[2 + 2] Photocycloadditions of Dichloromaleimide and Dichloromaleic Anhydride to Cyclic Olefins

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The photocycloaddition of dichloromaleimide to cyclohexadiene, cyclopentadiene, and cyclopentene on direct photolysis gave [2 + 2] addition products with the *cis,endo-* and *cis,exo-*configurations as the major products. However, a similar photocycloaddition to cyclohexene yielded the *trans*-fused cycloaddition product (between the four- and six-membered rings) as the major product in addition to the *cis,endo-* and *cis,exo-*isomers. The photocycloadditions of dichloromaleic anhydride to cyclopentadiene and cyclohexadiene were reinvestigated; two major products were obtained which were identified as the *cis,endo-* and *cis,exo-*addition products, while the reported *trans*-fused isomers were not isolated. The structures of these photoaddition products were investigated by 400 MHz n.m.r. spectroscopy to ascertain the configuration of the ring fusion. An X-ray crystallographic analysis established the stereochemistry of one product.

Photocycloadditions of [2 + 2] electron systems are a useful route to cyclobutane rings[1,2] and have been extensively studied with a wide variety of substrates.[3-8] As the model compounds (3), (4), (6), (7), and (13)—(16) were required for mechanistic studies, we investigated the photoaddition of maleimide and maleic anhydride to suitable olefins. The structural isomerism and the stereochemistry of the ring fusion in the photo-cycloaddition products was investigated by high-field n.m.r. spectroscopy and an X-ray crystallographic analysis. The results are reported herein.

Maleic anhydride derivatives react with olefins to form complexes which show new bands in the 280 nm region.[9-12] Irradiation of this charge-transfer band or sensitization by triplet sensitizers such as benzophenone initiates the [2 + 2] cycloaddition to give all the possible stereoisomers of the cyclobutane derivatives.[13-15] The photoadditions of maleimides to acyclic dienes are also known.[9,12]

Results and discussion

Photocycloadditon of Cyclohexadiene and Cyclohexene.— The direct photolysis of dichloromaleimide (1) in the presence of cyclohexene or cyclohexadiene in a Pyrex apparatus gave the cyclobutane derivatives (3)—(7) as the major products in which 7,8-dichloro-*cis*-bicyclo[4.2.0]oct-2-ene-*endo,cis*-7,8-di-carboximide (6) was related to 7,8-dichloro-*cis*-bicyclo[4.2.0]-octane-*endo,cis*-7,8-dicarboximide (3) by a mild hydrogen-ation; likewise the *exo,cis*-imide (7) was hydrogenated to give the *exo,cis*-imide (4). In the latter photoaddition, the bicyclo[2.2.2] products (8) and (9) were also formed as minor products presumably arising from a thermal [2 + 4] cycloaddition (Diels–Alder reaction); these compounds were not investigated. In the former photoaddition, 7,8-dichloro-*trans*-bicyclo-[4.2.0]octane-*cis*-7,8-dicarboximide (5) was the major product; it underwent methanolysis rapidly when heated in methanol with charcoal to give a single stereoisomer which was assigned the structure 7,8-dichloro-7-*trans*-carboxamido-8-*trans*-methoxycarbonyl-*trans*-bicyclo[4.2.0]octane (12) as nucleophilic attack of methanol would be expected to take place at the least hindered site at C-9. The formation of the imide (5) with the *trans*-ring fused isomer predominating indicates that the cycloaddition follows a stepwise mechanism as suggested previously.[10,11] The fact that the *endo,cis*-imide (3) is obtained in lower yield than the *exo,cis*-imide (4) (a ratio of 14:32) suggests that the reaction is significantly controlled by steric repulsion.

Table 1. ^{13}C N.m.r. spectral data ([$^2H_6$]acetone) (*J* in Hz)

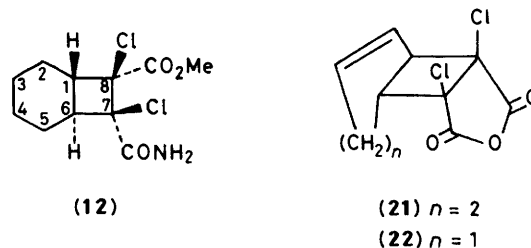| Compound	δ_C/p.p.m.
(3)	21.3 (t, *J* 130, C-3 and C-4), 22.44 (t, *J* 130, C-2 and C-5), 42.58 (d, *J* 145, C-1 and C-6), 69.46 (s, C-8 and C-7), 172.44 (s, C=O)
(4)	21.32 (t, *J* 130, C-3 and C-4), 23.09 (t, *J* 130, C-2 and C-5), 39.6 (d, *J* 148, C-1 and C-6), 71.47 (s, C-8 and C-7), 173.81 (s, C=O)
(5)	26.03 (t, *J* 130, C-4),^{a} 26.32 (t, *J* 130, C-3),^{a} 27.49 (t, *J* 130, C-2), 29.22 (t, *J* 130, C-5), 50.20 (d, *J* 136, C-6), 52.62 (d, *J* 136, C-1), 68.43 (d, *J* 8, C-8), 75.75 (s, C-7), 171.19 (d, *J* 8, C-10), 172.28 (d, *J* 4, C-4)
(6)	19.75 (t, *J* 128, C-5), 21.22 (tt, *J* 3.5, 129, C-4), 42.76 (d, *J* 149, C-1), 43.09 (d, *J* 143, C-6), 67.88 (s, br, C-7), 70.26 (d, *J* 7, C-8), 122.65 (dd, *J* 4, 162, C-2), 133.50 (d, *J* 158, C-3), 171.48 (s, C-9),^{a} 172.68 (d, *J* 4, C-10)^a
(7)	22.38 (t, *J* 128, C-4), 22.81 (t, *J* 130, C-5), 39.48 (d, *J* 146, C-6), 40.09 (d, *J* 140, C-1), 69.4 (s, br, C-7), 72.3 (d, *J* 8, C-8), 122.53 (d, *J* 165, C-2), 134.58 (d, *J* 170, C-3), 173.4 (d, *J* 3.6, C-9), 173.74 (d, *J* 3.7, C-10)
(12)	25.05, 25.61, 26.13, 28.16, 45.73, 52.15, 52.53, 75,15 76.20, 168.94, 169.28
(13)	27.78 (t, *J* 130, C-3), 28.43 (t, *J* 130, C-2 and C-4), 51.34 (d, *J* 150, C-1 and C-5), 68.21 (s, C-6 and C-7), 172.11 (s, C=O)
(14)	27.1 (t, *J* 132, C-3), 30.4 (t, *J* 133, C-2 and C-4), 47.15 (d, *J* 147, C-1 and C-5), 69.93 (s, C-6 and C-7), 174.40 (s, C=O)
(15)	35.15 (tt, *J* 9, 133, C-4), 47.31 (md, *J* 151, C-5), 57 (d, md, *J* 153, C-1), 68.44 (m, C-6), 71.4 (br s, C-7), 128.35 (md, *J* 168, C-2), 138.52 (md, *J* 165, C-3), 171.69 (s, C-8), 171.96 (d, *J* 3.9, C-9)
(16)	36.49 (tt, *J* 9, 133, C-4), 44.35 (dd, *J* 3.4, 147, C-5), 54.69 (md, *J* 147, C-1), 70.52 (s, C-7), 72.28 (m, C-6), 128.8 (md, *J* 172, C-2), 137.1 (md, *J* 165, C-3), 173.68 (d, *J* 3.2, C-8), 173.8 (d, *J* 3.8, C-9)

