# Acyl Rearrangements in Acylbenzoquinone Cycloadducts

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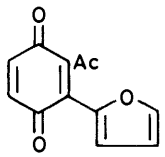
A number of cycloadducts between 2-acetyl- and 2-benzoyl-1,4-benzoquinones and dienes have been prepared and the direction of the subsequent acyl group migration has been shown to depend on the diene substituents. The initial adducts from 2-acetylnaphthoquinone and dienes either epimerised or yielded 9,10-anthraquinone on attempted rearrangement.

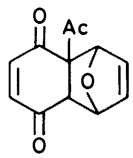
In 1963, in studies connected with site selectivity, Ansell and co-workers prepared the buta-1,3-diene and 2,3-dimethylbuta-1,3-diene adducts of 2-acetylbenzoquinone.[1] Around the same time Eugster and Bosshard described[2] the abnormal Diels–Alder reaction between certain furans and acylquinones in which the final product, *e.g.* (**1**), was considered to arise either by a direct nucleophilic addition of furan to the quinone and aerial oxidation, or by a dienone–phenol type rearrangement of the initially formed, normal (*i.e.* Diels–Alder) adduct (**1**). Recently, Bruce and his colleagues have also reported on the formation of such cycloadducts[3] but, prior to our work,[4] little had been published on the chemical behaviour of these cycloadducts, in particular on their ability, under certain conditions, to undergo acyl group migrations. Herein we detail our results in this area.

2-Acetyl-1,4-benzoquinone (**3**) was conveniently prepared, as required, by the oxidation of the corresponding quinol with silver oxide,[5] or by the preparation *in situ*, by this method, in the presence of the diene reactant. The corresponding 2-benzoyl-1,4-benzoquinone (**4**)[6] was similarly prepared.

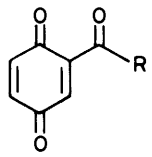
The acylquinones (**3**) and (**4**) were treated with a range of buta-1,3-dienes and the results are summarised in Table 1. Piperylene (**9**) and cyclopentadiene (**10**) reacted very readily, whilst the dienes (**7**), (**11**), and (**12**) required much longer periods, even when using an excess of the diene. The reaction of 1,4-diacetoxybuta-1,3-diene (**12**) with 2-benzoylbenzoquinone (**4**) did not produce an identifiable adduct under neutral or Lewis acid catalysed conditions. The site selectivity of all the adducts from 2-acetyl-1,4-benzoquinone (**3**) was shown to favour addition across the 2,3-quinone bond, the resulting adducts clearly showing, in their $^1$H n.m.r. spectra, an AB quartet for the remaining enedione protons. Similar characteristic signals were observed for the adducts of 2-benzoyl-1,4-benzoquinone (**4**), except for the butadiene adduct (**28**). In this adduct only three olefinic protons were observed in its $^1$H n.m.r. spectrum, explained by addition across the 5,6-double bond of the benzoquinone rather than across the benzoyl-substituted 2,3-double bond. This observation is in contrast to the result recently reported[7] when the reaction is carried out in the presence of an acid catalyst; under these conditions the angularly substituted adduct (**29**) is preferred. Evidently a delicate balance exists between steric and electronic factors for the combination between the benzoylquinone (**4**) and butadiene, steric effects winning out under neutral conditions when the bulky 2-benzoyl group is present, compared to the result obtained with the 2-acetyl substituent. Acid catalysis leads to formation of the 2,3-adduct (**29**) because it enhances the electron-deficiency of the 2,3-bond more than that of the 5,6-bond and to a sufficient degree to overcome the steric opposition of the benzoyl group. A similar situation has previously been noted by Kishi,[8] in which the oximino-ethylbenzoquinone (**30**) reacts with butadiene to yield either the 5,6- or the 2,3-cycloadduct depending on whether the reaction is carried out under neutral or acid-catalysed conditions respectively.

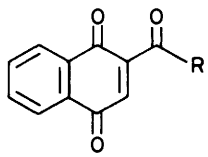



(**1**)

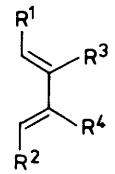



(**2**)




(**3**) R = Me (**5**)
(**4**) R = Ph (**6**)

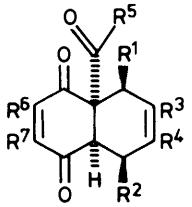



(**7**) $R^1 = R^2 = R^3 = R^4 = H$
(**8**) $R^1 = R^2 = H, R^3 = R^4 = Me$
(**9**) $R^1 = Me, R^2 = R^3 = R^4 = H$
(**10**) $R^1,R^2 = CH_2, R^3 = R^4 = H$
(**11**) $R^1 = OAc, R^2 = R^3 = R^4 = H$
(**12**) $R^1 = R^2 = OAc, R^3 = R^4 = H$
(**13**) $R^1 = OMe, R^2 = R^3 = H, R^4 = OSiMe_3$

Ansell and his colleagues[1] recognised three factors that help to determine which ethene linkage reacts: the electronic nature of the quinone substituents, the steric properties of such substituents, and the interaction of substituents in the two reacting components. Substituents at the 2,3-positions of the diene component tend to play a steric role in securing addition across the 2,3-double bond of the acylquinones. Since an *endo*-transition state is preferred, approaches of, for example, 2,3-dimethylbutadiene to the 5,6-bond of the quinone are deterred because of steric interaction between the acyl substituent on the quinone and the methyl groups on the diene; this steric compression is relieved on addition across the 2,3-double bond leading, in this case, to the observed adduct (**15**).

