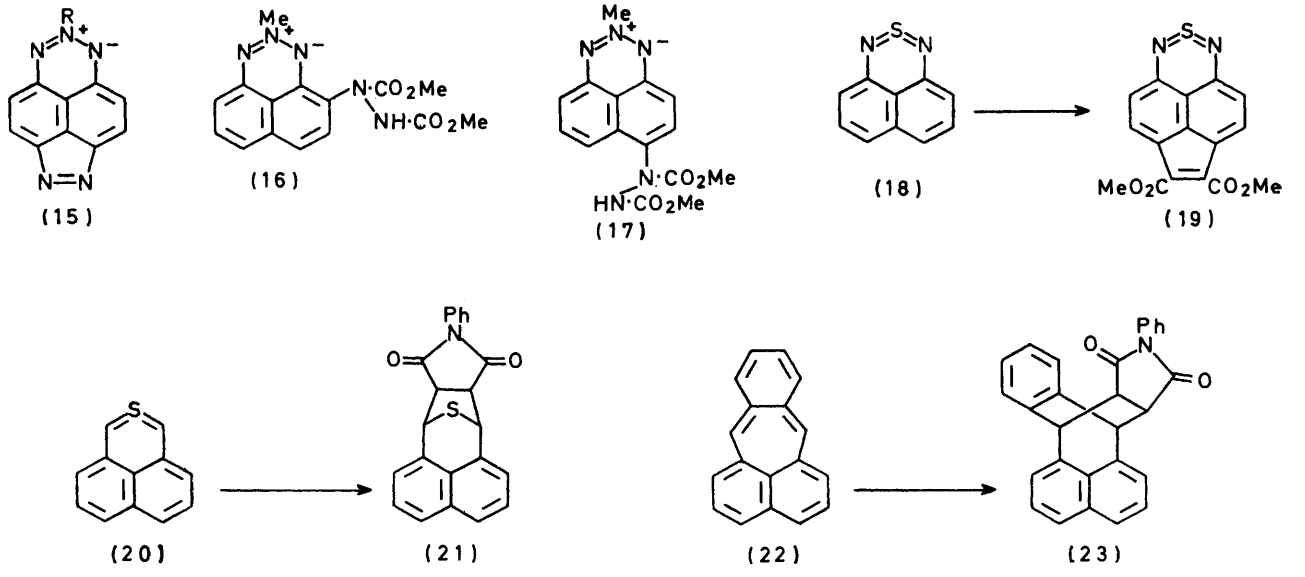
Gradual addition of dimethyl acetylenedicarboxylate (2 equiv.) to the 2-methylnaphthotriazine (12; R = Me) [20] in refluxing *o*-dichlorobenzene over 3 h gave the red methylacenaphtho[5,6-*de*]triazine (14; R = Me) in about 40% yield. The ^{1}H n.m.r. spectrum of this compound showed two identical ester groups (τ 5·88), an AB quartet (τ 1·05 and 2·19, *J* 8·5 Hz) of four protons in the aromatic region, and a singlet *N*-methyl absorption at τ 5·08. Its u.v. spectrum in ethanol [$\lambda_{max.}$ 247 (ε 18,500), 276 (13,200), 340sh (38,500), 352 (51,400), and 504 nm (6230)] was very similar to that reported for the unsubstituted 2-methylacenaphtho[5,6-*de*]triazine.[21]

Formation of the adduct (14) can be rationalised in terms of a novel 1,11-dipolar cycloaddition followed by dehydrogenation of the initial adduct (13) to give the stable, peripheral 14π aromatic system. Such a [12π +

[16] I. Tabushi, K. Takagi, M. Okano, and R. Oda, *Tetrahedron*, 1967, **23**, 2621.
[17] O. S. Rothenberger, R. T. Taylor, D. L. Dalrymple, and J. A. Moore, *J. Org. Chem.*, 1972, **37**, 2640.
[18] W. Reid and R. Dietrich, *Annalen*, 1963, **666**, 113, 135.
[19] N. D. Epiotis, *J. Amer. Chem. Soc.*, 1973, **95**, 1191 *et seq.*, *ibid.*, 1972, **94**, 1924 *et seq.*
[20] M. J. Perkins, *J. Chem. Soc.*, 1964, 3005.
[21] P. Flowerday, M. J. Perkins, and A. R. J. Arthur, *J. Chem. Soc.* (*C*), 1970, 290.