^{a} The pair of signals is interchangeable.

These cyclobutylimides (3)—(7) showed the appropriate i.r. absorptions, mass spectral fragments, and elemental analyses for the proposed molecular formulae. The i.r. and mass spectral data and elemental analyses are available as a Supplementary
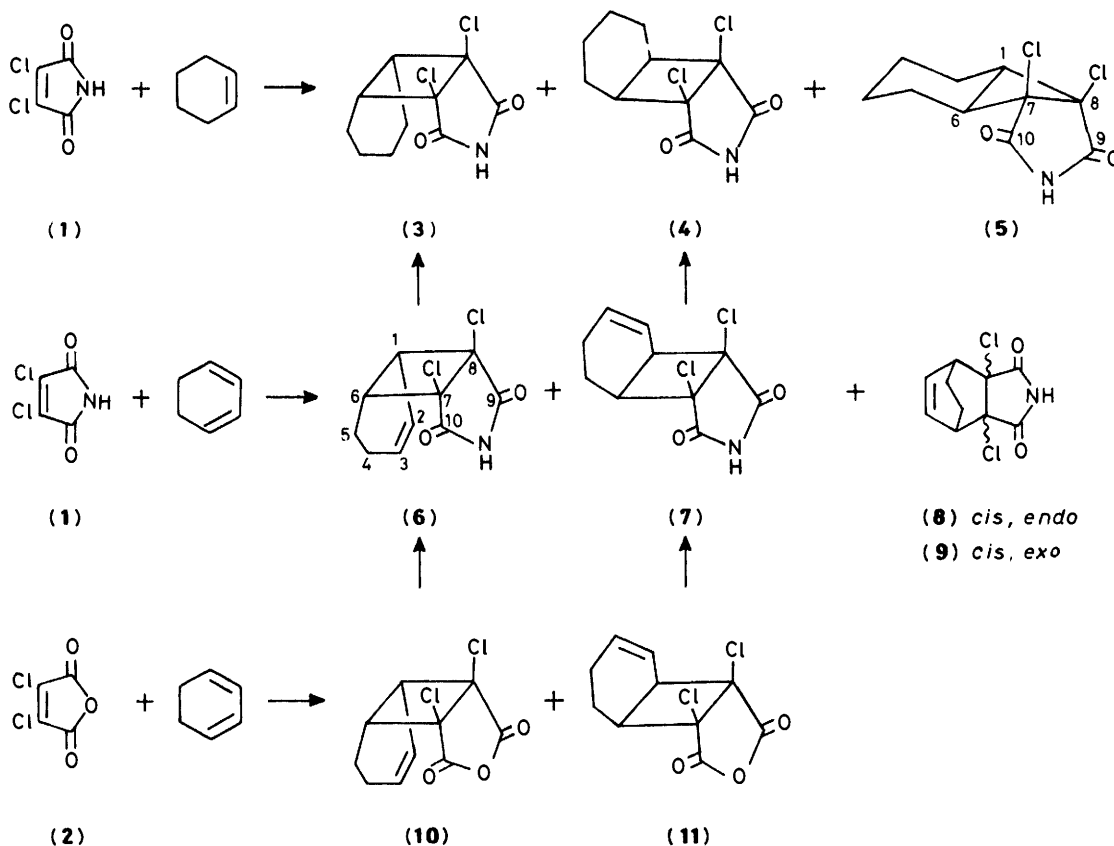
Scheme 1.

Publication (SUP No. 23900, 7 pp.).* The structural determination of compounds (3), (4), (6), and (7) were primarily concerned with the cis–trans configuration at the ring-junction and the endo–exo orientation of the dicarboximide group with respect to the cis-ring fusion of the bicyclic system. The ^{13}C n.m.r. spectra (Table 1) of compounds (3) and (4) show only five signals, indicating the molecular symmetry with respect to the plane bisecting the molecules through the nitrogen atom. Evidence for the endo–exo orientation may be obtained from the over-the-space electromagnetic effects of the carboximide group with respect to the protons of the molecule. For this purpose, the ^1H n.m.r. signals were identified using decoupling experiments. The details are described later. The pertinent arguments in support of the structural assignments are outlined below.

Firstly, the anisotropic effect of the carbonyl group[16] shifts the proton signal to higher fields if the proton is located in the shielding region of the cone (Table 2). Thus, the signals of 1-H and 6-H are shifted to higher fields in compounds (4) and (7) than the corresponding signals in (3) and (6). Conversely, the signal of the olefinic proton, 3-H, in compound (6) is shifted to higher field than that of the corresponding proton in (7). Similarly, shifts to higher field of several of the alkyl proton signals in (3) and (6) are revealed when their chemical shifts are compared with those of (4) and (7) (Table 2). Secondly, a distinct enhancement of the 1-H and 6-H signals [nuclear Overhauser effects (n.O.e.)] was observed when the NH proton in compounds (4) and (7) was irradiated, while a similar irradiation of compounds (3) and (6) did not cause a significant n.O.e.

* For details of the Supplementary Publications scheme see Instructions for Authors (1984) in J. Chem. Soc., Perkin Trans. 1, 1984, Issue 1.

(12)

(21) n = 2
(22) n = 1

Scheme 2.