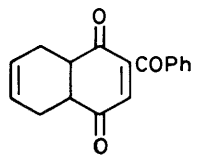
The reaction of 1-acetoxybuta-1,3-diene (**11**) with the 2-acetylbenzoquinone (**3**) afforded only one isolated adduct (**18**), the stereochemistry of which followed from $^1$H n.m.r. studies. Since the regioselectivity of addition was in agreement with

**Table 1.** Adducts from the reaction of compounds (3) and (4) with buta-1,3-dienes



| Adduct | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ | $R^7$ | Yield (%) | M.p. (° C) | Method[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| (14) | H | H | H | H | Me | H | H | 74 | 80—81[b] | A |
| (15) | H | H | Me | Me | Me | H | H | 78 | 79—81[c] | A |
| (16) | $-CH_2-$ | | H | H | Me | H | H | 81 | 70—71 | A |
| (17) | Me | H | H | H | Me | H | H | 79 | 100—101 | A |
| (18) | OAc | H | H | H | Me | H | H | 43 | 89—92 | A |
| (19) | OAc | OAc | H | H | Me | H | H | 40 | 168—169 | A |
| (20) | H | H | Me | Me | Ph | H | H | 48 | 182—184 | A |
| (21) | OAc | H | H | H | Ph | H | H | 65 | 145—147 | A |
| (22) | OAc | OAc | H | H | Ph | H | H | 0 | | A |
| (23) | OAc | H | H | H | Me | $-CH=CH-CH=CH-$ | | 74 | 108—110 | B |
| (24) | OAc | OAc | H | H | Me | $-CH=CH-CH=CH-$ | | 23 | 163 | B |
| (25) | OMe | H | H | $OSiMe_3$ | Me | $-CH=CH-CH=CH-$ | | 43 | 105—106 | B |
| (26) | OAc | H | H | H | Ph | $-CH_2-CH=CH-CH_2-$ | | 70 | 191 | B |
| (27) | Me | H | H | H | Ph | H | H | 61 | 112—114 | A |

[a] Method A: the quinone and diene reacted at or below room temperature in benzene. Method B: the hydroquinone was oxidised with silver(II) oxide in the presence of the diene in benzene at room temperature with the exclusion of light. [b] Lit.,[1] m.p. 85—87 °C. [c] Lit.,[1] m.p. 73—81 °C.



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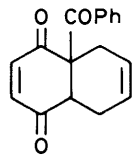

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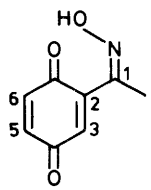

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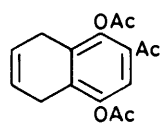
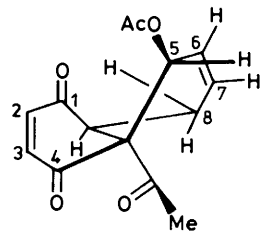


(31)

previous observations on the reactions of electron-deficient dienophiles with electron-rich dienes,[9] the preferred conformation of the adduct can be assigned as that shown in Figure 1. The fact that 8a-H couples with only one of the protons at position 8 ($J$ 9 Hz) indicates a pseudoaxial orientation of the former. Both 8a-H and the proton at position 8, to which it is coupled, are highly deshielded, their signals occurring at δ 3.95 and 3.1 respectively, indicating their closeness to the 4a-acetyl group. The proton at position 5, adjacent to the acetoxy group, occurs as a doublet ($J$ 6 Hz) at δ 6.0, reflecting a low dihedral angle between it and the olefinic hydrogen at position 6 to which it is coupled. These coupling constants and chemical shifts are best explained in terms of a model in which both rings adopt half-chair conformations, the acetoxy group being placed in a pseudoaxial position in which the methyl group (δ 1.84) is slightly shielded by the enedione group; the acetyl group sits with the methyl group pointing away from the bicyclic ring system, so that it is deshielded (δ 2.44) by the ketone formation at position 4.



(18)

Figure 1.

A similar stereoselectivity was observed for the adduct (19) between 1,4-diacetoxybuta-1,3-diene and 2-acetylbenzoquinone. The average conformation of this adduct is different, however, in that both acetoxy groups are held in pseudo-equatorial positions; no coupling was observed between the protons at positions 5 and 8 and the adjacent olefinic protons, indicating dihedral angles of approximately 90 °. Both rings appear to take up half-boat conformations (Figure 2).

Attempts to prepare 2-acetyl-1,4-naphthoquinone by literature methods[10] failed. This problem was resolved by using the *in situ* method for the preparation of sensitive quinones

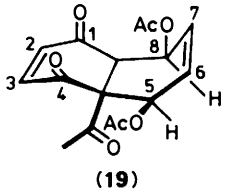


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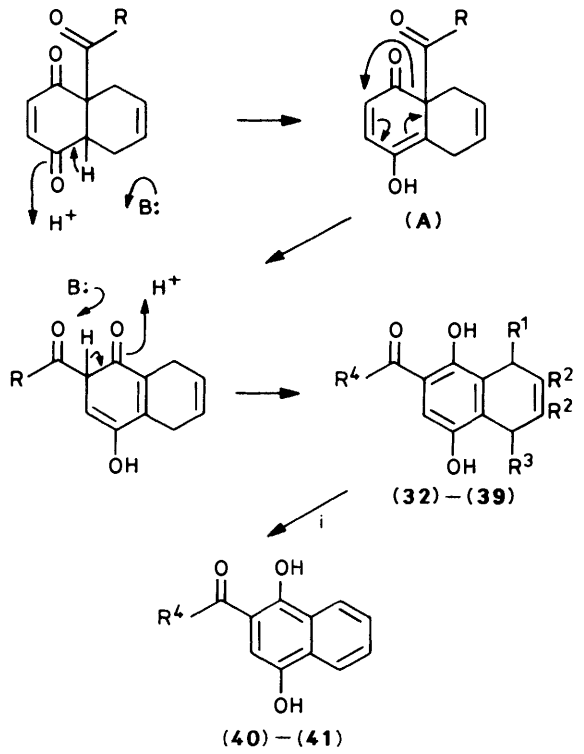
Figure 2.




(32) $R^4$ = Me, $R^1$ = $R^2$ = $R^3$ = H
(33) $R^1$ = $R^3$ = H, $R^2$ = $R^4$ = Me
(34) $R^1$, $R^3$ = $CH_2$, $R^2$ = H, $R^4$ = Me
(35) $R^1$ = $R^4$ = Me, $R^2$ = $R^3$ = H
(36) $R^1$ = OAc, $R^2$ = $R^3$ = H, $R^4$ = Me
(37) $R^1$ = $R^3$ = H, $R^2$ = Me, $R^4$ = Ph
(38) $R^1$ = OAc, $R^2$ = $R^3$ = H, $R^4$ = Ph
(39) $R^1$ = Me, $R^2$ = $R^3$ = H, $R^4$ = Ph
(40) $R^4$ = Me
(41) $R^4$ = Ph

**Scheme 1.** i, $R^1$ = OAc, $R^2$ = $R^3$ = H

described by Kraus.[11] In this method the quinol is oxidised by silver(I) oxide in the presence of the reacting diene with the exclusion of air and light and without isolation of the intermediate quinone. In this manner the adducts (**23**)—(**25**) of 2-acetyl-1,4-naphthoquinone with 1-acetoxy-, 1,4-diacetoxy- and 1-methoxy-3-trimethylsilyloxy-buta-1,3-diene, respectively were prepared. In a similar manner the adduct (**26**) was obtained from 2-benzoyl-5,8-dihydro-1,4-naphthoquinone (**28**) and 1-acetoxybuta-1,3-diene (**11**). The conformations of these naphthoquinone adducts may also be deduced from their $^1H$ n.m.r. spectra. For example, the introduction of the extra benzene nucleus in the adduct (**23**), as compared to the benzoquinone adduct (**18**) described above, shifts the acetoxy methyl group upfield by 0.7 p.p.m. owing to the extra shielding of this pseudoaxial substituent by the aromatic ring; in the diacetoxy adduct (**24**), in which the acetoxy substituents adopt a pseudoequatorial conformation, such shielding is not observed.