2π] addition is allowed and although we have no clear evidence that this cycloaddition is concerted, the fact that the reaction is insensitive to solvent polarity is at least consistent with a concerted mechanism. The known tendency [21] of 2-methylnaphthotriazine to undergo electrophilic attack at positions 4, 6, 7, and 9 makes a stepwise reaction through a zwitterion a reasonable alternative but this lack of solvent effect and our failure to observe products of substitutive addition with dimethyl acetylenedicarboxylate (see later for azodicarboxylic ester) argue against this. The first examples of [$12\pi + 2\pi$] cycloaddition have only recently been observed for all-carbon polyenes by Prinzbach and his co-workers.[22]

The conditions described for the addition of the acetylene to 2-methylnaphthotriazine were the best found after considerable experimentation involving variation of solvent, temperature, reaction time, and proportions of reactants. The addition of a dehydrogenating agent (palladium–charcoal, *o*-chloranil, or dichlorodicyano-*p*-benzoquinone) to the reaction mixture did not affect yields significantly although marginally



the best yield and cleanest reaction was observed in the presence of sulphur (3 equiv.). The adduct (14) was accompanied by large amounts of brown material which could not be purified. The n.m.r. spectrum of the crude material suggests that several ester molecules have been incorporated for each naphthotriazine molecule. This product is not formed by reaction of the adduct (14) with more acetylene and, together with other minor unidentified products, possibly arose by further reaction of unstable adducts initially formed by direct addition across the azimine system.

Analogous reactions occur with diethyl acetylenedicarboxylate (34%) and with dibenzoylacetylene (40%); the less reactive methyl propiolate gave only a trace of product (t.l.c.). With diphenylacetylene under forcing conditions (300°), 2-methylnaphthotriazine is consumed but no adduct was isolated. 2-Benzylnaphthotriazine (12; R = $PhCH_2$) gave the expected adduct with dimethyl acetylenedicarboxylate in 34% yield but reaction of 2-(2,4-dinitrophenyl)naphthotriazine gave no more than a trace of product (t.l.c.). Some reaction occurs between 2-methylnaphthotriazine and dipolarophiles such as tetracyanoethylene, malononitrile, diethyl fumarate, diethyl maleate, maleic anhydride, *N*-phenylmaleimide, and diphenylcyclopropenone but no adducts have yet been characterised.

Dimethyl azodicarboxylate seemed a particularly promising dipolarophile since any tendency for direct 1,3-dipolar addition to the nitrogen bridge would be strongly disfavoured because of the low N–N bond energy; furthermore addition across the *peri* (6,7-) carbon atoms would provide a simple entry into the interesting heterocyclic system (15). However the rapid reaction of dimethyl azodicarboxylate (1 equiv.) with 2-methylnaphthotriazine gave only a blue product resulting from substitutive addition, as shown by the presence of N–H stretching absorptions in its i.r. spectrum. The susceptibility of the 2-substituted naphthotriazine nucleus towards electrophilic attack is known [20] and probable structures for this adduct are (16) and (17). We favour structure (17) since the n.m.r. spectrum shows two high-field aromatic protons characteristic of the 4-hydrogen atoms of the 2-substituted naphthotriazine system. With an excess of the azo-ester two or more molecules of azo-compound were incorporated.

$2\lambda^4\sigma^2$-Naphtho[1,8-*cd*]thiadiazine (18),[23] isoelectronic with the 2-substituted naphthotriazines, also reacts with dimethyl acetylenedicarboxylate to give the acenaphthothiadiazine (19), (6%), again presumably by [$12\pi + 2\pi$] addition and aromatisation. The related thiocarbonyl

[22] H. Prinzbach and H. Knöfel, *Angew. Chem. Internat. Edn.*, 1969, **8**, 881; H. Prinzbach and H. Sauter, *ibid.*, 1972, **11**, 133; H. Prinzbach, *Pure Appl. Chem.*, 1971, **28**, 281.
[23] H. Beecken, *Chem. Ber.*, 1967, **100**, 2164.

ylide (20) [24] and pleiadene (22) [25] have been reported to give the [4π + 2π] cycloadducts (21) and (23) respectively with *N*-phenylmaleimide. However with this dipolarophile [12π + 2π] cycloaddition could not lead, after dehydrogenation, to a new aromatic system and the reactions of acetylenes with (20) and (22) therefore remain of interest.

