100 ml of water, two clear phases were separated. Treating the aqueous phase with concentrated potassium iodide solution gave a crude yellow solid. Recrystallization from ethanol gave 1.43 g (2.9 mmol, 72.5%) of fine yellow crystalline flakes of 4,4′-di(dimethylamino)diphenyliodonium iodide, mp 159° dec.

Anal. Calcd for $C_{16}H_{20}N_2I_2$: C, 38.87; H, 4.05; N, 5.66; I, 51.42. Found: C, 39.22; H, 3.91; N, 5.59; I, 51.38.

The infrared spectrum (KBr) has aliphatic C–H stretching at 2900 cm^{-1}, CH_3–N stretching at 2805 cm^{-1}, CH_3 rocking at 1500 and 1440 cm^{-1}, and an aromatic para-disubstitution pattern at 805 cm^{-1}.

The aqueous filtrate was then neutralized with dilute sodium hydroxide solution to give an off-white precipitate, which after recrystallization from water gave 1.02 g (6.1 mmol, 43% based on unexchanged 4-dimethylaminophenyllithium) of 4-dimethylaminobenzoic acid, mp 239–240° (lit.[12] mp 240–241°).

The acidic product in the organic phase was separated by acid–base extractions and esterified with diazomethane to give 0.595 g of methyl benzoate (2.29 mmol, 28.6% based on the milliequivalents of phenyl group in the starting diphenyliodonium salt, 57.2% based on the millimoles of diphenyliodonium chloride).

Dibenziodolium Iodide from Diphenyliodonium Chloride and 2,2′-Dilithiobiphenyl.—To a white suspension of 1.27 g (4 mmol) of diphenyliodonium chloride in 40 ml of tetrahydrofuran at −73°, there was added 4.25 mmol of 2,2′-dilithiobiphenyl in ether. The resulting bright yellow semitransparent solution was stirred at −73° for 15 min and filtered rapidly into aqueous potassium iodide with stirring. The pale yellow solid that separated between two phases was collected, washed with ether and water, and dried to give 1.2 g (2.86 mmol, 71.5%) of dibenziodolium iodide, mp 220° dec (lit.[13] mp 210–215°). The infrared spectrum was in agreement with that of an authentic sample. The pyrolysis product was pure 2,2′-diiodobiphenyl, identified by vpc peak enhancement with an authentic sample. Analysis of the ether layer also showed 27% of biphenyl, apparently arising from unreacted 2,2′-dilithiobiphenyl.

When a similar reaction mixture was treated first with carbon dioxide and then with aqueous acid, the yield of benzoic acid was only 2%.

Registry No.—**2**, 32174-73-5; **5**, 34220-01-4; phenyllithium, 591-51-5; diphenyliodonium chloride, 1483-72-3; 4-chlorophenyllithium, 14774-78-8; 4-dimethylaminophenyllithium, 13190-50-6; 4,4′-di(dimethylamino), diphenyliodonium iodide, 34220-05-8.

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[12] C. A. Bischoff, *Ber.*, **22**, 343 (1889).

[13] L. Mascarelli and G. Benati, *Gazz. Chim. Ital.*, **38**, 619 (1908).

Oxidation of Arylpropenes by 2,3-Dichloro-5,6-dicyanoquinone[1]

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Oxidation of anethole, estragole, or 1-phenylpropene by DDQ in benzene gives mono- and/or bis(arylpropenyl) ethers of dichlorodicyanohydroquinone (DDHQ). These highly reactive intermediates can be further oxidized by DDQ to arylpropenals, converted to allylically rearranged alkyl arylpropenyl ethers by alcoholysis, or converted to arylpropenyl chlorides by treatment with HCl. No esr or CIDNP evidence for free-radical intermediates could be detected, and it is assumed from solvent and substituent kinetic effects that the initial oxidation involves hydride ion abstraction by DDQ. Exclusive incorporation of ^{18}O-labeled water into the aldehyde oxidation product implicates an acetal intermediate in this transformation. The allylic rearrangement which takes place on alcoholysis is postulated to proceed *via* a cyclic S_N2' mechanism in which hydrogen bonding of the alcohol to the departing hydroquinone anion determines the geometry of the transition state.

