# Acyl Analogues of the Ene Reaction

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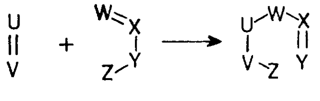
*Summary* The unsaturated lactones, 3-morpholino-1*H*-2-benzopyran-1-one (**6**), 2,3-dihydro-5-morpholinofuran-2-one (**19a**), and its 3-(diphenylmethylene) - derivative (**19b**) add to numerous compounds containing electron-deficient multiple bonds to give products arising from ene reactions in which acyl groups are transferred.

The ene reaction (Scheme) is the 'indirect substituting addition' of a component with a multiple bond, the 'enophile' (**1**), to an olefin, the 'ene' (**2**), possessing an allylic hydrogen atom (Z = H), which is transferred during the process.[1] The reaction and its reverse are very versatile,[2] comprising not only all-carbon systems but also components with diverse hetero-atoms: the enophile may be an aldehyde,



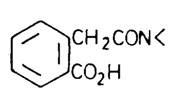
(1) (2) (3)

Scheme

ketone, keten, thioketone, carbon dioxide, oxygen, sulphur dioxide,[3] sulphur trioxide, selenium dioxide, or an azo compound, and the ene a vinyl alcohol, ketone, carboxylic acid, thiocarboxylic acid, or an aldehyde hydrazone.

We have found that certain enol esters (**2**; W = X = C, Y = O, Z = RCO) add to unsaturated electrophiles in a manner that constitutes an ene reaction, in which an acyl group is transferred.

3-Morpholino-1*H*-2-benzopyran-1-one (**6**),† obtained by the action of acetic anhydride on the substituted homophthalamic acid (**4**) or, better, by deprotonation of the derived isoimidium salt (**5**),[4] added to *p*-nitrobenzaldehyde to yield the dihydrobenzopyranone (**7**; R = *p*-$NO_2 \cdot C_6H_4$) (100%) as a 1:1 mixture of *cis*- ($J_{AB}$ 3 Hz) and *trans*- ($J_{AB}$ 11 Hz) isomers. The configuration of the former was confirmed and its conformation determined by *X*-ray analysis, which showed that the *p*-nitrophenyl group is equatorial and the morpholinecarbonyl substituent is in the axial position. Analogous geometrically isomeric adducts were formed in yields of 34–99% from the reactions of the morpholinobenzopyranone with benzaldehyde, *o*- and *m*-nitrobenzaldehyde, *p*-chlorobenzaldehyde, anisaldehyde, *m*- and *p*-hydroxybenzaldehyde, 2-furaldehyde, and thiophen-2-aldehyde. Phenylacetaldehyde yielded a mixture (28%) of *cis*- and *trans*- (**7**; R = $PhCH_2$) and cyclohexanone and diphenylketen gave the lactones (**8**; $R_2 = C_5H_{10}$) (18%) and (**8**; $R_2$ = $Ph_2C=$) (86%), respectively. Examples of addition to carbon–nitrogen double bonds include the formation of *cis*- and *trans*- (**9**) (77%) from benzylideneaniline and that of the isoquinolinedione (**10**) (31%) from phenyl isocyanate. The novel heterocycles (**11**) (95%) and (**12**) (37%) were obtained by reaction with nitrosobenzene and carbon disulphide, respectively, and 4-phenyl-1,2,4-triazoline-3,5-dione[5] yielded the adduct (**13**) (89%). Treatment of compound (**6**) with the appropriate arenediazonium fluoroborate in the presence of triethylamine gave the phthalazinones (**14**; R = Ph) (36%) and (**14**; R = *p*-$NO_2 \cdot C_6H_4$) (53%), which are thought to be formed by ene-addition, followed by deprotonation.



