

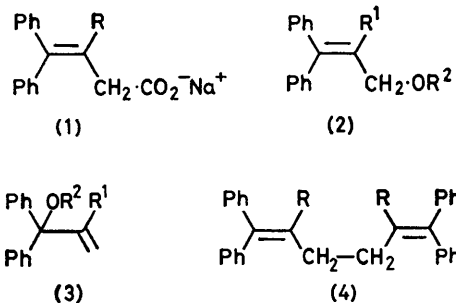
Anodic Oxidation. Part 16.¹ A Comparison of Chemical and Electrochemical Routes to Alkyl Diphenylallyl Ethers

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Electrolysis of 1-ethyl hydrogen 2-diphenylmethylenesuccinate, a Stobbe half-ester, in ethanol gives as the major products the two, readily separable, isomeric ethers ethyl 2-ethoxymethyl-3,3-diphenylprop-2-enoate and ethyl 2-[ethoxy(diphenyl)methyl]prop-2-enoate. 4,4-Diphenylbut-3-enoic acid on electrolysis in methanol gives the analogous methyl diphenylallyl ethers. Alternative chemical syntheses of the four ethers are also described; these illustrate the superiority of the electrochemical route.

HALF-ESTERS have proved very useful in the Kolbe electrosynthesis,² but one type of half-ester not hitherto investigated is the unsymmetrical type of half-ester formed by the Stobbe condensation.³ We now report on the electrolysis of 1-ethyl hydrogen 2-diphenylmethylenesuccinate and of 4,4-diphenylbut-3-enoic acid which is readily available from it. Few electrolyses of $\beta\gamma$ -olefinic acids have been reported,² but recently the electrolysis of *cis*-4-phenylcyclohex-2-enecarboxylic acid in methanol has been reported⁴ to give predominantly a mixture of all four possible ethers derived from the allylic cation resulting from the two-electron oxidative decarboxylation together with much smaller amounts of a mixture of the Kolbe dimers formed by the coupling of the radical arising by one-electron oxidative decarboxylation.

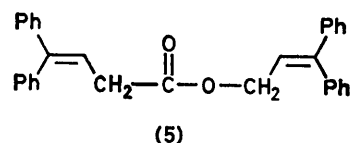
The electrolysis of sodium 1-ethyl-2-diphenylmethylenesuccinate (1; R = CO₂Et) in ethanol, using an undivided cell,⁵ a platinum anode, a mercury cathode, and an uncontrolled potential gave the two ethers (2; R¹ = CO₂Et, R² = Et) and (3; R¹ = CO₂Et, R² = Et) in 69



and 12% yield, respectively, together with a small amount of the Kolbe dimer formed by coupling of the intermediate radical at the primary site (4; R = CO₂Et). The two ethers could be readily separated by preparative t.l.c.; the Kolbe dimer crystallised from the solution at the end of the electrolysis. The products were identified from their spectroscopic properties and by direct comparison with authentic samples (see later).

The electrolysis of sodium 4,4-diphenylbut-3-enoate (1; R = H) in methanol, in the same cell, gave the two ethers (2; R¹ = H, R² = Me) and (3; R¹ = H, R² =

Me) in 48 and 19% yield, respectively, together with two minor products, the Kolbe dimer (4; R = H) and the ester (5). These products, too, were identified spectro-



scopically and by comparison with authentic samples (see later). The nature of the products is as expected. Two-electron oxidative decarboxylation is the predominant process, since the resultant cations are both allylic and benzylic, and the observed products (2), (3), and (5) arise by nucleophilic attack on the cations by the alcoholic solvent and in the case of (5) by the starting carboxylate anion; attack at the less hindered primary site is preferred in all cases. The isolated Kolbe dimers (4; R = H or CO₂Et) also correspond to coupling at the less hindered primary site.

Authentic samples of each isolated product were prepared by conventional chemical routes, which we now describe. It is clear from the multistep nature of the synthetic routes which had to be employed that the direct electrochemical synthesis is much more convenient for the preparation of the ethers (2; R¹ = CO₂Et, R² = Et), (2; R¹ = H, R² = Me), (3; R¹ = CO₂Et, R² = Et), and (2; R¹ = H, R² = Me).