In addition to its widespread use for the introduction of conjugated double bonds in steroidal ketones and hydroaromatic systems,[4] 2,3-dichloro-5,6-dicyanoquinone (DDQ) has been used to generate stable carbonium ions (*e.g.*, cycloheptatrienyl and triphenylcyclopropenyl) and free radicals (*e.g.*, perinaphthenyl) from the parent hydrocarbons.[5] In cases where an intermediate ion or radical is of lower stability and simple dehydrogenation to an alkene is blocked, the intermediate may either undergo rearrangement (*e.g.*, 1,1-dimethyltetralin to 1,2-dimethylnaphthalene[6]) or collapse to a covalent adduct (*e.g.*, 2,2-dimethylindan,[7] diphenylmethane[8]). We have characterized the reaction of DDQ with arylpropenes, which falls into the latter category. Because of the ability of DDQ to abstract either hydride ions or hydrogen atoms, we have also investigated briefly the mechanism of this reaction, as well as that of the oxidation to arylpropenals by excess DDQ. Finally, we have explored some synthetically useful transformations based on these reaction.

Results and Discussion

Reactions of DDQ with *trans*-1-(*p*-methoxyphenyl)-propene (anethole), 3-(*p*-methoxyphenyl)propene (estragole), *trans*-1-phenylpropene, 2-phenylpropene, and *p*-methoxystyrene were carried out under a variety of conditions. Intensely colored molecular complexes formed immediately in all cases, but oxidation rates varied widely; the reactions could be conveniently followed by observing the disappearance of color and precipitation of the quinone reduction product, 2,3-dichloro-5,6-dicyanohydroquinone (DDHQ). Reaction of anethole with tetrachloro-*p*-benzoquinone (chloranil) in benzene was also carried out for comparative purposes; in this case, no oxidation occurred within 5 days at room temperature. Since oxidation of anethole by DDQ under these conditions proceeds measurably within 1 sec (see below), it can be concluded that DDQ is at least 10^5 times as reactive as chloranil in this case.

2-Phenylpropene was not oxidized by DDQ within 8 days under the above conditions, nor was any po-

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[1] Abstracted from the Ph.D. thesis of F. E. Lutz, University of Hawaii, 1970. Parts of this work have been published in preliminary form[2,3] and presented at the 26th Northwest Regional Meeting of the American Chemical Society, Bozeman, Mont., June 17, 1971. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the U. S. Public Health Service, National Institutes of Health, for support of this research.

[2] F. E. Lutz and E. F. Kiefer, *Tetrahedron Lett.*, 4851 (1970).

[3] F. E. Lutz and E. F. Kiefer, *Chem. Commun.*, 1723 (1970).

[4] D. Walker and J. D. Hiebert, *Chem. Rev.*, **67**, 153 (1967).

[5] D. H. Reid, M. Frazer, B. B. Molloy, H. A. S. Payne, and R. G. Sutherland, *Tetrahedron Lett.*, 530 (1961).

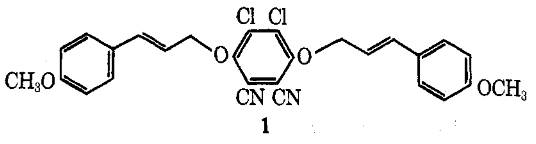
[6] R. P. Linstead, E. A. Braude, L. M. Jackman, and A. N. Beames, *Chem. Ind. (London)*, 1174 (1954).

[7] E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *J. Chem. Soc.*, 3123 (1960).

[8] H.-D. Becker, *J. Org. Chem.*, **34**, 1203 (1969).

lymerization observed. *p*-Methoxystyrene was substantially converted to a benzene-insoluble polymer within 20 hr by DDQ, probably *via* a change-transfer mechanism.[9] This type of polymerization was a minor side reaction in the oxidation of anethole by DDQ, and the only reaction observed with chloranil.