We believe that the extended dipolar cycloadditions discussed above, together with the 1,7-dipolar [$_{\pi}8_s$ + $_{\pi}2_s$] additions of diazocyclopentadienes to dimethyl acetylenedicarboxylate reported as long ago as 1963,[26] and the very recently reported [$_{\pi}6_s$ + $_{\pi}4_s$] addition of 1-substituted 3-oxidopyridiniums to dienes [27] clearly establish the generality of such processes. Their potential in the synthesis of medium-ring heterocycles is obvious. It may also be significant that the majority of these additions so far reported are ' allowed ' reactions, the exceptions being where alternative stepwise processes are highly favoured. We believe that all types of pericyclic reactions, now so familiar for polyenes, will become equally well recognised for the isoelectronic dipolar systems, as they are already for 1,3-dipolar cycloaddition and 1,5-dipolar cyclisation.

EXPERIMENTAL

Reaction of Benzo[c]*cinnoliniobisethoxycarbonylmethanide* (5) [12] *with Dimethyl Acetylenedicarboxylate.*—An equimolar mixture of the ylide (5) and dimethyl acetylenedicarboxylate in dimethylformamide was maintained at 60—70° until the green colour faded (30 min). The solution was then poured into water and the precipitate was filtered off, dried, and chromatographed on alumina. Elution with 75% ether–petroleum gave 1,1-*diethyl* 2,3-*dimethyl benzo*[c]*pyrazolo*[1,2-a]*cinnoline*-1,1,2,3-*tetracarboxylate* (6) as yellow prisms (42%), m.p. 171—173° (from ether–petroleum) (Found: C, 62·3; H, 5·0; N, 5·8. $C_{25}H_{24}N_2O_8$ requires C, 62·5; H, 5·0; N, 5·8%), $\nu_{max.}$ 1748, 1690, 1590, 1520, 1460, 1440, 1370, 1258, 1240, 1198, 1100, 1060, 778, and 745 cm^{-1}, $\lambda_{max.}$ (EtOH) 262 (ε 30,000) and 394 nm (12,000), τ ($CDCl_3$) 2·40—3·20 (8H, m), 5·79 (4H, q, *J* 7 Hz), 6·09 (3H, s), 6·33 (3H, s), and 8·82 (6H, t, *J* 7 Hz).

Reaction of 1-*Benzo*[c]*cinnolinio*-2-*ethoxycarbonyliminoethanides* (1) [12] *with Acetylenes to give Benzo*[c][1,2,5]*triazepino*[1,2-a]-*cinnolines* (*Yellow Adducts*).—The azomethine imine (1) was dissolved in the minimum of dimethylformamide and a small excess of the acetylene was added. The mixture was kept at room temperature for 16 h and then poured into water. The aqueous solution was extracted with ether and the extracts were washed with water, dried (Na_2SO_4), and concentrated; the residue was chromatographed on alumina. The azomethine imine (1; $R^1 = R^2 = CO_2Me$) with dimethyl acetylenedicarboxylate gave 3-*ethyl* 1,2,4,5-*tetramethyl* 3H-*benzo*[c][1,2,5]*triazepino*[1,2-a]*cinnoline*-1,2,3,4,5-*pentacarboxylate* (2; $R^1 = R^2 = R^3 = CO_2Me$) as yellow prisms (47%), m.p. 85—90° (followed by solidification and remelting at 215—218°) (from ether–petroleum) (Found: C, 59·0; H, 4·5; N, 7·6. $C_{27}H_{25}N_3O_{10}$ requires C, 58·8; H, 4·6; N, 7·6%), $\nu_{max.}$ 1720, 1640, 1610, 1458, 1380, 1278, 1235, 768, and 739 cm^{-1}, $\lambda_{max.}$ (EtOH) 244 (ε 20,000), 280 (14,100), and 308 nm (13,600), τ ($CDCl_3$) 2·24—2·42 (2H, m), 2·66—2·86 (4H, m), 2·98—3·18 (2H, m), 5·77 (2H, q, *J* 7 Hz), 6·22 (6H, s), 6·59 (6H, s), and 8·73 (3H, t, *J* 7 Hz).