A brief examination of the effect of Lewis acids on the reaction of 2-acetyl-1,4-benzoquinone (**3**) with 1-acetoxybuta-diene (**11**) was made. The regioselectivity of these reactions was the same as that observed for the uncatalysed reaction, but both the reactant diene and the resultant adduct (**18**) appeared to be unstable in the presence of the Lewis acids, and the product yields were always lowered.

The properties of the cycloadducts, listed in Table 1, were examined with a view to utilising a possible 1,5-sigmatropic

**Table 2.** Rearrangement products from the cycloadducts of 2-acetyl- and 2-benzoyl-1,4-benzoquinone[a]

| Adduct | Product | Yield (%)[b] | M.p. (° C) |
|---|---|---|---|
| (**14**) | (**32**) | 94 | 173 (subl.) |
| (**15**) | (**33**) | 86 | 175 (subl.) |
| (**16**) | *c* | 29 | 202—203[c] |
| (**17**) | (**35**) | 68 | 153 |
| (**18**) | (**40**) | 52 | 205—206[d] |
| (**19**) | (**43**) | 49 | 110—112 |
| (**20**) | (**37**) | 48 | 182—184 |
| (**21**) | (**41**) | 39 | 124 |
| (**27**) | (**39**) | 100 | 152—153 |

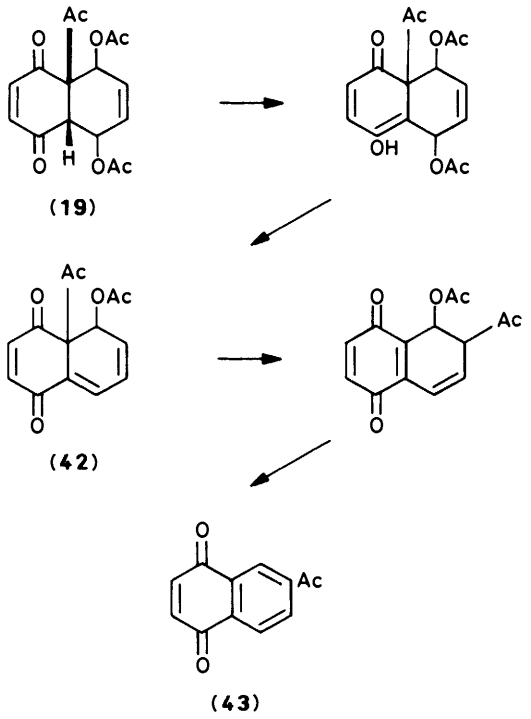
[a] Rearrangements were carried out in refluxing xylene containing pyridine (see Experimental section); reactions were carried out for 1—3 h. [b] Isolated yields. [c] Product 2,5-dihydroxyacetophenone, lit.,[19] m.p. 202—203 °C. [d] Lit.,[20] m.p. 206 °C; reaction carried out at 120 °C.

shift of the angular acyl substituents. The first reaction of this type was observed in 1967 by Cort and Rodriguez,[12] who observed that treatment of 2-acetyl-1,4-benzoquinone (**3**), with buta-1,3-diene (**7**) followed by boiling the product with acetic anhydride, afforded 2-acetyl-1,4-diacetoxy-5,8-dihydronaphthalene (**31**). This result was explained at the time by a retro-diene reaction, under thermodynamic control, leading to re-addition of the diene component across the 5,6-double bond of the resulting quinone, and enol acetylation. A more probable reaction path involves the initial enolisation of the adduct (Scheme 1), followed by a 1,5-acetyl shift in the enol (**A**) or its acetate. The migrating ability of acyl groups in similar environments to that existing in structure (**A**) has been reported.[13] 1,5-Acetyl shifts have been observed in competition with Claisen-type allyl migrations[14] and the relative rates of acyl group migration in 1-substituted cyclohexa-2,4-dienes[15] and substituted indenes[16] have been measured. The acyl-migrating properties of the adducts listed in Table 1 have therefore been studied and it has been shown that the direction of migration depends both on the conditions used to effect the transformations and the nature of the diene substituents. Subsequent to our preliminary note,[4] independent work has been published by Bruce *et al.*[17,18]

Except for the adduct (**16**), all the cycloadducts listed in Table 1 were stable, under neutral conditions, when heated in xylene solutions up to 140 °C for several days. For the adduct (**16**) a retro-Alder reaction occurs at about 120 °C leading to loss of starting material. On addition of a few drops of pyridine to solutions, in xylene heated to reflux, of representative adducts a rapid rearrangement occurred to produce new products. Thus the cycloadduct (**14**) reacted within 3 h at 140 °C to produce 2-acetyl-5,8-dihydro-1,4-dihydroxynaphthalene (**32**). The intramolecularity of the reaction was established by demonstrating the independence of the rate of reaction with concentration. Presumably the base catalyses the enolisation of the carbonyl group bearing an α-hydrogen atom in a pre-equilibration step, the rate-determining step being the 1,5-acyl transfer process.

Two reaction types could be recognised in these acyl migrations. The adducts derived from simple dienes, bearing only hydrogen or alkyl substituents, rearranged by a path involving prior enolisation of the carbonyl group, followed by the 1,5-acyl migration and a second enolisation of the remaining quinone-carbonyl group to produce the quinol (Scheme 1). The yields of the isolated rearrangement products were generally good (Table 2). For the adducts (**18**) and (**21**), derived from 1-acetoxybuta-1,3-diene, initial rearrangement was followed by elimination of acetic acid to afford the corresponding naphthoquinols (**40**) and (**41**) (Scheme 1).