The structural proof of the trans-imide (5) relied on extensive decoupling experiments and 2D ^1H n.m.r. spectra to establish the identity and pattern of signals (vide infra). These results indicate that the cyclohexane ring is fused to the cyclobutane ring with equatorial–equatorial bonding. The ten signals of the ^{13}C n.m.r. spectrum clearly indicate that compound (5) does not possess a plane of symmetry like those in (3) and (4). The proton signal due to 6-H (1.43 p.p.m.) resonates at higher field than that from 1-H (2.15 p.p.m.), showing that 6-H lies in the shielding cone of the C-10 carbonyl group.[16] The trans-fusion between the four- and six-membered rings is clearly shown by the facile methanolysis of the imide ring which partially relieves the molecular strain. Nucleophilic methanol must attack the C-9 carbonyl as this is the less sterically hindered site; the configuration of the amide ester (12) was assigned on the basis of mechanistic considerations.

The photocycloaddition of dichloromaleic anhydride (2) to cyclohexadiene has been reported by Scharf[15] to give the products (10) and (21): the latter, (21), is a trans-4,6-fused bicyclic compound with reported m.p. 158 °C.

Table 2. ¹H N.m.r. data (in CDCl₃)[a]

Compound	δ/p.p.m.	J/Hz
(3)	1.27 (m, 3-Hₙ and 4-Hₙ), 1.45 (m, 3-Hₓ) and 4-Hₓ), 1.57 (m, 2-Hₙ and 5-Hₙ), 1.83 (m, 2-Hₓ and 5-Hₓ), 3.11 (m, 1-H and 6-H), 8.18 (NH)	$J_{2n.2x} = J_{5n.5x} = 13.8$, $J_{2x.3n} = J_{2x.3x} = 5.1$, $J_{2n.3x}$ 8.7, $J_{2n.3n}$ 4.4
(4)	1.38 (m, 3-Hₙ and 4-Hₙ), 1.75 (m, 4-H), 1.86 (m, 2-Hₓ and 5-Hₓ), 2.84 (m, 1-H and 6-H), 8.83 (NH)	
(5)[b]	0.7 (m, 3-Hₙ and 3-Hₐ), 1.11 (dq, J 3.7, 12, 2-Hₐ), 1.19 (ddt, J 3.7, 10.7, 12.8, 5-Hₐ), 1.25 (m, 5-Hₑ and 4-Hₑ), 1.33 (qd, J 3.7, 12.5, 5-Hₑ), 1.43 (ddd, J 3.7, 10.12, 6-H), 1.67 (qd, J, 3.5, 12.5, 2-Hₑ), 2.15 (ddd, J 3, 12, 13, 1-H)	$J_{1.2e}$ 3, $J_{1.2a}$ 13, $J_{1.6}$ 12.5, $J_{2e.2a}$ 12.5, $J_{2e.3a}$ 3.8, $J_{2a.3}$ 12.8, $J_{4e.5a}$ 3.8, $J_{4a.5a}$ 12.8, $J_{5a.5e}$ 12.8, $J_{5e.6}$ 3.8, $J_{5a.6}$ 10.8
(6)	1.72 (tdd, J 6.4, 8.6, 14.6, 5-Hₓ), 1.95 (tdd, J 3.9, 6.2, 14.6, 5-Hₙ), 2.04 (m, 4-Hₙ and 4-Hₓ), 3.45 (ddd, J 4, 6.4, 11, 6-H), 3.48 (qdd, J 2, 3.6, 11, 1-H), 5.83 (tdd, J 2, 3.8, 10, 2-H), 6.05 (dddd, J 1.4, 3.2, 5, 10, 3-H), 9.05 (NH)	$J_{1.2}$ 3.8, $J_{1.3}$ 1.4, $J_{1.6}$ 11, $J_{2.3}$ 10, $J_{2.4n}$ 2, $J_{2.4x}$ 2, $J_{3.4x}$ 5, $J_{3.4n}$ 3.4, $J_{4x.4n}$ 17, $J_{4x.5n}$ 3.8, $J_{4n.5x}$ 3.8, $J_{4n.5n}$ 6.8, $J_{4x.5x}$ 6.5, $J_{5x.5n}$ 15, $J_{5n.6}$ 4, $J_{5x.6}$ 6.4
(7)	1.91 (m, 5-Hₙ and 5-Hₓ), 2.03 (m, 4-Hₙ), 2.29 (dqd, J 2, 5.4, 17, 4-Hₓ), 3.04 (td, J 8, 9, 6-H), 3.29 (dtdd, J 0.5, 2, 5, 8, 1-H), 5.64 (tdd, J, 2, 4.4, 10, 2-H), 6.27 (dddd, J 2, 3.4, 5.2, 10, 3-H), 8.54 (NH)	$J_{1.2}$ 4.4, $J_{1.3}$ 1.8, $J_{1.6}$ 8.8, $J_{2.3}$ 9.9, $J_{2.4x}$ 1.6, $J_{2.4n}$ 2.2, $J_{3.4x}$ 5.3, $J_{3.4n}$ 3.4, $J_{4n.4x}$ 17, $J_{4x.5x}$ 5.3, $J_{4x.5n}$ 5.1, $J_{4n.5n}$ 5.6, $J_{4n.5x}$ 9, $J_{5x.5n}$ 17.2, $J_{5x.6}$ 7.2, $J_{5n.6}$ 8
(8)	1.83 (md, J 8, 7-Hₐₙₜᵢ and 8-Hₐₙₜᵢ), 2.21 (md, J 8, 7-Hₛᵧₙ and 8-Hₛᵧₙ), 3.23 (m, 1-H and 4-H), 6.28 (m, 2-H and 3-H)	
(9)	1.45 (md, J 10, 7-Hₐₙₜᵢ and 8-Hₐₙₜᵢ), 1.67 (md, J, 10, 7-Hₛᵧₙ and 8-Hₛᵧₙ), 3.37 (m, 1-H and 4-H), 6.48 (m, 2-H and 3-H)	
(10)	1.77 (tdd, J 6.5, 10, 15, 5-Hₓ), 2.05 (tdd, J 3, 6.5, 15, 5-Hₙ), 2.1 (m, 4-Hₓ), 2.18 (m, 4-Hₙ), 3.48 (m, 1-H and 6-H), 5.87 (md, J 10, 2-H), 6.15 (dtd, J 1.8, 4, 10, 3-H)	
(11)	1.93 (m, 5-Hₙ and 5-Hₓ), 2.05 (m, 4-Hₙ), 2.32 (qd, J 4.5, 17, 4-Hₓ), 3.10 (td, J 7, 9, 6-H), 3.37 (m, 1-H), 5.65 (tdd, J 1.8, 4, 10, 2-H), 6.28 (dddd, J, 2, 3, 5.5, 10, 3-H)	
(12)	1.36 (m, 3-H and 4-H), 1.43 (dq, J, 3.5, 12, 5-Hₐ), 1.53 (dq, J 3.5, 12, 2-Hₐ), 1.82 (m, 3-H, 4-H, 5-Hₑ), 1.92 (qd, J, 3, 12, 2-Hₑ), 2.37 (ddd, J, 3.5, 12, 13, 6-H), 2.85 (dddd, J 3.5, 11, 13, 1-H), 3.72 (s, Me), 5.72 (NH), 6.55 (NH)	$J_{1.6}$ 13, $J_{1.2a}$ 12, $J_{1.2e}$ 3.5, $J_{6.5a}$ 12
(13)	1.76 (m, 3 H), 1.82 (m, 1 H), 2.04 (m, 2 H), 3.45 (m, 1-H and 5-H), 8.75 (NH)	
(14)	1.73 (m, 2 H), 1.83 (m, 1 H), 1.9 (m, 1 H), 2.22 (m, 2 H), 3.18 (m, 1-H and 5-H), 8.57 (NH)	
(15)	2.62 (qdd, J 2.2, 8.8, 19, 4-Hₓ), 2.78 (md, J 18.6, 4-Hₙ), 3.62 (dt, J 1.8, 9, 5-H), 3.92 (md, J 9, 1-H), 5.75 (qd, J 2.2, 5.8, 2-H), 6.02 (qd, J 2, 5.6, 3-H), 8.58 (NH)	$J_{1.2}$ 2.3, $J_{1.3}$ 2, $J_{1.4n}$ 3, $J_{1.4x}$ 2.2, $J_{1.5}$ 8.8, $J_{2.3}$ 5.6, $J_{2.4n}$ 2.3, $J_{2.4x}$ 2.3, $J_{3.4n}$ 2.4, $J_{3.4x}$ 2.2, $J_{4n.4x}$ 18.6, $J_{4n.5}$ 1.8, $J_{4x.5}$ 8.8
(16)	2.72 (tddd, J 1.8, 2.2, 8.6, 18, 4-Hₓ), 3.0 (md, J 18, 4-Hₙ), 3.37 (ddd, J 2, 6.4, 8, 5-H), 3.87 (m, 1-H), 5.72 (qd, J 2.4, 5.6, 2-H), 6.08 (qd, J 2.2, 5.6, 3-H), 8.27 (NH)	$J_{1.2}$ 2.6, $J_{1.3}$ 2.7, $J_{1.4n}$ 1.5, $J_{1.4x}$ 2.5, $J_{1.5}$ 6.2, $J_{2.3}$ 5.7, $J_{2.4n}$ 2.4, $J_{2.4n}$ 2.0, $J_{3.4n}$ 2.3, $J_{3.4x}$ 2, $J_{4n.4n}$ 18.4, $J_{4n.5}$ 1.5, $J_{4x.5}$ 8.6
(17)[c]	1.62 (md, J 11, 7-Hₛᵧₙ), 1.9 (md, J, 11, 7-Hₐₙₜᵢ), 3.35 (m, 1-H and 4-H), 6.52 (m, 2-H and 3-H)	
(18)	2.67 (qdd, J 2, 8, 19, 4-Hₓ), 2.87 (md, J 19, 4-Hₙ), 3.67 (t, J 8.5, 5-H), 3.95 (md, J 8, 1-H), 5.83 (qd, J 2, 6, 2-H), 6.13 (m, 3-H)	$J_{1.2}$ ca. 2, $J_{1.4x}$ ca. 2, $J_{1.5}$ 8.5, $J_{2.3}$ 6, $J_{2.4x}$ ca. 2, $J_{3.4x}$ ca. 2, $J_{4n.4x}$ 19, $J_{5.4x}$ 8
(19)	2.8 (qdd, J 2, 8, 18.5, 4-Hₓ), 3.05 (md, J 18, 4-Hₙ), 3.43 (t, J 7.5, 5-H), 3.93 (m, 1-H), 5.77 (qd, J 2, 5.5, 2-H), 6.13 (m, 3-H)	$J_{1.2}$ ca. 2, $J_{1.4x}$ ca. 2, $J_{1.5}$ 7.5, $J_{2.3}$ 5.5, $J_{2.4x}$ ca. 2, $J_{3.4x}$ ca. 2, $J_{4x.4n}$ 18.5, $J_{5.4x}$ 8
(20)	2.18 (md, J 10, 7-Hₐₙₜᵢ), 2.5 (md, J 10, 7-Hₛᵧₙ), 3.42 (m, 1-H and 4-H), 6.32 (m, 2-H and 3-H)	