The azomethine imine (1; $R^1 = R^2 = CO_2Et$) with dimethyl acetylenedicarboxylate gave 1,2,3-*triethyl* 4,5-*dimethyl* 3H-*benzo*[c][1,2,5]*triazepino*[1,2-a]*cinnoline*-1,2,3,4,5-*pentacarboxylate* (2; $R^1 = R^2 = CO_2Et$, $R^3 = CO_2Me$) as yellow prisms, unstable to warming (Found: C, 60·1; H, 5·1; N, 7·3. $C_{29}H_{29}N_3O_{10}$ requires C, 60·1; H, 5·0; N, 7·2%), $\nu_{max.}$ 1729, 1610, 1465, 1445, 1375, 1280, 1230, 1030, 770, and 738 cm^{-1}, $\lambda_{max.}$ (EtOH) 245 (ε 19,850), 283 (17,000), and 309 nm (16,800), τ ($CDCl_3$) 2·22—2·44 (2H, m), 2·67—2·89 (4H, m), 2·97—3·16 (2H, m), 5·76 (2H, q, *J* 7 Hz), 5·77 (2H, q, *J* 7 Hz), 6·16 (2H, q, *J* 7 Hz), 6·23 (3H, s), 6·55 (3H, s), 8·72 (3H, t, *J* 7 Hz), 8·73 (3H, t, *J* 7 Hz), and 9·14 (3H, t, *J* 7 Hz).

The azomethine imine (1; $R^1 = CO_2Me$, $R^2 = H$) with dimethyl acetylenedicarboxylate gave 3-*ethyl* 1,2,5-*trimethyl* 3H-*benzo*[c][1,2,5]*triazepino*[1,2-a]*cinnoline*-1,2,3,5-*tetracarboxylate* (2; $R^1 = R^3 = CO_2Me$, $R^2 = H$) as yellow prisms (41%), m.p. 157—159° (from ether–petroleum) (Found: C, 60·8; H, 4·6; N, 8·7. $C_{25}H_{23}N_3O_8$ requires C, 60·9; H, 4·7; N, 8·5%), $\nu_{max.}$ 1732, 1720, 1645, 1470, 1450, 1380, 1330, 1250, 1228, 778, and 747 cm^{-1}, $\lambda_{max.}$ (EtOH) 247 (ε 19,600), 276 (20,000), and 305 nm (14,600), τ ($CDCl_3$) 1·96 (1H, s), 2·20—2·38 (2H, m), 2·62—3·04 (4H, m), 3·37—3·50 (2H, m), 5·68 (2H, q, *J* 7 Hz), 6·37 (3H, s), 6·40 (3H, s), 6·87 (3H, s), and 8·70 (3H, t, *J* 7 Hz).

The azomethine imine (1; $R^1 = CO_2Me$, $R^2 = H$) with diethyl acetylenedicarboxylate gave 1,2,3-*triethyl* 5-*methyl* 3H-*benzo*[c][1,2,5]*triazepino*[1,2-a]*cinnoline*-1,2,3,5-*tetracarboxylate* (2; $R^1 = CO_2Me$, $R^2 = H$, $R^3 = CO_2Et$) as yellow prisms (17%), m.p. 145—146° (from ether–petroleum) (Found: C, 62·0; H, 5·2; N, 8·0. $C_{27}H_{27}N_3O_8$ requires C, 62·2; H, 5·2; N, 8·1%), $\nu_{max.}$ 1739, 1720, 1645, 1469, 1459, 1375, 1322, 1248, 1220 1028, 770, and 742 cm^{-1}, $\lambda_{max.}$ (EtOH) 249 (ε 18,750), 277 (20,000), and 306 nm (14,700), τ ($CDCl_3$) 1·95 (1H, s), 2·12—2·40 (2H, m), 2·53—2·94 (4H, m), 3·18—3·50 (2H, m), 5·73 and 5·74 (4H, two overlapping q, *J* 7 Hz), 6·33 (2H, q, *J* 7 Hz), 6·35 (3H, s), 8·67 (3H, t, *J* 7 Hz), 8·82 (3H, t, *J* 7 Hz), and 9·28 (3H, t, *J* 7 Hz).