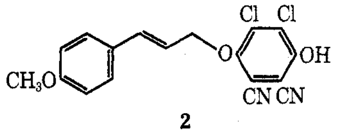
The DDQ oxidation of anethole has been described previously.[2] Benzene is the preferred solvent owing to the relatively high solubility (68 g/l.)[4] of DDQ and the very low solubility (0.6 g/l.)[4] of DDHQ. The immediate oxidation product, 2,3-dichloro-5,6-dicyano-1,4-bis(3-*p*-anisyl-2-propenyloxy)benzene (**1**), can be isolated only with difficulty (most conveniently after repeated extraction with aqueous dioxane) owing to its high reactivity toward polymerization and solvolysis; higher overall yields are obtained in subsequent transformations starting with the initial yellow solution of **1** in benzene after filtration of DDHQ. Further oxidation to *p*-methoxycinnamaldehyde is best accomplished by stirring a benzene solution of anethole and 2 equiv of DDQ with a small amount of water, and destroying unreacted DDQ by titration with aqueous sodium borohydride. Conversion to aldehyde may be nearly quantitative; the isolated yield in one run on a less than 1-g scale was 85%.



1

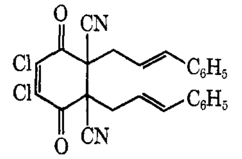
The DDQ oxidation of estragole also gives *p*-methoxycinnamaldehyde under the above conditions, though about 50 times as slowly. The difference in rate is attributed to the absence of extended conjugation in estragole, which significantly lowers the equilibrium constant for π-complex formation with DDQ. The aldehyde yield from estragole was remarkably constant at about 50% under a variety of conditions.

p-Methoxycinnamaldehyde is also produced when DDQ and estragole are present in equimolar amounts. In this case, the major oxidation product isolated was the mono ether of DDHQ, 2,3-dichloro-5,6-dicyano-4-(3-*p*-anisyl-2-(propenyloxy)phenol (**2**, below). Since **2** is presumably an intermediate in the formation of **1** from anethole also, its more rapid disproportionation to **1** in the anethole reaction might be rationalized on the basis of acid catalysis: the very high initial reaction rate in the anethole reaction might produce a temporarily supersaturated solution of the strong acid DDHQ. Indeed, a tendency of DDHQ to precipitate only slowly from benzene solution has been noted in our work, and can be inferred in this case by the fact that the color change in the reaction substantially precedes DDHQ precipitation.



2

The DDQ oxidation of 1-phenylpropene, which serves to demonstrate that an activating substituent is not essential in this reaction, resembled that of estragole in rate and product distribution. In this case, both mono and bis ether products analogous to **1** and **2** were isolated, along with cinnamaldehyde, when the reagents were present in equimolar amounts. In addition, a small yield of a high-melting orange solid was obtained which was isomeric with the bis ether and was assigned the structure **3** on the basis of its spectral properties. The enedione chromophore is evident from the ir and uv-visible spectra, and the presence of two cinnamyl units per molecule is indicated by the uv extinction coefficient, microanalysis, and mass spectra. The nmr spectrum shows both cinnamyl units to be in identical environments and bonded to carbon rather than oxygen. Somewhat surprisingly, the methylene groups appear as a simple doublet rather than the expected AB quartet of doublets, in spite of the fact that the adjacent pseudoasymmetric carbon atoms bear highly anisotropic substituents. The cinnamyl groups are assigned to the cyano- rather than chloro-substituted carbon atoms (with unknown stereochemistry) largely because no thermal dehydrohalogenation could be observed at the melting point (217°).



3

Mechanism.—Because of the proven ability of DDQ to generate free radicals by hydrogen atom abstraction[5] and a proposed free-radical mechanism for the DDQ oxidation of diphenylmethane,[8] a careful search was made for evidence of a free-radical intermediate in the oxidation of anethole. Simultaneous injection of benzene solutions of DDQ and of anethole into an esr probe with rapid scanning[10] produced no esr signal attributable to a free radical derived from anethole. The broadened singlet due to semiquinone radical (DDSQ), together with a weak, superimposed triplet of unknown origin, were the only signals detected. Both signals were time- and concentration-independent and also shown to be present when DDQ and DDHQ were mixed in the absence of anethole.