A different reaction path occurred with the 1,4-diacetoxy-

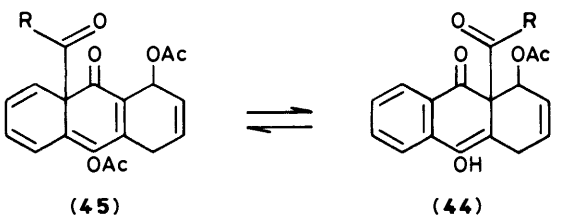



Scheme 2.

buta-1,3-diene adduct (**19**). For this, extrusion of one molecule of acetic acid preceded acetyl group migration, to produce the alternative cyclohexadiene unit (**42**) (Scheme 2), allowing transposition of the acetyl group to position 6; final loss of a second molecule of acetic acid produced the 6-acetyl-1,4-naphthoquinone (**43**) in 49% yield.

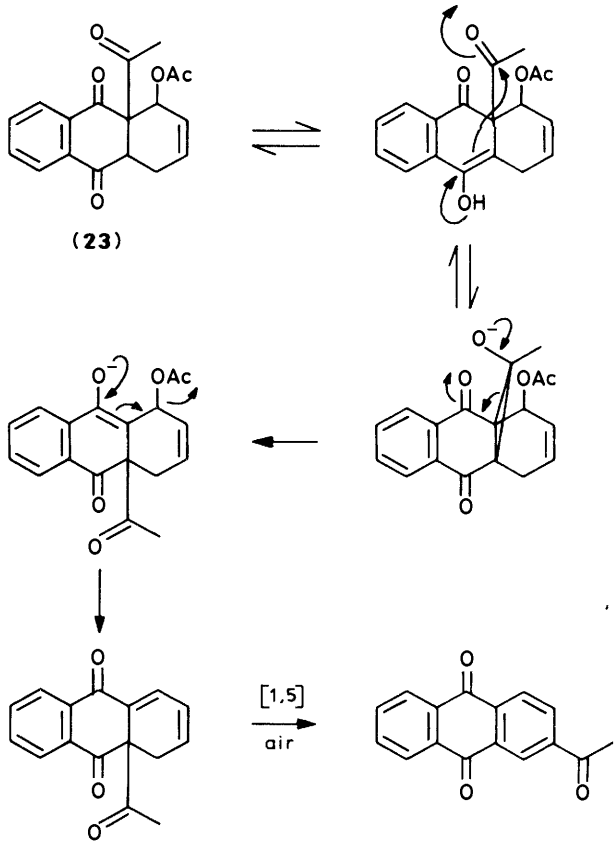
The benzoyl-substituted adducts (**20**)—(**22**) reacted in a similar manner to the corresponding acetyl adducts. The cyclopentadiene adduct (**16**), however, again gave the retro-diene reaction leading to the formation of 2,5-dihydroxy-acetophenone rather than the expected product (**34**).

An examination of the cycloadducts obtained from 2-acetyl-1,4-naphthoquinone, (**23**)—(**25**), was of interest. In these adducts the presence of the benzo ring was expected to preclude acyl transfer across the central cyclohexadienone ring since, in the product (**45**) of such rearrangements, derived from the enol (**44**), the aromatic stabilisation associated with the benzene ring

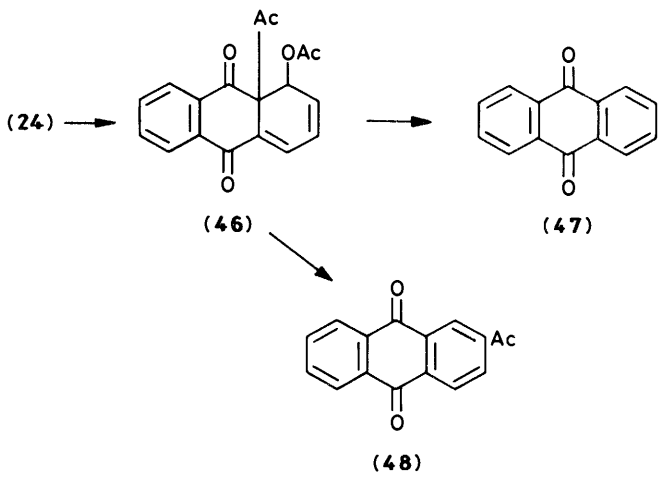



is lost. For the adducts (**23**)—(**25**), the process depicted in Scheme 3 was expected, leading to the corresponding 2-acetylanthraquinone. However, on heating the adduct (**23**) in xylene containing pyridine, only 9,10-anthraquinone (**47**) was obtained (97%).

On changing to 1 : 1 methanol–pyridine as solvent, conditions said to favour the 1,2-acyl shift,[18] again only the anthraquinone was isolated. Use of the non-nucleophilic base, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in xylene produced a quantitative yield of anthraquinone within 5 min at room temperature.

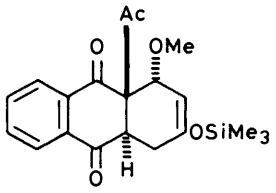



Scheme 3.




Scheme 4.

Presumably, for the system (**23**), elimination of acetic acid is favoured as a fast, first step. The acetate ion thus produced can then attack the angular acetyl function to liberate acetic anhydride and the quinol, which can be rapidly air oxidised to produce quinone. For the adduct (**24**) a preliminary 1,2-acetyl shift (*cf.* Scheme 3) is unnecessary and elimination of one molecule of acetic acid could generate the cyclohexadiene system (**46**) needed to initiate a 1,5-acetyl migration. In the event, using rigorously dry conditions, a very low yield (3%) of 2-acetyl-9,10-anthraquinone (**48**) was isolated (Scheme 4), together with the unsubstituted anthraquinone (**47**) (75%), the




(49)

latter probably forming by nucleophilic deacetylation of the intermediate; no further work on the latter cycloadduct was carried out. Heating the cycloadduct (**25**) with pyridine in xylene did not lead to acetyl migration but, instead, epimerisation to form the isomer (**49**). Further heating of this product slowly produced a complex mixture of products.

A brief study of the effect of acid-catalysed rearrangements failed to produce improved yields of products.

In conclusion, we have described a new type of 1,5-acyl group migration in cycloadducts from 2-acylbenzoquinones; for the corresponding naphthaquinone adducts, bearing acetoxy groups, nucleophilic deacylation effectively competes with acyl migration.