Reaction of 1-*Benzo*[c]*cinnolinio*-2-*ethoxycarbonyliminoethanides* (1) [12] *with Acetylenes to give Dibenz*[e,g]*imidazo*[1,2-a][1,4]*diazocines* (4) (*Colourless Adducts*).—A small excess of the acetylene and the azomethine imine (1) were dissolved in the minimum volume of dimethylformamide and the mixture was maintained at 60—70° until the green colour had disappeared (0·5—2 h). The mixture was then poured into water and the precipitate was filtered off, dried, and recrystallised from ether–petroleum (charcoal). The reaction was also carried out as above, using benzocinnoline *N*-ethoxycarbonylimide and 2 mol. equiv. of the acetylene.

The azomethine imine (1; $R^1 = R^2 = CO_2Me$) and dimethyl acetylenedicarboxylate gave 11-*ethyl* 10,10a,12,13-*tetramethyl dibenz*[e,g]*imidazo*[1,2-a][1,4]*diazocine*-10,10a,-11,12,13-*pentacarboxylate* (4; $R^1 = R^2 = R^3 = CO_2Me$) as needles (67%), m.p. 223° (Found: C, 59·0; H, 4·6; N, 7·9. $C_{27}H_{25}N_3O_{10}$ requires C, 58·8; H, 4·6; N, 7·6%), $\nu_{max.}$ 1740, 1670, 1470, 1447, 1385, 1300, 1270, 1235, 782, and 770 cm^{-1},

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$\lambda_{max.}$ (EtOH) 231 (ε 25,800), 254 (19,500), and 290 nm (9400), τ ($CDCl_3$) 2·47—2·93 (8H, m), 5·88 (2H, q, *J* 7 Hz), 6·16 (3H, s), 6·34 (3H, s), 6·39 (3H, s), 6·41 (3H, s), and 8·82 (3H, t, *J* 7 Hz).

The azomethine imine (1; $R^1 = R^2 = CO_2Et$) and diethyl acetylenedicarboxylate gave *pentaethyl dibenz*[e,g]*imidazo*[1,2-a][1,4]*diazocine*-10,10a,11,12,13-*pentacarboxylate* (4; $R^1 = R^2 = R^3 = CO_2Et$), as needles (37%), m.p. 116—118° (Found: C, 61·2; H, 5·5; N, 6·9. $C_{31}H_{33}N_3O_{10}$ requires C, 61·3; H, 5·5; N, 6·9%), $\nu_{max.}$ 1718, 1640, 1450, 1375, 1330, 1290, 1258, 1207, 1110, 1080, 1040, 780, 770, and 750 cm^{-1}, $\lambda_{max.}$ (EtOH) 230 (ε 25,400), 252 (18,500), and 289 nm (10,300), τ ($CDCl_3$) 2·29—3·07 (8H, m), 5·50—6·17 (10H, 5 overlapping q, *J* 7 Hz), and 8·35—9·08 (15H, 5 overlapping t, *J* 7 Hz).

The azomethine imine (1; $R^1 = R^2 = CO_2Me$) with diethyl acetylenedicarboxylate and the azomethine imine (1; $R^1 = R^2 = CO_2Et$) with dimethyl acetylenedicarboxylate gave identical mixtures of 10,10a,11-*triethyl* 12,13-*dimethyl* and 11,12,13-*triethyl* 10,10a-*dimethyl dibenz*[e,g]*imidazo*[1,2-a][1,4]*diazocine*-10,10a,11,12,13-*pentacarboxylate* (4; $R^1 = R^2 = CO_2Me$, $R^3 = CO_2Et$) and 4; $R^1 = R^2 = CO_2Et$, $R^3 = CO_2Me$). N.m.r. spectra of the crude reaction mixtures from each experiment were identical, both showing 5 different ethyl ester groups, 4 different methyl groups, and aromatic protons, all in identical ratios. Recrystallisation of the mixtures from ether–petroleum gave the major pure isomer (50%), m.p. 159—161° (Found: C, 59·9; H, 5·1; N, 7·5. $C_{29}H_{29}N_3O_{10}$ requires C, 60·1; H, 5·0; N, 7·3%), $\nu_{max.}$ 1745, 1720, 1632, 1470, 1383, 1300, 1270, 1220, 1040, 800, 780, and 762 cm^{-1}, $\lambda_{max.}$ (EtOH) 229 (ε 26,200), 251 (21,000), and 289 nm (10,800), τ ($CDCl_3$) 2·32—2·90 (8H, m), 5·60—6·02 (6H, 3 overlapping q), 6·14 (3H, s), 6·38 (3H, s), and 8·57—9·00 (9H, 3 overlapping t).