[a] In the assignments the subscripts n and x stand for endo and exo, and a and e are axial and equatorial. [b] In C₆D₆. [c] In a mixture of (16) and (17).
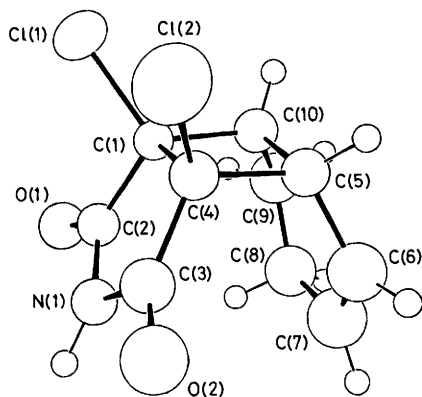
Figure. The perspective view of compound (6) from crystallographic measurements showing the crystallographic numbering scheme (different from the numbering scheme shown in the reaction schemes and used in the names). Atoms are represented as 50% thermal ellipsoids with the exception of the H atoms which are drawn in an arbitrary size

In our hands, the photocycloaddition of compound (2) to cyclohexadiene gave the product (10) and a fraction with physical constants (e.g. m.p. and 60 MHz n.m.r. spectrum) corresponding to those reported for compound (21). The fraction was a mixture and could not be purified, but contained one major compound (70%) which was readily converted into the lactam (7) by ammonolysis followed by cyclization; the major component is therefore 7,8-dichloro-cis-bicyclo-[4.2.0]oct-2-ene-exo,cis-7,8-dicarboxylic acid anhydride (11), but can not have structure (21). Compounds which are trans-4,6-fused with a carbon–carbon double bond, such as (21), are relatively difficult to form owing to ring strain, but have been isolated in the analogous photoaddition of dimethylmaleic anhydride to cyclohexadienes.[13,14] The ring-strain in these is shown by the facile nucleophilic hydrolysis of the imide ring which is also shown by the trans-imide (5). Our results show that, if such compounds are formed at all, the yields are insignificant in both photocycloadditions to cyclohexadiene. The conversion of compound (10), via ammonolysis and cyclization, into (6) relates the stereochemistry of these two compounds. Finally, the structure of compound (6) was determined by X-ray crystallography* and is shown in the Figure.