## Experimental

All m.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257G spectrometer using solutions of samples in chloroform, unless otherwise stated. $^1$H N.m.r. spectra were obtained on a Perkin-Elmer R32 instrument for solutions in deuteriochloroform using tetramethylsilane as internal standard. Peaks are reported using the following abbreviations: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Accurate mass measurements were recorded using an AEI/Kratos 905 high resolution spectrometer. In general, solvents were redistilled before use. Diethyl ether was dried over sodium wire then distilled from lithium aluminium hydride. Benzene, xylene, and tetrahydrofuran were dried by distillation from sodium; pyridine was dried by refluxing over sodium before distillation. Dried solvents were stored over Linde 4A molecular sieves. Extracts were dried over either anhydrous sodium sulphate or dry magnesium sulphate and evaporated under reduced pressure using a Büchi rotary evaporator. Reactions were routinely carried out under nitrogen.

Thin layer chromatography (t.l.c.) was carried out on Merck precoated plates of 0.1 mm Kieselgel $60F_{254}$ silica. Preparative layer chromatography (p.l.c.) was carried out on plates, 20 × 20 × 0.1 cm, coated with Kieselgel $60F_{254}$ silica. Column chromatography was carried out using columns packed with Merck G60 silica gel, eluting with solvent under a slightly positive pressure. The eluant was monitored by t.l.c., the silica gel to compound loading ratio was usually in the range 50—100:1.

2-Acetyl-1,4-benzoquinone was prepared according to the method of Kloetzel *et al.*,[5] m.p. 64—66 °C (lit.,[5] 65.5—66.5 °C) and 2-benzoyl-1,4-benzoquinone by a similar method, m.p. 85—86 °C (lit.,[6] 85 °C). Buta-1,3-diene, penta-1,3-diene, 2,3-dimethylbutadiene, and cyclopentadiene were freshly distilled before use. Light petroleum refers to the fraction of boiling range 40—60 °C.

*General Procedures for the Cycloadditions.*—The 2-acylquinone (2 mmol) in benzene (5—10 ml) was stirred with the diene (2—4 mmol) at room temperature under dry nitrogen for periods of 2 h—1 week, reactions being monitored by t.l.c. until no further change could be detected. The solvent was removed under reduced pressure and the residue triturated with light petroleum before the residue was crystallised from an organic solvent. Reactions involving buta-1,3-diene were carried out in a stainless steel bomb at room temperature overnight. The reaction involving cyclopentadiene was carried out in tetrahydrofuran as solvent. M.p.s and % yields of adducts are quoted in Table 1. The adducts showed the following properties:

4a,5-trans-4a,8a-cis-4a-*acetyl*-4a,5,8,8a-*tetrahydro*-5-*methyl*-1,4-*naphthoquinone* (**17**), $\nu_{max.}$ (Nujol) 1 720, 1 690, 1 670, and 1 610 cm$^{-1}$; δ 0.95 (3 H, d, *J* 8 Hz, 5-Me), 2.4 (3 H, s, 4a-MeCO), 5.66 (2 H, m, 6-, 7-H), 6.66 (1 H, d, *J* 10 Hz, 2-H), and 6.82 (1 H, d, *J* 10 Hz, 3-H) (Found: C, 71.4; H, 6.6. $C_{13}H_{14}O_3$ requires C, 71.5; H, 6.4%).

4a,8a-cis-4a-*Acetyl*-4a,5,8,8a-*tetrahydro*-5,8-*methano*-1,4-*naphthoquinone* (**16**), $\nu_{max.}$ 1 720, 1 705, 1 670, and 1 610 cm$^{-1}$; δ 1.38, 152 (2 H, ABq, *J* 9 Hz, 5.8 $CH_2$), 2.38 (3 H, 3 H, s, 4a-MeCO), 3.5 (1 H, br m, 8a-H), 3.74 (2 H, m, 5-, 8-H), 6.15 (2 H, m, 6-, 7-H), and 6.59 (2 H, s, 2-, 3-H) (Found: C, 72.4; H, 5.6. $C_{13}H_{12}O_3$ requires C, 72.2; H, 5.6%).

4a,5-trans-4a,8a-cis-5-*Acetoxy*-4a-*acetyl*-4a,5,8,8a-*tetrahydro*-1,4-*naphthoquinone* (**18**), $\nu_{max.}$ 3 020, 1 745, 1 710, and 1 685; δ 1.85 (3 H, s, acetate), 2.05 (2 H, dd, *J* 20, 9 Hz, 8-H), 2.42 (3 H, s, MeCO), 3.10 (1 H d, *J* 20 Hz, 8-H), 3.92 (1 H, d, *J* 9 Hz, 8a-H), 5.77—6.0 (3 H, m, 5-H, 6-H, 7-H), 6.66 (1 H, d, *J* 11 Hz, 2-H), and 6.92 (1 H, d, *J* 11 Hz, 3-H) (Found: C, 64.1; H, 5.3. $C_{14}H_{14}O_5$ requires C, 64.1; H, 5.3%).

4a,5-trans-4a,8a-cis-8,8a-trans-5,8-*Diacetoxy*-4a-*acetyl*-4a,5,8,8a-*tetrahydro*-1,4-*naphthoquinone* (**19**), $\nu_{max.}$ 2 800, 1 740, and 1 660 cm$^{-1}$; δ 1.97 (3 H, s, OAc), 2.05 (3 H, s, OAc), 2.34 (3 H, s, 4a-MeCO), 4.2 (1 H, d, *J* 7 Hz, 8a-H), 5.19 (1 H, br d, *J* 7 Hz, 8-H), 5.71 (1 H, br s, 5-H), 5.39 (2 H, br s, 6-, 7-H), and 6.78 (2 H, br s, 2-, 3-H) (Found: C, 65.0; H, 5.0. $C_{16}H_{16}O_7$ requires C, 65.0; H, 5.0%).

4a,8a-cis-2-*Benzoyl*-4a,5,8,8a-*tetrahydro*-1,4-*naphthoquinone* (**28**) (65%); m.p. 125 °C (decomp.), $\nu_{max.}$ 1 685, 1 600, and 1 570 cm$^{-1}$; δ 2.0—2.8 (4 H, m, 5-, 8-$CH_2$), 3.2—3.6 (2 H, m, 4a-, 8a-H), 5.72 (2 H, s, 6-, 7-H), 6.7 (1 H, s, 3-H), and 7.2—8.0 (5 H, m, Ph) (Found: C, 76.5; H, 5.4. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%).