In an even more sensitive test, rapid scanning of the pmr spectrum of a freshly mixed solution of DDQ and anethole also failed to detect any nmr emission or enhanced absorption due to nuclear polarization by unpaired electrons (CIDNP).[11] Further indirect evidence against a radical meechanism can be found in kinetic substituent and solvent effects: a *p*-methoxy substituent causes an approximately 100-fold rate enhancement, compared with typical factors of only 2–3 for analogous free-radical reactions,[12] and more polar solvents also exert substantial rate enhancements. It can thus be concluded with reasonable assurance that the initial step in this reaction is hydride ion abstrac-

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(9) H. Nomori, M. Hatano, and S. Kambara, *J. Polym. Sci. Part B*, **4**, 623 (1966); H. Scott, G. A. Miller, and M. M. Labes, *Tetrahedron Lett.*, 1073 (1963).

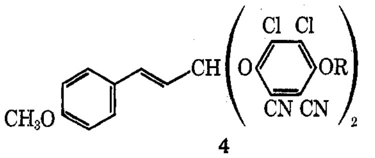
(10) I. Yamazaki and L. H. Piette, *J. Amer. Chem. Soc.*, **87**, 986 (1965), and earlier papers. We wish to thank Professor Piette for his assistance in performing the esr experiments.

(11) K. H. Hausser and D. Stehlik, *Advan. Mag. Res.*, **3**, 79 (1968), and references cited therein.

(12) R. L. Huang and S. Singh, *J. Chem. Soc.*, 3183 (1959); C. Walling, "Free Radicals in Solution", Wiley, New York, N. Y., 1957, p 139.

tion, as is the case in typical dehydrogenation reactions. Since subsequent proton transfer in our case is energetically disfavored, the initially formed ion pair[13] collapses to the ether **2**. As indicated above, the disproportionation of **2** to **1** and DDHQ appears to be acid catalyzed, though no studies bearing specifically on this point were made.

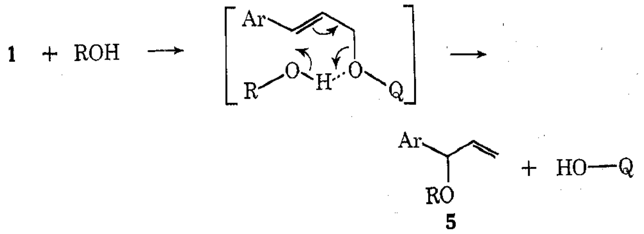
The further oxidation of **1** or **2** to aldehyde may be assumed to proceed initially by a repetition of the above steps, leading to an acetal, *e.g.*, **4** (R = H or *p*-methoxycinnamyl).[2] As might be expected, **4** is extremely labile; attempts to isolate it failed. Addition of ^{18}O-enriched water to the reaction gave an 85% yield of *p*-methoxycinnamaldehyde in which at least 94% of the carbonyl oxygen was derived from water. The rate of oxidation of **1** or **2** to **4** by DDQ appears to be about 50 times as slow as that of anethole; *i.e.*, comparable to that of estragole.



4

Enedione **3** is believed to arise *via* alkylation of DDHQ or mono ether of type **2** by the cinnamyl carbonium ion, since no tendency for the biscinnamyl ether of DDHQ to rearrange to **3** could be observed. The fact that the *p*-methoxy analog of **3** was not found is presumably a reflection of the greater stability (*i.e.*, higher selectivity) of the *p*-methoxycinnamyl cation.

Conversion to Other Products.—The alcoholysis of **1** has been previously noted.[3] In this reaction, which is advantageously carried out starting with anethole and DDQ without isolation of **1**, allylically rearranged ethers (**5**) are produced *via* a proposed[3] SN2′ mechanism involving the cyclic, hydrogen-bonded transition state shown below (Ar = *p*-methoxyphenyl). The yield of rearranged ethers **5** drops from 65–70% with methanol (**5a**) and ethanol (**5b**) to 2% with 2-methyl-2-propanol (**5d**), while the yield of unrearranged alkyl *p*-methoxycinnamyl ethers (**6**) correspondingly rises from 4–5% to 17%. As the unconjugated ethers **5** could be quantitatively isomerized to the more stable conjugated ethers by treatment with dilute acid, this reaction constitutes a useful synthesis of both types of compound. The uniqueness of this system as a precursor for the unconjugated 1-arylallyl ethers was demonstrated by the ethanolysis of *p*-methoxycinnamyl chloride, which gave only the conjugated isomer, 3-*p*-methoxycinnamyl ethyl ether.