3-Methoxy-3,3-diphenylpropene (3; R¹ = H, R² = Me) was prepared by methylation of 1,1-diphenylprop-2-en-1-ol, which was conveniently obtained by the action of vinylmagnesium bromide on benzophenone. 3-Methoxy-1,1-diphenylpropene (2; R¹ = H, R² = Me) was prepared by the action of methanolic sodium methoxide on 3-bromo-1,1-diphenylpropene; none of the isomeric ether (3; R¹ = H, R² = Me) was detected in this reaction. The ester (5) was prepared from 3,3-diphenylprop-2-enol, using *NN'*-dicyclohexylcarbodi-imide to effect coupling with 4,4-diphenylbut-3-enoic acid, after attempts using the acyl chloride had been unsuccessful. The 3,3-diphenylprop-2-enol was prepared by Bouveault-Blanc reduction of ethyl 3,3-diphenylpropenoate, after problems of

¹ Part 15, R. Brettle and J. R. Sutton, *J.C.S. Perkin I*, 1975, 1955.

² J. H. P. Utley in 'Technique of Electro-organic Synthesis, Part 1', ed. N. L. Weinberg, Wiley, New York, 1974, ch. VI.

³ W. S. Johnson and G. H. Daub, *Org. Reactions*, 1951, **6**, 1.

⁴ G. E. Hawkes, J. H. P. Utley, and G. B. Yates, *J.C.S. Chem. Comm.*, 1973, 305.

⁵ R. Brettle and D. Seddon, *J. Chem. Soc. (C)*, 1970, 2175.

partial reduction of the double bond had been encountered using lithium tetrahydridoaluminate as reductant.⁶ The Kolbe dimer (4; R¹ = CO₂Et) was prepared in good yield by coupling of ethyl 2-bromomethyl-3,3-diphenylpropenoate with tetracarbonylnickel. The necessary substituted allylic bromide was prepared by bromination with *N*-bromosuccinimide of ethyl 2-methyl-3,3-diphenylpropenoate, obtained by dehydration of the Reformatskii product from benzophenone and ethyl 2-bromopropanoate. Reaction of ethyl 2-bromomethyl-3,3-diphenylpropenoate with ethanolic sodium ethoxide gave the ether (2; R¹ = CO₂Et, R² = Et) uncontaminated with the isomeric ether (3; R¹ = CO₂Et, R² = Et).

The synthesis of (3; R¹ = CO₂Et, R² = Et) proved more difficult, but the following method was eventually successful, although the overall yield was low. When ethyl 2,3-epoxy-3,3-diphenylpropanoate was heated under reflux for 18.5 h with ethanol containing a small amount of concentrated sulphuric acid, and the product was worked up at room temperature, ethyl 3-ethoxy-2-hydroxy-3,3-diphenylpropanoate was formed by regio-specific opening of the oxiran ring in the expected direction; the reaction was not complicated by any acid-catalysed molecular rearrangement of the glycidic ester. The protons of the ethoxy-group at C-3 in ethyl 3-ethoxy-2-hydroxy-3,3-diphenylpropanoate give rise to an ABX₃ system in the ¹H n.m.r. spectrum. Oxidation of ethyl 3-ethoxy-2-hydroxy-3,3-diphenylpropanoate to ethyl 3-ethoxy-2-oxo-3,3-diphenylpropanoate was achieved in good yield by use of Collins reagent [chromium(vi) oxide-pyridine-dichloromethane] but cleavage to benzophenone occurred with chromium(vi) oxide-pyridine-acetic acid. Wittig methylenation of the α-oxo-ester then gave the ether (3; R¹ = CO₂Et, R² = Et). The yield, as in other cases⁷ of the reaction of α-oxo-esters with Wittig reagents, was quite low.