4a,8a-cis-4a-*Benzoyl*-4a,5,8,8a-*tetrahydro*-6,7-*dimethyl*-1,4-*naphthoquinone* (**20**), $\nu_{max.}$ 1 690, 1 665, 1 595, and 690 cm$^{-1}$; δ ($C_6D_6$) 1.32 (3 H, br s, 6-Me), 1.4 (3 H, br s, 7-Me), 1.8—2.3 (3 H, m, 5-H, 8-$CH_2$), 3.1 (1 H, d, *J* 17 Hz, 5-H), 3.5 (1 H, br q, *J* 1, 7 Hz, 8a-H), 5.9 (1 H, d, *J* 10 Hz, 3-H), 6.15 (1 H, dd, *J* 1, 10 Hz, 2-H), 6.9—7.1 (3 H, m, aromatic), and 7.8—8.0 (2 H, m, aromatic) (Found: C, 77.3; H, 6.1. $C_{19}H_{18}O_3$ requires C, 77.5; H, 6.1%).

4a,8a-cis-4a,5-trans-4a-*Benzoyl*-4a,5,8,8a-*tetrahydro*-5-*methyl*-1,4-*naphthoquinone* (**27**), $\nu_{max.}$ (Nujol) 1 690, 1 675, and 1 595 cm$^{-1}$; δ ($C_6D_6$) 0.95 (3 H, d, *J* 7 Hz, 5-Me), 1.75 (1 H, m, 8-H), 2.7 (1 H, m, 8-H), 3.23 (1 H, m, 5-H), 3.83 (1 H, dd, *J* 2.5, 7.5 Hz, 8a-H), 5.4—5.8 (2 H, m, 6-, 7-H), 6.9 (2 H, s, 2-, 3-H), and 7.3—7.8 (5 H, m, Ph) (Found: C, 77.1; H, 5.7. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.7%).

4a,8a-cis-4a,5-trans-5-*Acetoxy*-4a-*benzoyl*-4a,5,8,8a-*tetrahydro*-1,4-*naphthoquinone* (**21**), $\nu_{max.}$ (Nujol) 1 740, 1 675, 1 640, and 1 610 cm$^{-1}$; δ 1.85 (1 H, m, 8-H), 1.93 (3 H, s, 5-OAc), 2.95 (1 H, m, 8-H), 3.9 (1 H, m, 8-H), 5.7—6.1 (3 H, m, 5-, 6-, 7-H), 6.95 (1 H, d, *J* 8 Hz, 2-H), 7.12 (1 H, d, *J* 8 Hz, 3-H), and 7.4—7.8 (5 H, m, Ph) (Found: C, 70.2; H, 5.0. $C_{19}H_{16}O_5$ requires C, 70.3; H, 5.0%).

1,9a-trans-4a,9a-cis-1-*Acetoxy*-9a-*acetyl*-1,4,4a,9a-*tetrahydro*-9,10-*anthraquinone* (**23**).—Naphthalene-1,4-diol (0.5 g, 2.9 mmol) in benzene (20 ml) was treated with anhydrous sodium sulphate (0.5 g) and the mixture stirred rapidly at 10 °C whilst 1-acetoxybuta-1,3-diene (**11**) (0.35 g, 3.1 mmol) and

silver(I) oxide (*ex.* silver nitrate; 3 g) were added. The mixture was stirred in the dark at room temperature and under oxygen-free nitrogen for 16 h, when a further portion of the diene (0.1 g, 1.0 mmol) was added and stirring continued for a further 7 h. The solids were filtered off through Celite, washing with chloroform, and the combined filtrates evaporated under reduced pressure. The red residue was triturated with ethanol to afford a white solid, which was recrystallised from dichloromethane–light petroleum to yield the *title adduct* (**23**) (0.57 g, 74%), m.p. 108—110 °C, $\nu_{max.}$ 1 740, 1 705, 1 680, and 1 595 $cm^{-1}$; δ 1.3 (3 H, s, OAc), 2.10 (1 H, dd, *J* 7, 20 Hz, 4-H), 2.47 (3 H, s, 9a-MeCO), 3.25 (1 H, d, *J* 20 Hz, 4-H), 4.04 (1 H, d, *J* 7 Hz, 4a-H), 5.8—6.1 (3 H, m, s, 2-H), and 7.6—8.2 (4 H, m, aromatic H) (Found: C, 69.1; H, 5.1. $C_{18}H_{16}O_5$ requires C, 69.2; H, 5.1%).

1,9a-trans-4,4a-trans-4a,9a-cis-1,4-*Diacetoxy*-9a-*acetyl*-1,4,4a,9a-*tetrahydro*-9,10-*anthraquinone* (**24**).—This was prepared in a manner similar to that described for compound (**23**), except that the reaction time was extended to 7 days, adding small portions of fresh diene each day (total, 2 equiv.). The *acetyl adduct* (**24**) (23%) showed m.p. 163 °C, $\nu_{max.}$ 1 735, 1 705, and 1 690 $cm^{-1}$; δ 1.68 (3 H, s, OAc), 1.82 (2 H, s, OAc), 2.29 (3 H, s, 9a-MeCO), 4.30 (1 H d, *J* 7 Hz, 4a-H), 5.31 (1 H, d, *J* 7 Hz, 4-H), 5.78 (1 H, br s, 1-H), 5.98 (2 H, br s, 2-, 3-H), and 7.7—8.2 (4 H, m, aromatic *H*) (Found: C, 64.9; H, 5.0. $C_{20}H_{18}O_7$ requires C, 64.9; H, 4.9%).

1,9a-trans-4a,9a-cis-9a-*Acetyl*-1,4,4a,9a-*tetrahydro*-1-*methoxy*-3-*trimethylsilyloxy*-9,10-*anthraquinone*.—In the usual manner 2-acetylnaphthalene-1,4-diol (0.9 g, 5.0 mmol) was treated with 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (**13**)[20] (0.9 g, 5.1 mmol) and the silver(I) oxide from silver nitrate (13 g), in benzene (25 ml) in the dark, under nitrogen for 3 days. Work-up, followed by recrystallisation from ether–light petroleum gave the *title adduct* (43%), m.p. 105—106 °C, $\nu_{max.}$ (Nujol) 1 710, 1 680, 1 650, and 1 595 $cm^{-1}$; δ 0.23 (9 H, s, $Me_3Si$), 2.0—2.4 (1 H, ddd, *J* 2, 9, 18 Hz, 4-H), 2.59 (3 H, s, 9a-MeCO), 3.05 (3 H, s, MeO), 3.3 (1 H, d, *J* 18 Hz, 4-H), 4.12 (1 H, d, *J* 9 Hz, 4a-H), 4.68 (1 H, d, *J* 8 Hz, 1-H), 5.30 (1 H, d, *J* 8 Hz, 2-H), and 7.7—7.9 and 8.0.8.3 (4 H, m, aromatic H) (Found: C, 64.5; H, 6.5. $C_{20}H_{21}O_5Si$ requires C, 64.5; H, 6.4%).