5

DDQ oxidation of anethole to **1** in benzene solution followed by treatment with aqueous hydrochloric acid gave *p*-methoxycinnamyl chloride in approximately 50% yield, the remainder being converted to a hexane-insoluble polymer. Reaction of **1** with diethylamine or aniline in benzene solution required prolonged heating and gave only intractable products. In a single experiment, crude **1** reacted at room temperature with excess pyrrolidine in acetonitrile to produce traces of a compound tentatively identified as N-(*p*-methoxycinnamyl)pyrrolidine on the basis of its ir spectrum and basicity. Compound **1** failed to react with cyanide ion in the absence of added acid, even in dimethyl sulfoxide. It thus appears that nucleophilic displacement on **1** requires the presence of a proton donor, *i.e.*, that the anion of DDHQ (or its mono ether) is a poor leaving group.

Experimental Section

Uv, ir, nmr, esr, and mass spectra were recorded on Cary 14, Beckman IR-5A, Varian HA-100, Varian E4, and Hitachi Perkin-Elmer RMU-6D spectrometers, respectively. Glpc separations were carried out on a Varian Aerograph Model 200 gas chromatograph, using a 0.25 in. × 5 ft stainless steel column packed with 20% SE-30 silicone fluid on 60–80 mesh Chromosorb W at 185°. Melting points were determined on a Fisher-Johns apparatus and are uncorrected; boiling points were determined by the inverted capillary method and are corrected. Mass spectral analyses were performed by Sr. Mary Roger Brennan and microanalyses by the Berkeley Analytical Laboratory unless otherwise noted. Arylpropenes were the best available commercial grade, redistilled before use. DDQ (Arapahoe Chemical Co.) was recrystallized from 3:2 benzene–petroleum ether (bp 30–60°) and displayed the expected spectral properties.[4] Analytical reagent grade solvents were used without further purification.

2,3-Dichloro-5,6-dicyano-1,4-bis(3-*p*-anisyl-2-propenyloxy)-benzene (1).—A solution of 3.72 ml (25 mmol) of anethole in 20 ml of benzene was added to a solution of 5.67 g (25 mmol) of DDQ in 230 ml of benzene. Within 1 min, the initially black color of the molecular complex had faded a bright yellow, whereupon 2.84 g (50%) of precipitated DDHQ was collected by filtration and identified by its mass spectrum (*m/e* 228, base, M^+) and by conversion to the diacetate,[14] mp 182–183°. The filtrate was used directly for the conversion of **1** to other products (see below). For the isolation of **1**, 50 ml of dioxane was added to the filtrate, which was then washed with five 50-ml portions of water, dried ($MgSO_4$), and evaporated to dryness *in vacuo*. The residue, after brief trituration with 50 ml of ice-cold MeOH to remove residual DDHQ and colored polymeric material, weighed 3.0–3.5 g (45–55%) and displayed erratic melting behavior. Six recrystallizations from 1:3 dioxane–hexane were required to obtain a 20% yield of pure **1** of constant melting point (124°) uv max (dioxane) 268 nm (ϵ 44,200), 325 (4980); ir (KBr) 972 (*trans*-CH=CH), 1244 (COC), 2222 cm^{-1} (CN); nmr ($CDCl_3$) δ 7.08 (q, 4, J = 9.0, C_6H_4), 6.59 (d, 1, J = 16.0 Hz, CH=CHCH$_2$), 6.29 (d of t, 1, J = 16.0, 6.5 Hz, CH=CHCH$_2$), 4.87 (d, 2, J = 6.5 Hz, CH_2), and 3.78 (s, 3, OCH_3).

Anal. Calcd for $C_{28}H_{22}Cl_2N_2O_4$: C, 64.60; H, 4.27; Cl, 13.64; N, 5.38. Found: C, 64.52; H, 4.00; Cl, 13.71; N, 5.40.

Independent synthesis of **1** was accomplished in 40% yield by stirring a solution of the disodium salt of DDHQ in 50% aqueous dioxane with a benzene solution of 2 equiv of *p*-methoxycinnamyl chloride (see below) at 60° for 20 min, followed by isolation and purification as described above. This sample was identical (mixture melting point, ir, uv, nmr) with that prepared by the oxidation of anethole.