Photocycloaddition to Cyclopentene and Cyclopentadiene.— Irradiation of the solutions of dichloromaleimide (1) in the presence of either cyclopentadiene or cyclopentene smoothly afforded 6,7-dichloro-cis-bicyclo[3.2.0]hept-2-ene-endo,cis-6,7-dicarboximide (15) and its exo,cis-isomer (16), and 6,7-dichloro-cis-bicyclo[3.2.0]heptane-endo,cis-6,7-dicarboximide (13) and its exo,cis-isomer (14) respectively. These compounds were formed as the major products. In the former addition a minor amount of 2,3-dichlorobicyclo[2.1.1]hept-5-ene-exo,cis-2,3-dicarboximide (17) was obtained; the compound exhibited distinctly different physical properties from those of the endo,cis-isomer (20) which was the sole product from the Diels–Alder reaction. The stereochemistries of the exo,cis-pair of isomers (14) and (16) and the endo,cis-pair (13) and (15) were readily related by mild hydrogenation. These compounds exhibited the expected i.r., mass, and ¹³C and ¹H n.m.r. spectra as shown in the Supplementary Publication and Tables 1 and 2. Both

compounds (13) and (14) have a plane of symmetry and therefore showed simple five-peak patterns in their ¹³C n.m.r. spectra which contrasted with the nine-peak patterns of the isomers (15) and (16).

Owing to some ambiguity in the decoupling experiments, we were unable to obtain the complete coupling patterns of compounds (13) and (14) and could only partially assign the signals in these spectra. The chemical shifts of 1-H and 5-H in compounds (14) and (16) are clearly located to higher field than those of (13) because of the anisotropic effects of the carbonyl groups.[16] Also, irradiation of the NH proton in (14) enhanced the intensities of 1-H and 5-H. Both these observations support the structural assignment shown. However, the electromagnetic effects of the carbonyl group on 2-H, 3-H, and 4-H are relatively small in these compounds. This may be because the imido group and the pentane ring are rigidly held in these molecules and the carbonyl groups and the ring protons are further apart than those in the 4,6-ring-fused system.

The benzophenone-sensitized photoaddition of dichloromaleic anhydride (2) to cyclopentadiene in dioxane gave the cis,endo-isomer (18) and the cis,exo-isomer (19) in a 1:1 ratio, in addition to a small amount of an unknown compound. Owing to partial hydrolysis, the recovery of these isomers (18) and (19) from flash chromatography was low. Compounds (18) and (19) were directly converted into (15) and (16), respectively, by ammonolysis and cyclization, thus relating their structures. It is also obvious that both isomers (18) and (19) are cis-ring-fused on the basis of the coupling constant $J_{1,5}$ (8.5 and 7.5 Hz, respectively). The same photoaddition was reported by Scharf[15] who assigned the two major products as the cis,endo-isomer (18) (m.p. 93 °C) and the trans-4,5-fused isomer (22) (m.p. 122 °C; higher g.c. retention time): the structure of (18) was established by a series of chemical reactions. Our second major product, though not obtained in the pure state, exhibited a similar n.m.r. pattern (at 60 MHz) to that of Scharf's sample and was directly correlated to the cis,exo-isomers (16) and (14). In view of the five-line pattern in the ¹³C n.m.r. spectrum of (14) and of the strain inherent in a trans-4,5-ring-fused molecule with a carbon–carbon double bond, as shown by Dreiding models, we conclude that the second major product in this [2 + 2] photocycloaddition is (19), and Scharf's proposed structure[15] (22) is incorrect.

The N.M.R. Spectra of the Photocycloaddition Products.— The n.m.r. spectra of some of the addition products were examined at 400 MHz by extensive decoupling and n.O.e. experiments. These allowed us to assign the proton and carbon signals and the stereochemistry of the products. The details of the experiments are described in the thesis to be presented by Y.M.A.N.;† the salient points are given below.

For the imides (6) and (7), irradiation of the signal due to 2-H caused changes in the 1-H and 3-H signals, irradiation of the signal due to 3-H caused changes in the 2-H,1-H (allylic couplings) and 4-H signals, and irradiation of the 4-H signals caused changes in the 1-H, 2-H, 3-H, and 5-H signals. Irradiation of the 1-H and 6-H signals selectively simplified the 2-H and 5-H signals, respectively, and also enhanced the intensity of the 2-H and 5-H$_{exo}$ signals. For the imide (7), a n.O.e. was also observed for 1-H when 6-H was irradiated and vice versa. The coupling constants were obtained from these experiments on the basis of the conformation given by the X-ray analysis of (6); in particular, the value of $J_{1,6}$ (11 and 8.8 Hz) for (6) and (7) indicates that the 4,6-ring system is cis-fused. The ¹³C n.m.r. signals of (6) and (7) were assigned by off-resonance decoupling experiments; the results are summarized in Table 3.