1,9a-trans-4a,9a-cis-1-*Acetoxy*-9a-*benzoyl*-1,4,4a,5,8,10a-*hexahydro*-9,10-*anthraquinone* (**26**).—2-Benzoyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (**28**) (0.21 g, 0.8 mmol) in benzene (20 ml) containing anhydrous sodium sulphate (0.25 g) was treated with silver(I) oxide (*ex.* silver nitrate; 3 g) and 1-acetoxybuta-1,3-diene (0.1 g, 0.9 mmol) in the manner described above. Further portions of diene (3 × 0.05 g) were added at intervals during the total reaction time of 3 days, before work-up. The crude product was recrystallised from dichloromethane–light petroleum to give the *title product* (0.21 g, 70%), m.p. 191 °C, $\nu_{max.}$ 1 735 and 1 690 $cm^{-1}$; δ 1.80 (3 H, s, OAc), 2.8—3.0 (1 H, br m, 4-H), 3.0—3.4 (5 H, m, 4-H, 5-$CH_2$, 8-$CH_2$), 3.8—4.0 (1 H, d, *J* 7 Hz, 4a-H), 5.7—6.1 (5 H, m, 1-H and vinylic H), and 7.9—8.1 (5 H, m, aromatic H) (Found: C, 73.3; H, 5.6. $C_{23}H_{20}O_5$ requires C, 73.4; H, 5.4%).

*General Procedure for Acyl Rearrangements*.—The cycloadduct (0.5 mmol) was heated in refluxing xylene (5 ml) containing pyridine (0.2—0.5 ml) for 1—3 h, reactions being monitored by t.l.c. The resulting solution was either cooled and the crystalline deposit harvested, or the solvent removed under reduced pressure and the residue crystallised from a suitable organic solvent. Occasionally, product isolation was performed by p.l.c. using ether–light petroleum mixtures as solvent. Yields and m.p.s are described in Table 2. Other properties of the new compounds prepared were as follows: 2-*acetyl*-5,8-*dihydro*-*naphthalene*-1,4-*diol* (**32**), $\nu_{max.}$ (Nujol) 3 350, 1 610, and 1 505 $cm^{-1}$; δ ($CD_3COCD_3$) 2.55 (3 H, s, MeCO), 3.25 (4 H, m, 5-$CH_2$, 8-$CH_2$), 5.89 (2 H, br s, 6-, 7-H), 7.15 (1 H, s, 3-H), 8.0 (1 H, br s, 4-OH), and 12.28 (1 H, s, 1-OH) (Found: C, 70.6; H, 5.8. $C_{12}H_{12}O_3$ requires C, 70.6; H, 5.9%).

2-*Acetyl*-5,8-*dihydro*-6,7-*dimethylnaphthalene*-1,4-*diol* (**33**), $\nu_{max.}$ 3 600, 1 685, and 1 610 $cm^{-1}$; δ 1.78 (6 H, s, 2 × Me), 2.54 (3 H, s, MeCO), 3.20 (4 H, br s, 5-, 8-$CH_2$), 7.10 (1 H, s, 3-H), 7.88 (1 H, br s, 4-OH), and 12.28 (1 H, s, 1-OH) (Found: C, 72.1; H, 6.9. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9%).

2-*Acetyl*-5,8-*dihydro*-8-*methylnaphthalene*-1,4-*diol* (**35**), $\nu_{max.}$ (Nujol) 3 340 and 1 610 $cm^{-1}$; δ 1.24 (3 H, d, *J* 8 Hz, 8-Me), 2.55 (3 H, s, MeCO), 5.87 (2 H, m, 6-, 7-H), 7.15 (1 H, s, 3-H), 7.91 (1 H, br s, 4-OH), and 12.40 (1 H, s, 1-OH) (Found: C, 71.6; H, 6.5. $C_{13}H_{16}O_3$ requires C, 71.6; H, 6.4%).

6-*Acetyl*-1,4-*naphthoquinone* (**43**), $\nu_{max.}$ (Nujol) 1 695, 1 675, 1 606, and 840 $cm^{-1}$; δ 2.72 (3 H, s, MeCO), 7.05 (2 H, s, 2-, 3-H), 8.25 (2 H, m, 7-, 8-H), and 8.59 (1 H, br s, 5-H) (Found: C, 72.0; H, 4.0. $C_{12}H_8O_3$ requires C, 72.0; H, 4.0%).

2-*Benzoyl*-5,8-*dihydro*-6,7-*dimethylnaphthalene*-1,4-*diol* (**37**), $\nu_{max.}$ (Nujol) 3 420 and 1 620 $cm^{-1}$; δ 1.83 (6 H, s, 6-, 7-Me), 3.22 (4 H, br s, 5-, 7-$CH_2$), 4.48 (1 H, s, 4-OH), 6.84 (1 H, s, 3-H), 7.4—7.8 (5 H, m, Ph), and 12.15 (1 H, s, 1-OH) (Found: C, 72.3; H, 6.2. $C_{19}H_{18}O_3$ requires C, 72.5; H, 6.1%).

2-*Benzoyl*-5,8-*dihydro*-8-*methylnaphthalene*-1,4-*diol* (**39**), $\nu_{max.}$ (Nujol) 3 340 and 1 620 $cm^{-1}$; δ 1.28 (3 H, d, *J* 8 Hz, 8-Me), 3.2—3.4 (2 H, m, 5-$CH_2$), 3.78 (1 H, m, 8-H), 4.68 (1 H, br s, 4-OH), 5.7—6.1 (2 H, m, 6-, 7-H), 6.78 (1 H, s, 3-H), 7.4—7.7 (5 H, m, Ph), and 12.20 (1 H, s, 1-OH) (Found: C, 77.3; H, 5.7. $C_{18}H_{16}O_3$ requires C, 77.2; H, 5.7%).