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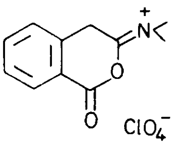

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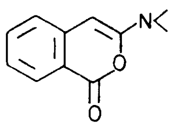

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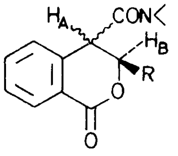

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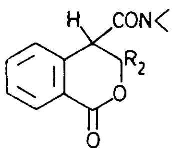

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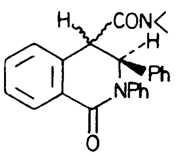

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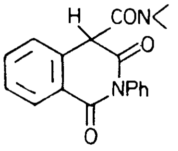

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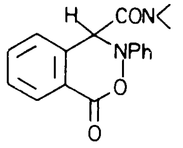

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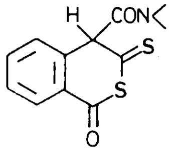

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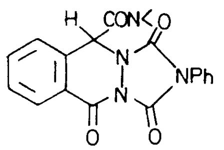

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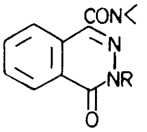

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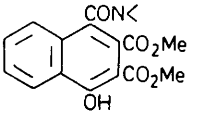
N < = morpholino

Reaction of the benzopyranone with the carbon enophiles, dimethyl acetylenedicarboxylate, *N*-phenylmaleimide, and (*E*)-β-nitrostyrene afforded, respectively, the naphthol (**15**) (35%), *cis*- and *trans*- (**16**) (91%), and the ketone (**17**) (13%) as a 4:1 mixture of geometrical isomers. The formation of only two products in this case is significant; n.m.r. spectroscopy indicates that in the major isomer the hydrogen atoms labelled $H_A$ and $H_B$ are situated *cis* to each other ($J_{AB}$ 6 Hz), whereas in the other they have the *trans*-configuration ($J_{AB}$ 12 Hz); in both $J_{BC}$ = 13 Hz, so that the *trans*-geometry of the enophile is maintained in the products, a result consistent with a concerted mechanism for the reaction. Application of the Frontier Molecular Orbital theory[6] shows that concerted suprafacial–suprafacial addition is allowed and that the correct orientation is predicted.



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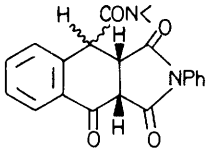

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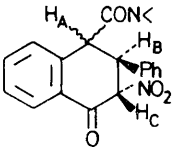

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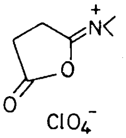

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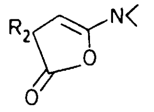

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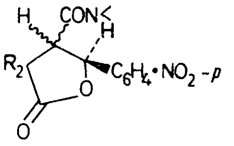

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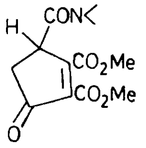
a: R = H
b: $R_2$= $Ph_2C=$



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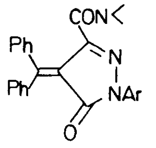

(22)

N < = morpholino

The butenolide (**19a**), generated from the succinisoimidium salt (**18**) in the presence of *p*-nitrobenzaldehyde, gave 75% of a mixture of geometrically isomeric adducts (**20a**); analogous products were obtained from *o*-nitrobenzaldehyde

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† Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

(58%) and *p*-chlorobenzaldehyde (52%), while dimethyl acetylenedicarboxylate yielded the cyclopentenone (**21**) (0·5%). The isolable diphenylmethylene-derivative (**19b**) afforded a mixture (72%) of *cis*- and *trans*-adducts (**20b**) with *p*-nitrobenzaldehyde; reaction with benzenediazonium, *p*-nitrobenzenediazonium, and *p*-chlorobenzenediazonium fluoroborates gave the (diphenylmethylene)pyrazolinones (**22**) in 83—92% yields.

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[1] K. Alder, F. Pascher, and A. Schmitz, *Ber.*, 1943, **76**, 27.

[2] For an excellent review, see H. M. R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 556.

[3] P. E. Peterson, R. Brockington, and M. Dunham, *J. Amer. Chem. Soc.*, 1975, **97**, 3517.

[4] G. V. Boyd, *Chem. Comm.*, 1969, 1147.

[5] It has been reported (K. B. Wagener, S. R. Turner, and G. B. Butler, *J. Org. Chem.*, 1972, **37**, 1454) that this compound adds vinyl esters to form 1-acyl-2-formylmethyl-4-phenyl-1,2,4-triazolidine-3,5-diones, together with variable amounts of 1,3,5-triazabicyclo[3.2.0]heptane-2,4-diones and polymers.

[6] For a recent summary and leading references, see K.-L. Mok and M. J. Nye, *J.C.S. Perkin I*, 1975, 1810.