The imides (3) and (4) exhibited complex n.m.r. patterns
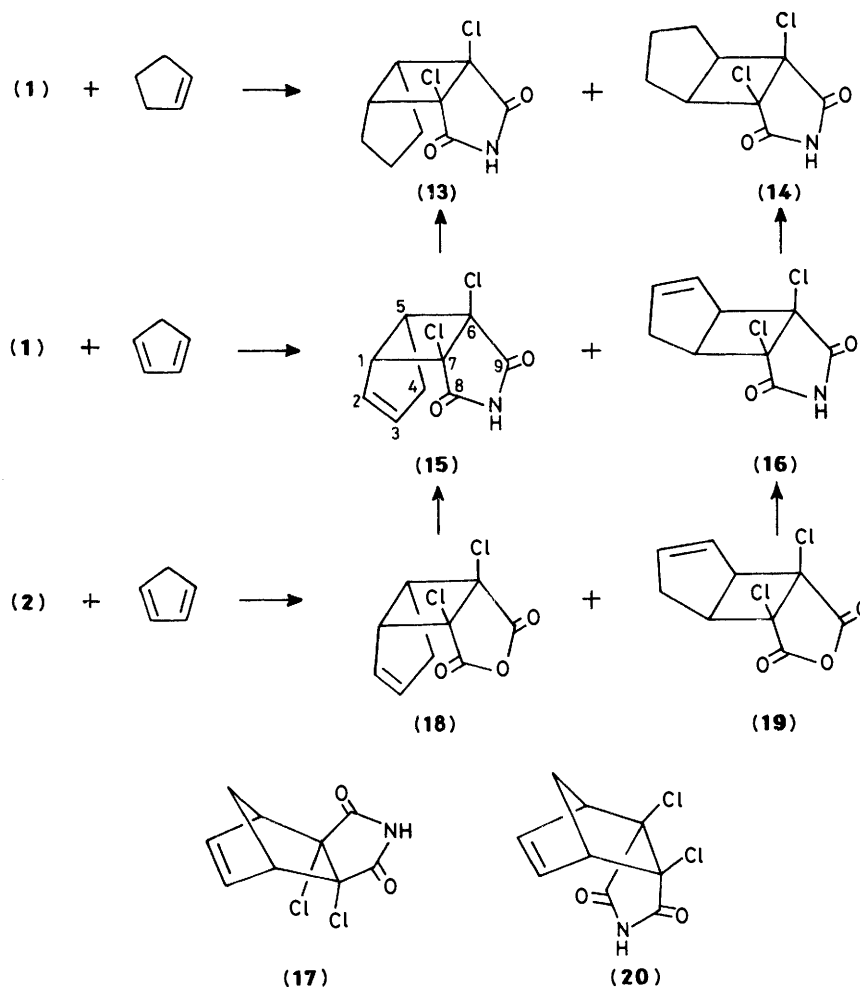
Scheme 3.

Table 3. Off-resonance decoupling[a] of the ^{13}C n.m.r. spectra of (6) and (7)

^{13}C N.m.r. signals	(6)	(7)
C-1 and C-6	C-1 enhanced on decoupling of 2-H and 3-H	C-1 collapsed on decoupling of 1-H
C-2 and C-3	C-2 collapsed on decoupling of 2-H	C-2 collapsed on decoupling of 2-H
C-4 and C-5	C-5 collapsed to a doublet on decoupling of either 5-H_x or 5-H_n	C-4 enhanced on decoupling of 2-H and 3-H
C-9 and C-10	[b]	C-9 enhanced on decoupling of 1-H C-10 enhanced on decoupling of 6-H
C-7 and C-8	C-7 enhanced on decoupling of 5-H	C-8 enhanced on decoupling of 1-H C-7 enhanced on decoupling of 6-H

[a] The 'enhancement' arises from the removal of long-range coupling (see ref. 17). [b] The two signals are overlapped with solvent peaks and can not be differentiated.

which could not be analysed precisely. However, irradition of the 1-H (or 6-H) signal changed the pattern of the 2-H (or 5-H) signals, but not that of the 3-H (or 4-H) signal, and also caused

an intensity enchancement of the 2-H_{exo} (or 5-H_{exo}) signal. Most of the coupling constants of the *trans*-4,6-fused imide (5) were obtained by 2D n.m.r. spectroscopy; they suggest that the cyclohexane ring is frozen in a chair conformation. In the ^1H n.m.r. spectrum of compound (5), irradiation of the 1-H signal changed the patterns of the 6-H, 2-H_{ax}, and 2-H_{eq} signals; the signals due to 3-H_{ax}, 4-H_{ax}, 5-H_{ax}, and 5-H_{eq} were consecutively located *via.* a series of decoupling experiments in which the immediately neighbouring proton signals were irradiated. The ^{13}C n.m.r signals of (5) were assigned by the following experiments. Irradiation of the 1-H signal collapsed the C-1 doublet signal to a singlet and enhanced the intensities of the C-8 and C-9 signals.[17] Separate irradiation of the 2-H_{eq}, 3-H_{ax}, and 4-H_{ax} signals collapsed the C-2, C-3, and C-4 signals, respectively, to doublets.

Both the imides (15) and (16) showed well-resolved ^1H n.m.r. spectra which were completely resolved by decoupling experiments to afford the coupling constants shown in Table 2, and the signals were easily assigned from these results and also from the results of the n.O.e. experiments. For example, irradiation of the 1-H signal caused enhancement of the 2-H and 5-H signals, and irradiation of the 5-H signal enhanced the 4-H_{exo} and 1-H signals, but not the 4-H_{endo} signal. The ^{13}C n.m.r. signals of (15) and (16) were assigned by off-resonance experiments in which the intensity of the C-8 and C-9 signals were enhanced when the 1-H and 5-H signals were irradiated, respectively.[17] The C-5 signal was shown to be weakly coupled with the 4-H protons by decoupling experiments.

Owing to the molecular symmetry, the imides (13) and (14) showed simple five-line ^{13}C n.m.r. patterns, but complex patterns in their ^{1}H n.m.r. spectra arising from second-order couplings; only a few proton–proton coupling contents were obtained from decoupling experiments.

Experimental

General Conditions.—Unless specified otherwise, the following experimental conditions were used. M.p.s were determined on a Fisher-Johns apparatus and were uncorrected. I.r. spectra were recorded on a Perkin-Elmer 599B spectrometer using Nujol mulls. U.v. spectra were obtained on a Unicam SP 800 spectrometer. Mass spectra and gas chromatography–mass spectra were taken on a Hewlett-Packard 5985 mass spectrometer using a SE-30 capillary column. Elemental analyses were performed by Mr. M. A. Yang on a Perkin-Elmer 240 spectrometer. Gas chromatographic (g.c.) analyses were performed on a Varian 1400 (F.I.D.) instrument with an SE-30 capillary column (J & W, 13.7 m × 0.28 mm) or a Hewlett-Packard 5792 A instrument with an OV-1 capillary column (HP, 12.5 m × 0.20 mm) coupled with a HP 3390 integrator. Preparative g.c. was carried out with a Varian 1700 (thermal conductivity detector) instrument on a 10% SE-30 (3 m × 6.4 mm) column.

Separations by column chromatography were carried out using silica gel (Baker; 60—200 mesh). Flash chromatographic separations were carried out as described by Still[18] using silica gel (230—400 mesh).