*Attempted Rearrangement of the Adduct* (**25**).—Heating the adduct (0.20 g, 0.57 mmol) in dry xylene (5 ml) containing pyridine (0.2 ml) for 2 h caused the disappearance of the starting material with the formation of one major product. The solvent was removed under reduced pressure to produce, as a yellow solid, 1,9a-trans-4a,9a-trans-9a-*acetyl*-1,4,4a,9a-*tetrahydro*-1-*methoxy*-3-*trimethylsilyloxy*-9,10-*anthraquinone* (**49**) (94 mg, 47%), m.p. 149—151 °C; $\nu_{max.}$ (Nujol) 1 705, 1 695, and 1 595 $cm^{-1}$; δ 0.23 (9 H, s, $Me_3Si$), 2.18 (3 H, s, MeCO), 2.68—2.76 (2 H, m, 4-$CH_2$), 3.45 (3 H, s, MeO), 3.65—3.87 (1 H, m, 4a-H), 5.32 (1 H, br d, *J* 7 Hz, 2-H), 4.91 (1 H, d, *J* 7 Hz, 1-H), 7.65—7.62 (2 H, m, 6-, 7-H), and 8.0—8.3 (2 H, m, 5-, 8-H) (Found: C, 64.5; H, 6.6. $C_{20}H_{24}SiO_5$ requires C, 64.5; H, 6.5%).

*Attempted Rearrangement of the Adduct* (**23**).—(*a*) *Pyridine–xylene*. The adduct (0.1 g, 0.53 mmol) was heated for 2 h with xylene containing pyridine. After 2 h the solution was cooled to deposit crystals of 9,10-anthraquinone (50 mg, 75%), m.p. 215—217 °C (decomp.) [lit.,[22] 218 °C (decomp.)].

(*b*) *Pyridine–methanol*. The adduct (0.1 g, 0.53 mmol) in 1:1 methanol–pyridine (5 ml) was heated to 50 °C for 7 days. The solvent was removed under reduced pressure and the residue chromatographed through silica gel, using 3:7 dichloromethane–light petroleum as eluant, to afford 9,10-anthraquinone (40 mg, 60%).

(*c*) *With DBN*. The adduct (0.10 g, 53 mmol) in xylene (5 ml) was treated with DBN (40 mg) at room temperature. After 5 min the solution was washed with 2M-HCl, whereupon a pale yellow solid precipitated. The organic solvent was removed under reduced pressure and the residue, containing the solid, was recrystallised from dichloromethane to produce yellow needles of 9,10-anthraquinone (65 mg, 97%).

*Attempted Rearrangement of the Adduct* (**24**).—The adduct (0.69 g, 1.8 mmol) was dissolved in 1:1 xylene–pyridine and heated to reflux for 3 h. On cooling, crystals of 9,10-anthraquinone deposited (0.29 g, 75%). The filtrate was

evaporated and the residue subjected to column chromatography to yield 2-acetyl-9,10-anthraquinone (14 mg, 3%), m.p. 140 °C (lit.,[23] 140—142 °C), $\nu_{max.}$ 1 695, 1 670, and 1 605 cm $^{-1}$; δ 2.76 (3 H, s, MeCO), 7.8—7.95 (2 H, m, aromatic H), 8.2—8.55 (4 H, m, aromatic H), and 8.82 (1 H, m, aromatic H) (Found: $M^+$ 250.062 59. Calc. for $C_{16}H_{10}O_3$: $M^+$ 250.062 99).

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## References

1 M. F. Ansell, B. W. Nash, and D. A. Wilson, *J. Chem. Soc.*, 1963, 3012.
2 C. H. Eugster and P. Bosshard, *Helv. Chim. Acta*, 1963, **46**, 815.
3 J. M. Bruce in 'Benzoquinones and Related Compounds,' in 'Rodds Chemistry of Carbon Compounds,' ed. S. Coffey, Elsevier, Amsterdam, 1974, vol. III, B, ch. 8.
4 S. C. Cooper and P. G. Sammes, *J. Chem. Soc., Chem. Commun.*, 1980, 633.
5 M. C. Kloetzel, R. P. Dayton, and B. Y. Abadir, *J. Org. Chem.*, 1955, **20**, 38.
6 M. J. Bojert and H. P. Howells, *J. Am. Chem. Soc.*, 1930, **52**, 837.
7 R. Al Hamdany, J. M. Bruce, R. T. Pardasari, and I. Watt, *J. Chem. Soc., Chem. Commun.*, 1981, 171.
8 Y. Kishi, F. Nakatsubo, M. Aratani, T. Goto, S. Inoue, H. Kakoi, and S. Sugiura, *Tetrahedron Lett.*, 1970, 5127.
9 *Cf.* I. A. Kaye and R. S. Matthews, *J. Org. Chem.*, 1964, **29**, 1341; K. Alder, and W. Vogt, *Liebigs Ann. Chem.*, 1949, **564**, 120.
10 C. Escobar, F. Fariña, R. Martinez-Utrilla, and M. C. Paredes, *J. Chem. Res.*, 1980; (*S*), 156.
11 G. A. Kraus and M. J. Taschner, *J. Org. Chem.*, 1980, **45**, 1176.
12 L. A. Cort and P. A. B. Rodriguez, *J. Chem. Soc.* C, 1967, 949.
13 J. H. Berson and R. G. Solomon, *J. Am. Chem. Soc.*, 1971, **93**, 4621; R. A. Baylouny, *J. Am. Chem. Soc.*, 1971, **93**, 4620.
14 C. P. Falshaw, S. A. Lane, and W. D. Ollis, *J. Chem. Soc., Chem. Commun.*, 1973, 491.
15 P. Schiess and P. Fünfschilling, *Tetrahedron Lett.*, 1972, 5195.
16 D. J. Field, D. W. Jones, and G. Kneen, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1050.
17 F. B. H. Ahmad, J. M. Bruce, J. Khalafy, V. Pejanovic, K. Sabetian, and I. Watt, *J. Chem. Soc., Chem. Commun.*, 1981, 166.
18 F. B. H. Ahmad, J. M. Bruce, J. Khalafy, and K. Sabetian, *J. Chem. Soc., Chem. Commun.*, 1981, 169.
19 C. J. P. Spruit, *Recl. Trav. Chim.*, 1947, **66**, 655.
20 C. G. Amin and N. M. Shah, *Org. Synth.* Coll. Vol. III, 1955, 280.
21 S. Danishefsky and Y. Kitahowa, *J. Am. Chem. Soc.*, 1974, **96**, 7807.
22 'Dictionary of Organic Compounds,' Roger and Spottiswoode, London, 1965.
23 A. Luttringhaus and F. Kacer, U.S. Pat., 1 730 081 (*Chem. Abstr.* 1936, **23**, 5474).

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