***p*-Methoxycinnamaldehyde.**—In the best preparative procedure a solution of 6 mmol of anethole in 20 ml of benzene was added to a solution of 12 mmol of DDQ in 230 ml of benzene to which 1 ml of water had been added. The heterogeneous mixture was stirred vigorously for 1 hr at room temperature and 1 hr at 50°, cooled, and treated dropwise with 2% aqueous sodium borohydride to reduce excess DDQ (yellow end point). After removal of DDHQ by filtration, the benzene solution was concentrated to about 20 ml and chromatographed on a 1.7 × 38 cm silica gel column. Elution with chloroform gave, after an

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[13] B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 1847 (1967).

[14] J. Thiele and F. Günther, *Justus Liebigs Ann. Chem.*, **349**, 55 (1906).

initial, bright orange oil (0.06 g, discarded), 0.79 g (78% yield) of *p*-methoxycinnamaldehyde: mp 58–59° after sublimation [50° (0.1 mm)]; uv (dioxane) max 314 nm (ϵ 22,700); ir (KBr) 1670 (C=O), 968 cm^{-1} (*trans*-CH=CH); nmr (CCl_4), δ 9.71 (d, 1, CHO); mass spectrum (70 eV) *m/e* 162 (M$^+$, base), 161. Reaction of the purified bis ether **1** with equimolar DDQ in benzene also gave *p*-methoxycinnamaldehyde in 73% yield, identical in all respects with that prepared directly from anethole.

_p_-Methoxycinnamaldehyde-^{18}*O*.—The above procedure was followed except that 0.905 g of water containing 20.0% ^{18}O (Bio-Rad Laboratories) was used, and the excess DDQ was destroyed by adding 0.4 ml of anethole before work-up instead of aqueous sodium borohydride. The yield of aldehyde was 0.86 g (85%). Comparison of the relative intensities due to the ions at *m/e* 162 and 164 with those of unlabeled material indicated 18.8% ^{18}O-containing ions, corresponding to 94% incorporation of oxygen from water.

2,3-Dichloro-5,6-dicyano-4-(3-*p*-anisyl-2-propenyloxy)phenol (2).—Reaction of estragole with equimolar DDQ under the conditions and on the same scale described for anethole gave a 72% yield of DDHQ after 1 hr. Dioxane–water extraction of the filtrate and solvent removal gave a benzene-insoluble solid (2.0 g) which could not be recrystallized without decomposition to DDHQ. This was purified by precipitation from chloroform solution by slow addition of hexane to give white, crystalline **2** mp 100° dec, distinguishable from the bis ether **1** by its ir [3195 cm^{-1} (OH)] and uv [$\lambda_{max}^{dioxane}$ 267 nm (ϵ 24,800), 340 (5850)] spectra, and by microanalysis. Neither **1** nor **2** gave a usable mass spectrum.

Anal. Calcd for $C_{18}H_{12}Cl_2N_2O_3$: C, 57.80; H, 3.23; N, 7.50; Cl, 18.95. Found: C, 57.58; H, 3.18; N, 7.42; Cl, 18.91.

Other compounds isolated from the benzene filtrate by silica gel chromatography were *p*-methoxycinnamylaldehyde (0.7 g, 17% yield) and unreacted estragole (0.8 g, 22% recovery). The yield of aldehyde increased to 50% with 2 equiv of DDQ and to 60% with 3 equiv and was essentially unchanged by changing the reaction solvent to dioxane or dichloromethane or by dropwise addition of reagents or a nitrogen atmosphere.