N.m.r. spectra were recorded at 400 MHz on a Bruker WH400 spectrometer in the Fourier Transform (FT) mode, and an internal lock (deuterium) was used. The chemical shifts in the ^{1}H n.m.r. spectra were referred to the solvent signals (δ 7.24, 7.15, and 2.04 p.p.m. for $CDCl_3$, C_6D_6, and $[^2H_6]$acetone, respectively). The peak positions of the ^{13}C signals were measured relative to the solvent signals at δ 77.0, 128.0, and 30.2 p.p.m. for $CDCl_3$, C_6D_6, and $[^2H_6]$acetone, respectively.

The n.O.e. experiments were performed at 400 MHz, using difference spectroscopy, on degassed solutions containing *ca.* 5 mg of a sample in 0.5 ml of solvent. Ether refers to diethyl ether and light petroleum to that fraction with b.p. 35—60 °C.

Preparation of Dichloromaleimide (1).—A mixture of dichloromaleic anhydride (19.4 g, 0.12 mol), urea (7.4 g. 0.12 mol), and sodium chloride (24.2 g, 0.42 mol) was placed in a round-bottomed flask fitted with an oil trap. The mixture melted at *ca.* 90 °C and reacted vigorously at *ca.* 120 °C. It was stirred at 120 °C for 20 min, and was added to water (50 ml) at 100 °C. The precipitate of the cold mixture was collected and recrystallized from methanol–water (2:1 v/v) to give dichloromaleimide (1) (11.5 g, 59%); m.p. 174—177 °C (lit.,[19] m.p. 178—180 °C); $\lambda_{max.}$ 235 nm (ϵ 7.2 × 10^4); $\nu_{max.}$ 3 200 (s), 1 730 (s,br), 1 610 (s), 1 050 (s), and 850 cm^{-1} (s).

The Photolysis Procedure.—Irradiation of a dioxane solution containing the olefin and maleimide (or maleic anhydride) was carried out in an immersion type Pyrex apparatus using a 450-W Hanovia medium-pressure Hg lamp. The whole apparatus was cooled externally with a water-bath at 10—15 °C. The solution was magnetically stirred and purged with a stream of nitrogen. The progress of the reaction was monitored by g.c. at suitable intervals to follow the decrease of the maleimide. The photolysate was evaporated under reduced pressure and the crude product separated by chromatography using g.c. to monitor the separation.

Photoaddition of Dichloromaleimide (1) *to Cyclohexa-1,3-diene.*—A solution of (1) (4 g, 0.024 mol) and cyclohexa-1,3-

diene (2.1 g, 0.026 mol) in anhydrous dioxane (350 ml) was irradiated for 1.5 h. The crude residue showed g.c. peaks corresponding to compounds (6) (R_t, 4.5 min; 50%), (7) (5.3 min; 48%), (8) (4.8 min; 5%), and (9) (5.0 min, 2%). Flash chromatography, using ether–light petroleum (1:2) as the eluant, of the crude product gave four fractions. The first fraction was *endo,cis*-amide (6) (1.3 g, 22%) which was recrystallized from CH_2Cl_2–cyclohexane as white crystals; m.p. 160—162 °C. The second fraction (0.32 g) consisted of (6) and (8) with a g.c. peak ratio of 1:1. The ^{1}H n.m.r. spectrum showed, in addition to signals due to (6), signals at δ 1.38 (md, *J* 8 Hz, 2 H), 2.20 (md, *J* 8 Hz, 2 H), 3.2 (m, 2 H), and 6.28 (m, 2 H) ascribed to (8). The third fraction (0.73 g) was a mixture of all four compounds and showed ^{1}H n.m.r. signals at δ 1.45 (md, *J* 10 Hz, 2 H), 1.67 (md, *J* 10 Hz, 2 H), 3.37 (m, 2 H), and 6.48 (m, 2 H) attributed to (9). The fourth fraction (1.4 g. 24%) was recrystallized from CH_2Cl_2–cyclohexane to give white crystals of *exo,cis*-imide (7); m.p. 173—179 °C.

Photoaddition of the Maleimide (1) *to Cyclohexene.*—A solution of (1) (0.93 g, 5.6 mmol) and cyclohexene (1.62 g, 19.7 mmol) in anhydrous dioxane (150 ml) was irradiated for 4 h. The photolysate showed three g.c. peaks corresponding to the *trans*-imide (5) (R_t 5.77 min, 49%), *endo,cis*-imide (3) (6.13 min, 14%), and *exo,cis*-imide (4) (7.84 min, 32%) in addition to other minor peaks. The crude product was taken up in hot methanol; the filtrate showed a new g.c. peak for *trans*-imide ester (12) in addition to those of (3) and (4) and the much decreased (5). Flash chromatography (ethyl acetate–light petroleum) of the crude product gave four fractions. The first (110 mg, 8%) and third (200 mg, 14%) fractions were recrystallized from CH_2Cl_2–cyclohexane to give *endo,cis*-imide (3) and *exo,cis*-imide (4). The compounds were identified by mixed m.p. and the i.r. and n.m.r. spectra.

The second fraction (340 mg, 24%) was recrystallized from CH_2Cl_2–cyclohexane to give white crystals of the *trans*-imide (5); m.p. 189—192 °C. The last fraction (90 mg) was recrystallized from chloroform to give white crystals of the *trans*-amide ester (12); m.p. 161—167 °C. A methanol solution of (5) was refluxed with a small amount of charcoal; the solution gave (12) (56%) by g.c. analysis.

Hydrogenation of Compounds (6) *and* (7).—A methanol solution of (6) (96 mg) containing 5% palladium–charcoal (10 mg) was stirred under hydrogen (1 atm) at room temperature for 3 h. The solution was filtered and evaporated to give a solid (89 mg) which was recrystallized from CH_2Cl_2–cyclohexane to give white crystals of (3); m.p. 169—171 °C.

Similar hydrogenation of (7) (86 mg) under similar conditions gave (4) (73 mg); m.p. 176—181 °C.