Reaction of 2-*Methyl*-2λ⁵σ³-*naphtho*[1,8-de]*triazine* [20] *with Acetylenes*.—(*a*) Dimethyl acetylenedicarboxylate (2·84 g, 20 mmol) in *o*-dichlorobenzene (40 ml) was added dropwise over 5 h to a refluxing solution of 2-methyl-2λ⁵σ³-naphtho[1,8-*de*]triazine (1·83 g, 10 mmol) in *o*-dichlorobenzene (10 ml). After a further 2 h, the solution was allowed to cool and the solvent was removed under reduced pressure. The residue was chromatographed on neutral alumina to give, on elution with chloroform–benzene (20 : 80) or ethyl acetate–ether (30 : 70), the crude red *dimethyl* 2-*methyl*-2λ⁵σ³-*acenaphtho*[5,6-de]*triazine*-6,7-*dicarboxylate* (14; R = Me). This was triturated with boiling ethanol for 5 min, filtered off, and crystallised from benzene–petroleum to give bright red needles (1·20 g, 37%), m.p. 225—226° (Found: C, 63·1; H, 4·3; N, 13·1. $C_{17}H_{13}N_3O_4$ requires C, 63·2; H, 4·1; N, 13·0%), $\nu_{max.}$ 1747, 1716, 1663, 1618, 1400, 1281, 1249, 1146, 1080, 969, and 817 cm^{-1}, $\lambda_{max.}$ (EtOH) 247 (ε 18,500), 276 (13,200), 340sh (38,500), 352 (51,400), and 504 nm (6230), τ ($CDCl_3$) 1·05 and 2·19 (4H, ABq, *J* 8·5 Hz), 5·08 (3H, s, NMe), and 5·88 (6H, s, 2 equivalent Me), *m/e* 323 (M^+).

The yield was slightly improved (43%) when the reaction was carried out in the presence of sulphur (3 equiv.), though it was unchanged by palladium–charcoal and lowered by *o*-chloranil and dichlorodicyano-*p*-benzoquinone. When the reaction was carried out in neat dimethyl acetylenedicarboxylate or in toluene, xylene, dimethylformamide, or nitrobenzene as solvent, the yield was equal to or less than that in *o*-dichlorobenzene. The procedure described above was therefore used for the following cycloadditions.

(*b*) 2-Methylnaphthotriazine and diethyl acetylenedicarboxylate gave *diethyl* 2-*methyl*-2λ⁵σ³-*acenaphtho*[5,6-de]-*triazine*-6,7-*dicarboxylate* (34%) as red needles, m.p. 161—162° (from benzene–petroleum) (Found: C, 65·2; H, 5·1; N, 12·1. $C_{19}H_{17}N_3O_4$ requires C, 65·0; H, 4·9; N, 12·0%), $\nu_{max.}$ 1730, 1704, 1662, 1616, 1405, 1251, 1207, 1080, 813, and 734 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 276 (ε 16,190), 311sh (9090), 344sh (45,900), 353 (57,000), and 494 nm (6110), τ ($CDCl_3$) 0·90 and 2·06 (4H, ABq, *J* 8·5 Hz), 5·02 (3H, s, NMe), 5·36 (4H, q, *J* 7 Hz), and 8·43 (6H, t, *J* 7 Hz), *m/e* 351 (M^+).

(*c*) 2-Methylnaphthotriazine and dibenzoylacetylene gave 6,7-*dibenzoyl*-2-*methyl*-2λ⁵σ³-*acenaphtho*[5,6-de]*triazine* (40%) as dark red needles, m.p. 230—231° (from benzene–petroleum) (Found: C, 78·4; H, 4·4; N, 9·9. $C_{27}H_{17}N_3O_2$ requires C, 78·1; H, 4·1; N, 10·1%), $\nu_{max.}$ 1638, 1613, 1600, 1382, 1318, 1251, 1227, 1080, 950, 831, 763, 722, 693, and 660 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 260 (ε 18,800), 278 (16,570), 365 (45,700), and 522 nm (8050), τ ($CDCl_3$) 1·22 and 2·29 (4H, ABq, *J* 8·5 Hz), 2·45—2·90 (10H, m, aromatic H), and 5·09 (3H, s, NMe), *m/e* 415 (M^+).