DDQ Oxidation of 1-Phenylpropene.—In a typical experiment, a solution of 3.23 ml (0.025 mol) of 1-phenylpropene in 20 ml of benzene was added to 5.67 g (0.025 mol) of DDQ in 230 ml of benzene. Precipitation of DDHQ began within 2 min; filtration after 20 hr yielded 2.2 g (38%) of DDHQ. Concentration of the filtrate to a volume of about 20 ml caused precipitation of a pale green solid (2.2 g), identified as the monocinnamyl ether of DDHQ (**7**), mp 130° dec, on the basis of the following evidence: uv max (dioxane) 254 nm (ϵ 26,250) 340 (6050); ir (KBr) 969 (*trans*-CH=CH), 1195 (CO), 2227 (CN), 3245 cm^{-1} (OH); nmr (DMSO-d_6), δ 7.36 (m, 5, C_6H_5), 6.76, 6.50, 4.82 (ABX_2, 1, 1, 2, J_{AB} = 16.0 Hz, J_{BX} = 6.0 Hz, $CH{=}CHCH_2$). Like the *p*-methoxy analog **2**, **7** could not be crystallized, but was precipitated from chloroform–hexane; it did not give satisfactory analytical data.

Silica gel chromatography of the filtrate from **7** yielded four fractions (A–D), the first three of which contained cinnaldehyde and traces of 1-phenylpropene. Cinnamaldehyde was isolated by fractional distillation of fraction B combined with the hexane-soluble portion of semisolid fraction A, total yield 0.5 g (15%), bp 41° (0.15 mm), identified by nmr, ir, and uv spectra. The solid hexane-insoluble portion of fraction A (0.8 g) was further separated by fractional crystallization. Addition of 3 vol. of hexane to an acetone solution of the solid caused long, white needles, mp 148–149°, to separate within 1 hr at 4°, followed after addition of hexane to turbidity by short, orange needles, mp 216–217°. The white compound was identified as the biscinnamyl ether of DDHQ by its uv, ir, and nmr spectra, which resembled those of **7** except for the absence of features attributed to the phenolic hydroxyl group, and by microanalyses.

Anal.[15] Calcd for $C_{26}H_{18}Cl_2N_2O_2$: C, 67.69; H, 3.93. Found: C, 68.03; H, 3.71. (Calcd for **7**: C, 59.15; H, 2.92.)

The orange compound above was assigned the structure 2,3-dichloro-5,6-dicyano-5,6-dicinnamyl-2-cyclohexene-1,4-dione (**3**) on the basis of the following evidence: nmr (acetone-d_6) δ 7.33 (m, 5, C_6H_5), 6.71, 6.06, and 3.39 (d, d of t, d, ABX_2, 1, 1, 2, J_{AX} = 16.0 Hz, J_{BX} = 7.5 Hz, *trans*-$CH{=}CHCH_2$); uv max (dioxane) 257 nm (ϵ 39,000), 370 (1100); ir (KBr) 1560, 1704 (enedione), 2222 cm^{-1} in addition to the expected cinnamyl bands; mass spectrum (20 eV) *m/e* 460 (M$^+$), 117 (base).

TABLE I

Compd (R)	Reflux, hr	% **5**	% **6**
a (CH_3)	0.5	65	5
b (C_2H_5)	0.5	68	4
c (*i*-C_3H_7)	1.0	31	14
d (*tert*-C_4H_9)	3.0	2	17

Anal.[15] Calcd for $C_{26}H_{18}Cl_2N_2O_2$: see above. Found: C, 68.77; H, 4.26.

The total yield of isomers **7** and **3** was 14%, in the approximate ratio of 4:1.