Photoaddition of Dichloromaleic Anhydride (2) *to Cyclohexa-1,3-diene.*—A solution of dichloromaleic anhydride (3 g, 18 mmol) and cyclohexa-1,3-diene in anhydrous dioxane (350 ml) was irradiated for 17 h. The crude product showed two major g.c. peaks at R_t 5.2 and 5.8 min in the ratio of 1.5:1 in addition to four minor peaks (<5%). This was separated by preparative g.c. on SE-30 at 200 °C to give (10) (R_t 16 min) and a fraction containing (11) (20 min). (10) was recrystallized fom CCl_4 as white crystals; m.p. 106—109 °C (lit.,[15] 108 °C). The other fraction was recrystallized from CCl_4 to give a white solid containing (11) (70%), m.p. 141—152 °C, (10) (15%), and an unknown compound. In ref. 15, this white solid was assigned a different structure [*i.e.*, (21)].

Conversion of the Anhydrides (10) *and* (11) *into the Imides* (6) *and* (7).—Ammonia was bubbled through a solution containing the anhydride (10) (100 mg) in dioxane for 10 min. The

precipitate was collected and refluxed in acetic anhydride (3 ml) for 3 h. Acetic acid was evaporated under reduced pressure to give a crude product which showed g.c. peaks corresponding to the anhydride (10) (70%) and the imide (6) (15%) by peak matching with authentic samples, in addition to an unknown compound. The crude product was chromatographed twice to give the imide (6); m.p. and mixed m.p. with the authentic sample, 158—160 °C: the i.r. and n.m.r. spectra were superimposable with those of the authentic sample.

The semi-pure fraction of (11) was treated in a similar manner as above to afford a crude product which showed g.c. peaks of the imide (7) (R_t 4.7 min; 34%) and the anhydride (11) (R_t 2.4 min; 50%) in addition to two minor peaks. The crude product was separated by preparative t.l.c. to afford the imide (7); the i.r. and n.m.r. spectra were superimposable with those of the authentic sample.

Photoaddition of the Maleimide (1) *to Cyclopentadiene.*—A solution of (1) (0.52 g, 3 mmol) and cyclopentadiene (0.25 g, 4 mmol) in anhydrous dioxane (300 ml) was irradiated for 1/2 h. The crude product showed three g.c. peaks at R_t 8.7 (47%), 9.1 (10%), and 9.7 min (43%) corresponding to (15), (17), and (16). The product was chromatographed on a silica-gel column (MeOH–CH_2Cl_2) to give the first fraction which was recrystallized from methanol–water to afford *endo,cis*-imide (15) (42 mg); m.p. 195—198 °C. The second fraction was rechromatographed to afford (15) (95 mg) and *exo,cis*-imide (16) (189 mg) which was recrystallized from methanol–water as white crystals; m.p. 202—207 °C.

A large-scale photolysis and flash chromatography of the crude product afforded, in addition to compounds (15) and (16), a fraction containing (17) and a small amount of (16).

Thermal Addition of Dichloromaleimide (1) *to Cyclopentadiene.*—A solution of (1) (18 mg) and cyclopentadiene (15 mg) in dimethoxyethane was stirred overnight at room temperature. The crude product was recrystallized from methanol–water to give (20) (30 mg) as white needles; m.p. 196—213 °C (decomposition).

Hydrogenation of the Imides (15) *and* (16).—The imide (15) (110 mg) was hydrogenated as above in methanol to afford a crude product (90 mg) which was recrystallized from CH_2Cl_2–cyclohexane to afford *endo,cis*-imide (13); m.p. 154—155 °C.

Similarly, the imide (16) (102 mg) was hydrogenated and recrystallized to give the *exo,cis*-imide (14); m.p. 209—213 °C.

Photoaddition of Dichloromaleimide (1) *to Cyclopentene.*—A dioxane solution containing (1) (3 g, 18 mmol) and cyclopentene (3.1 g, 45 mmol) was irradiated for 4 h. The photolysate showed two g.c. peaks at R_t 4.9 (43%) and 6.47 min (57%) corresponding to products (13) and (14). The crude product was flash chromatographed (EtOAc–light petroleum, 1:5) to give a fraction (1.6 g. 38%) which was recrystallized from CH_2Cl_2–cyclohexane to afford the *endo,cis*-imide (13); m.p. 156—158 °C. The second fraction (2.1 g, 49%) was recrystallized from CH_2Cl_2–cyclohexane to afford the *exo,cis*-imide (14); m.p. 209—212 °C. These samples showed identical i.r. and n.m.r. spectra with those obtained from the above hydrogenation.

Photoaddition of Dichloromaleic Anhydride (2) *to Cyclopentadiene.*—A solution of (2) (3.5 g, 20 mmol), cyclopentadiene (4 g, 60 mmol), and benzophenone (0.49 g, 2.5 mmol) in dioxane (350 ml) was irradiated for 10 h. The photolysate showed two major peaks at R_t 1.88 (45%) and 2.15 min (42%) in addition to a peak at 2.82 min (10%). The crude product was flash chromatographed (ethyl acetate–light petroleum) to afford two fractions. The first one (0.69 g) was recrystallized from carbon tetrachloride to give *endo,cis*-anhydride (18) as white crystals:

m.p. 88—91 °C (lit.,[15] m.p. 93 °C). The second fraction was recrystallized from carbon tetrachloride to afford the *exo,cis*-anhydride (19) mixed with (18) (*ca.* 34%); the ^1H n.m.r. spectrum showed signals at 2.8 (qdd, J 2, 8, 18.5 Hz), 3.05 (md, J 18 Hz), 3.43 (t, J 7.5 Hz), 3.93 (m), 5.77 (m), and 6.13 (m) (each 1 H).

The recovery of the products from the column chromatography was low owing to the hydrolysis of the anhydrides to dicarboxylic acids[15] which was not investigated.

Conversion of the Anhydrides (18) *and* (19) *into the Imides* (15) *and* (16).—The anhydride (18) (20 mg) was treated with ammonia in dry dioxane to give a precipitate which was refluxed in acetic anhydride for 3 h to give a crude product. G.c. showed (15) to be the major component (peak matching) and the presence of other minor peaks. Preparative t.l.c. of the crude product on silica gel with EtOAc–light petroleum (1:2) as the eluant gave (15) (7 mg) which had m.p., and i.r. and n.m.r. spectra identical with those of the authentic sample.

Similarly, a mixture of (18) and (19) (3:7 ratio; 20 mg) was treated as above to give a mixture which showed g.c. peaks corresponding to (15) and (16) (by peak matching). Preparative t.l.c. (silica gel; EtOAc–light petroleum, 1:2) gave pure samples of both products (15) and (16), identical by comparsion of their mixed m.p., and n.m.r. and i.r. spectra with authentic samples.

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