(*d*) Similarly 2-benzyl-2λ⁵σ³-naphtho[1,8-*de*]triazine [28] (12; R = $PhCH_2$) and dimethyl acetylenedicarboxylate gave *dimethyl* 2-*benzyl*-2λ⁵σ³-*acenaphtho*[5,6-de]*triazine*-6,7-*dicarboxylate* (34%) as bright red needles, m.p. 225—226° (from benzene) (Found: C, 69·3; H, 4·5; N, 10·6. $C_{23}H_{17}N_3O_4$ requires C, 69·2; H, 4·3; N, 10·5%), $\nu_{max.}$ ($CHCl_3$) 1703, 1663, 1611, 1441, 1398, 1316, and 1156 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 276 (ε 14,340), 311sh (7140), 350sh (51,600), 359 (59,600), and 497 nm (6190), τ ($CDCl_3$) 0·96 and 2·03 (4H, ABq, *J* 8·5 Hz), 2·22—2·84 (5H, m, aromatic H), 3·84 (2H, s, CH_2), and 5·89 (6H, s, 2 identical Me), *m/e* 399 (M^+).

Reaction of 2-*Methyl*-2λ⁵σ³-*naphtho*[1,8-de]*triazine with Dimethyl Azodicarboxylate*.—A mixture of 2-methylnaphthotriazine (549 mg, 3 mmol) and dimethyl azodicarboxylate (448 mg, 3 mmol) in dichloromethane (8 ml) was kept at room temperature for 48 h. The solvent was removed and the residue chromatographed on silica gel. Elution with ether gave 6-(*NN'-bismethoxycarbonylhydrazino*)-2-*methyl*-2λ⁵σ³-*naphtho*[1,8-de]*triazine* (17), which crystallised from benzene–petroleum as dark blue microcrystals (700 mg, 71%), m.p. 194—196° (Found: C, 54·9; H, 4·7; N, 21·1. $C_{15}H_{15}N_5O_4$ requires C, 54·7; H, 4·6; N, 21·3%), $\nu_{max.}$ 3262, 1760, 1704, 1628, 1534, 1255, 1073, 828, 758, and 709 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 355 (ε 14,800), 370sh (8600), 387sh (4300), 544 (1060), 590 (1090), and 640 nm (743), τ ($CDCl_3$) 2·48br (1H, s, NH), 2·77 [1H, dd, *J* 8 and 1 Hz, C(7)H], 2·93 [1H, d, *J* 8 Hz, C(5)H], 3·15 [1H, m, C(8)H], 3·65 [1H, dd, *J* 8 and 1 Hz, C(9)H], 3·74 [1H, d, *J* 8 Hz, C(4)H], 6·19 (3H, s), and 6·27 (6H, s, 2 × Me), *m/e* 329 (M^+).

Reaction of 2λ⁴σ²-*Naphtho*[1,8-cd][1,2,6]*thiadiazine* [23] *with Dimethyl Acetylenedicarboxylate*.—This reaction was carried out in refluxing *o*-dichlorobenzene as described for 2-methylnaphthotriazine. *Dimethyl* 2λ⁴σ²-*acenaphtho*[5,6-cd]-[1,2,6]*thiadiazine*-6,7-*dicarboxylate* was obtained as dark blue needles (6%) (from benzene–petroleum), m.p. 173—174° (Found: C, 59·1; H, 3·1; N, 8·4. $C_{16}H_{10}N_2O_4S$ requires C, 58·9; H, 3·1; N, 8·6%), $\nu_{max.}$ ($CHCl_3$) 1708, 1630, 1593, 1443, 1393, 1348, 1298, 1160, and 855 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 262 (ε 21,990), 368 (51,800), and 520 nm (1480), τ ($CDCl_3$) 0·87 and 1·95 (4H, ABq, *J* 8·5 Hz) and 5·89 (6H, s, 2 equivalent Me), *m/e* 362 (M^+).

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