3-*p*-Anisyl-3-alkoxypropenes (5) and 1-*p*-Anisyl-3-alkoxypropenes (6).—In the standard procedure for the conversion of anethole to the above ethers, the initial filtrate containing **1** (see above) was treated with 50 ml of an alcohol and heated under reflux for 0.5–3 hr (see below). After removal of the solvent *in vacuo*, benzene was added to facilitate removal of DDHQ by filtration and the filtrate was passed through a Florisil column (chloroform eluent) to remove polymeric materials, distilled *in vacuo*, and analyzed by glpc. Preparative separation of **5** and **6** was accomplished by collecting and analyzing *ca.* thirty 30-ml fractions from a 1.7 × 40 cm silica gel column with benzene as eluent; the unconjugated ethers **5** eluted first. Spectral data below are given for the ethyl ethers **5b** and **6b**. The nmr chemical shifts for the other six ethers are the same as those below within ±0.08 ppm except for the R groups and the benzylic proton in **5**, which shifts 0.38 ppm to lower field as the size of R increases from methyl to *tert*-butyl as would be expected from conformational considerations. The ir, uv, and mass spectra of these spectra of these homologues also show the expected similarities and differences. **5b**: nmr (CCl_4) δ 6.92 (q, 4, *J* = 9.0 Hz, C_6H_4), 5.80 (octet, 1, *J* = 17, 10, and 6 Hz, $CHC\mathbf{H}{=}CH_2$), 5.10 and 5.00 (m, 2, *J* = 17, 10, 2, 1.5, and 1.3 Hz, $CHCH{=}\mathbf{CH_2}$), 4.53 (octet, 1, *J* = 6, 1.5, and 1.3 Hz, $\mathbf{C}\mathbf{H}CH{=}CH_2$), 3.71 (s, 3, OCH_3), 3.40 and 3.30 (q_{AB} of q, 2, *J* = 9 and 7 Hz, $O\mathbf{CH_2}CH_3$), 1.16 (t, 3, *J* = 7 Hz, $CH_2\mathbf{CH_3}$); mass spectrum (70 eV) *m/e* (rel intensity) 192 (90 M$^+$), 163 (50), 147 (100), 135 (90). **6b**: nmr (CCl_4) δ 6.95 (q, 4, *J* = 9.0 Hz, C_6H_4), 6.39 (d of t, 1, *J* = 16 and 1.0 Hz, $C\mathbf{H}{=}CHCH_2$), 6.01 (d of t, 1, *J* = 16 and 5.5 Hz, $CH{=}C\mathbf{H}CH_2$), 3.98 (d of d, *J* = 5.5 and 1.0 Hz, $CH{=}CH\mathbf{CH_2}$), 3.72 (s, 3, OCH_3), 3.42 (q, 2, *J* = 7 Hz, $\mathbf{CH_2}CH_3$), 1.18 (t, 3, *J* = 7 Hz, $CH_2\mathbf{CH_3}$); uv max (cyclohexane) 263 nm (ϵ 17,200); mass spectrum (70 eV) *m/e* (rel intensity) 192 (25, M$^+$), 136 (50), 135 (100). The reflux times for the preparation of isomeric ethers **5** and **6** are given in Table I along with isolated yields of chromatographically purified products. None of those compounds has been previously characterized.

Isomerization of 5b to 6b.—A solution of **5b** (1 g) in 20 ml of ethanol was treated with 5 ml of 0.1 *M* perchloric acid and heated under reflux for 1 hr. After evaporation of most of the ethanol, the solution was extracted three times with ether and the combined ether solution was washed with water, dried ($MgSO_4$), and distilled, providing gas chromatographically pure **6b**, bp 76–78° (1.0 mm), identified by its ir and nmr spectra.

_p_-Methoxycinnamyl Chloride.—The initial benzene solution of compound **1** (see above) was stirred vigorously with 40 ml of concentrated HCl for 30 min and chilled in ice, and the acid was neutralized cautiously with 6 *N* NaOH to dissolved suspended DDHQ. The organic phase was washed twice with water, dried ($MgSO_4$), and evaporated at aspirator pressure. The oily residue was triturated thoroughly with warm hexane, and the hexane solution was evaporated to yield 2.36 g (52%) of solid *p*-methoxycinnamyl chloride, which after sublimation at 50° (0.1 mm) had mp 73.5–74.5° (lit.[16] mp 73°); uv max (cyclohexane) 268 nm (ϵ 20,400); ir (KBr) 654 (CCl), 972 (*trans*-CH=CH), 1645 cm^{-1} (C=C); nmr (CCl_4) δ 4.11 (d, 2, *J* = 6.5 Hz, CH_2Cl), otherwise similar to that of **1**; mass spectrum (70 eV) *m/e* 182 (M$^+$), 147 (base).

Registry No.—**1**, 33904-07-3; **2**, 31186-79-5; **3**, 33904-09-5; **5b**, 30225-71-9; **6b**, 33904-11-9; **7**, 33904-12-0; *p*-methoxycinnamaldehyde, 24680-50-0; biscinnamyl ether of DDHQ, 33904-14-2.

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[15] This analysis was by C. F. Geiger, Ontario, Calif.

[16] W. N. White and W. K. Fife, *J. Amer. Chem. Soc.*, **83**, 3846 (1961).