The synthesis of a monoether of a dihydroxy-ester from a glycidic ester is a convenient method which has apparently only once before been used;⁸ we record a third example of it, in the preparation of ethyl 3-ethoxy-2-hydroxy-2-methyl-3,3-diphenylpropanoate from ethyl 2,3-epoxy-2-methyl-3,3-diphenylpropanoate. Careful attention to the reaction conditions (see Experimental section) is necessary, as a minor alteration in the procedure causes a rearrangement to ethyl 2-oxo-3,3-diphenylbutanoate. In the ¹H n.m.r. spectrum of ethyl 3-ethoxy-2-hydroxy-2-methyl-3,3-diphenylpropanoate both ethyl groups behave as ABX₃ spin systems.

EXPERIMENTAL

¹H N.m.r. spectra were recorded with a Perkin-Elmer R12A or R34 instrument or a Varian HA 100 instrument for

⁶ R. Glenat and R. Heilman, *Bull. Soc. chim. France*, 1955, 1586.

⁷ H. O. House and G. H. Rasmusson, *J. Org. Chem.*, 1961, **26**, 4278; J. D. Edwards, jun., T. Mase, and T. Matsumoto, *J. Org. Chem.*, 1967, **32**, 244.

⁸ L. J. Dry and F. L. Warren, *J. S. African Chem. Inst.*, 1953, **6**, 14.

⁹ W. S. Johnson, J. W. Petersen, and W. P. Schneider, *J. Amer. Chem. Soc.*, 1947, **69**, 74.

solutions in CDCl₃, unless otherwise stated (Me₄Si as internal standard). In all cases integration agreed with assignments. I.r. spectra were measured with a Perkin-Elmer 137 or 457 instrument.

Light petroleum refers to the fraction having b.p. 60–80 °C, unless otherwise stated. Solutions in organic solvents were dried over anhydrous sodium sulphate unless otherwise stated.

Starting Materials and Reference Compounds.—1-Ethyl hydrogen 2-diphenylmethylenesuccinate, m.p. 123–124° (lit.,⁹ 123–124°), was prepared from benzophenone and diethyl succinate. 1-Methyl hydrogen 2-diphenylmethylenesuccinate, m.p. 129–130° [from benzene-light petroleum (b.p. 40–60 °C)], δ 3.54 (s, CH₂), 3.50 (s, CO₂Me), 7.29 (m, 2 × Ph), and 8.4 (s, CO₂H) (Found: C, 73.2; H, 5.5. C₁₈H₁₆O₄ requires C, 73.0; H, 5.4%), was similarly prepared (with Miss S. FRENCH) from benzophenone and dimethyl succinate, in 81% yield and converted into 4,4-diphenylbut-3-enoic acid, m.p. 115–116° (lit.,⁹ 115–116°), in 61% yield by a procedure analogous to that described⁹ for its preparation from 1-ethyl hydrogen 2-diphenylmethylenesuccinate. Ethyl 2-methyl-3,3-diphenylpropenoate, m.p. 86° (lit.,¹⁰ 87–88°), was prepared¹⁰ by dehydration of ethyl 3-hydroxy-2-methyl-3,3-diphenylpropanoate¹¹ with phosphoryl chloride. 1,1,6,6-Tetraphenylhexa-1,5-diene, m.p. 104–106° (lit.,¹² 108°), δ 2.26 (m, 2 × CH₂), 6.05 (m, 2 × CH), and 7.25 (s, 4 × Ph) was obtained by dehydration of 1,1,6,6-tetraphenylhexane-1,6-diol.¹²

3-Methoxy-3,3-diphenylpropene.—1,1-Diphenylprop-2-en-1-ol¹³ was prepared by the action of vinylmagnesium bromide on benzophenone in tetrahydrofuran and was separated from benzophenone by chromatography on activated alumina. It showed δ 2.52 (s, OH), 5.29–5.54 (m, CH₂), 6.43–6.68 (m, CH), and 7.93 (m, 2 × Ph). The alcohol (2.7 g, 0.013 mol) in dry tetrahydrofuran (100 ml) was treated with sodium hydride (0.32 g, 0.013 mol) followed by iodomethane (1.85 g, 0.013 mol) in dry tetrahydrofuran (25 ml). The mixture was stirred for 2 h at the ambient temperature, and then refluxed with stirring for 43 h. The crude product was placed on an alumina column. Elution with benzene-ether (9:1) gave 3-methoxy-3,3-diphenylpropene (2.0 g, 68%), b.p. 89° at 0.5 mmHg, ν_{\max} 3 000, 2 950, 2 820, 1 645, 1 600, 1 440, 1 310, 1 275, 1 210, 1 175, 1 070, 935, 925, and 700 cm⁻¹, δ 3.16 (s, OMe), 5.29–5.54 (m, CH₂), 6.43–6.68 (m, CH), and 7.2 (m, 2 × Ph) (Found: C, 85.4; H, 7.0. C₁₆H₁₆O requires C, 85.7; H, 7.1%).

1-Methoxy-3,3-diphenylpropene.—1-Bromo-3,3-diphenylpropene,¹⁴ m.p. 44–45° (lit.,¹⁴ 44–45°) (4.2 g, 0.0154 mol), was refluxed for 12 h with methanolic 1.85M-sodium methoxide (80 ml, 0.015 mol) under nitrogen. The solvent was distilled off at atmospheric pressure and the residue was diluted with water (100 ml) and extracted with ether (2 × 100 ml). The combined extracts were washed with water (3 × 100 ml) and dried. Distillation gave 1-methoxy-3,3-diphenylpropene (2.95 g, 85%), b.p. 149–150° at 0.4 mmHg, ν_{\max} 3 050, 2 920, 2 830, 1 490, 1 440, 1 375, 1 190, 1 110, 1 080, 1 030, 960, 920, and 700 cm⁻¹, δ 3.28 (s, OMe), 3.98

¹⁰ W. S. Johnson and A. Goldmann, *J. Amer. Chem. Soc.*, 1945, **67**, 430.

¹¹ J. F. J. Dippy and J. C. Parkins, *J. Chem. Soc.*, 1951, 1570; E. Bergmann and H. Weiss, *Annalen*, 1930, **480**, 64.

¹² M. Bouvet, *Bull. Soc. chim. France*, 1915[4], **17**, 202.

¹³ P. Martinet and H. Doupeux, *Compt. rend.*, 1964, **259**(14), 1224.

¹⁴ M. Charest, D. Herr, and R. H. Thomas, *J. Medicin. Chem.*, 1967, **10**, 627.

(d, J 7 Hz, CH_2) 6.34 (t, J 7 Hz, CH), and 7.25 (m, $2 \times \text{Ph}$) (Found: C, 85.5; H, 7.1. $\text{C}_{16}\text{H}_{16}\text{O}$ requires C, 85.7; H, 7.1%).

3,3-Diphenylprop-2-en-1-ol.—Ethyl 3,3-diphenylpropenoate,⁶ b.p. 152—156° at 0.1 mmHg (lit.,⁶ 157—158° at 3.0 mmHg), dissolved in dry ethanol (100 ml), was slowly treated with sodium (0.58 g, 0.025 g atom). The mixture was then refluxed with stirring for 1 h, until all the sodium had been consumed, and concentrated under diminished pressure. Water (100 ml) and ether (100 ml) were added, and the ether layer was separated. The aqueous layer was extracted with ether (100 ml) and the combined ethereal solutions were washed with water (2×100 ml) and dried (CaSO_4). Distillation gave 3,3-diphenylprop-2-en-1-ol (4.73 g, 90%), b.p. 148—153° at 0.5 mmHg (lit.,⁶ 153—155° at 0.3 mmHg).

3,3-Diphenylprop-2-enyl 4,4-Diphenylbut-3-enoate (5).—*NN'*-Dicyclohexylcarbodi-imide (0.865 g, 4.17 mmol) in ether (50 ml) was added to 4,4-diphenylbut-3-enoic acid (0.985 g, 4.17 mmol) and 3,3-diphenylprop-2-en-1-ol (0.875 g, 4.17 mmol) in dry ether (200 ml) dropwise, with stirring. Stirring was continued for 6 h, then *NN'*-dicyclohexylurea was filtered off and the solution was washed with *m*-hydrochloric acid (2×100 ml) and water (100 ml), and dried. Evaporation left a solid, which on crystallisation from trichloromethane–light petroleum afforded 3,3-diphenylprop-2-enyl 4,4-diphenylbut-3-enoate, m.p. 87.5—88.5°, δ 3.15 (d, J 7 Hz, $\text{CH}_2\cdot\text{CO}_2$), 4.63 (d, J 7 Hz, CH_2O), 6.24 (t, J 7 Hz, $\text{CH}\cdot\text{CH}_2\text{O}$), 6.15 (t, J 7 Hz, $\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2$), and 7.22 (m, $4 \times \text{Ph}$) [Found: C, 86.3; H, 6.3. $\text{C}_{31}\text{H}_{26}\text{O}_2$ requires C, 86.5; H, 6.05%].

Ethyl 2-Bromomethyl-3,3-diphenylpropenoate.—Ethyl 2-methyl-3,3-diphenylpropenoate (5.32 g, 0.02 mol), *N*-bromosuccinimide (3.56 g, 0.02 mol), and benzoyl peroxide (10 mg) were heated for 16 h in refluxing tetrachloromethane (150 ml). The mixture was cooled in ice, washed with water (3×100 ml), and dried. Evaporation left a solid, which on crystallisation from benzene–light petroleum gave the bromo-derivative (6.3 g, 94%), m.p. 105—106°, δ 0.88 (t, J 7 Hz, CH_2Me), 3.98 (q, J 7 Hz, CH_2Me), 4.27 (s, CH_2Br), and 7.27 (m, $2 \times \text{Ph}$) (Found: C, 62.5; H, 5.1; Br, 23.2. $\text{C}_{18}\text{H}_{17}\text{BrO}_2$ requires C, 62.6; H, 4.9; Br, 23.2%).

Ethyl 2-Ethoxymethyl-3,3-diphenylpropenoate.—A solution of the foregoing bromo-derivative (3.45 g, 0.01 mol) in ethanolic 0.24*M*-sodium ethoxide (50 ml, 0.012 mol) was refluxed for 18.5 h under nitrogen. The ethanol was distilled off, and the residue was treated with ether (100 ml). The solution was washed with water (3×100 ml) and the combined aqueous washings were extracted with ether (100 ml). The combined ethereal solutions were dried and evaporated. Distillation gave the ether (2; $\text{R}^1 = \text{CO}_2\text{Et}$, $\text{R}^2 = \text{Et}$) (2.75 g, 90%), b.p. 182—186° at 0.2 mmHg, δ 0.88 (t, J 3 Hz, $\text{CO}_2\cdot\text{CH}_2\text{Me}$), 1.19 (t, J 7 Hz, $\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\text{Me}$), 3.48 (q, J 7 Hz, $\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\text{Me}$), 3.98 (q, J 7 Hz, $\text{CO}_2\cdot\text{CH}_2\text{Me}$), 4.19 (s, $\text{CH}_2\cdot\text{OEt}$), and 7.28 (m, $2 \times \text{Ph}$) (Found: C, 77.5; H, 7.0. $\text{C}_{20}\text{H}_{22}\text{O}_3$ requires C, 77.4; H, 7.1%).

Ethyl 3-Ethoxy-2-hydroxy-3,3-diphenylpropenoate.—A solution of ethyl 2,3-epoxy-3,3-diphenylpropenoate¹⁵ (10 g) in ethanol (100 ml) containing concentrated sulphuric acid (0.5 ml) was refluxed for 18 h. The solution was evaporated to ca. 25 ml at room temperature, and diluted with water

(100 ml). The organic layer was separated, and the aqueous layer extracted with ether (2×100 ml). The combined ethereal layers were washed with saturated aqueous sodium hydrogen carbonate (50 ml) and water (100 ml), and dried. Removal of the solvents left a solid which on crystallisation from light petroleum gave ethyl 3-ethoxy-2-hydroxy-3,3-diphenylpropenoate, m.p. 58—59°, δ (CDCl_3) 1.13 (t, J 7 Hz, $\text{CO}_2\cdot\text{CH}_2\text{Me}$ and X_3 of AMX_3 system, $\text{O}\cdot\text{CH}_2\text{Me}$) [δ (C_6D_6) 0.87 (t, J 7 Hz, Me) and 1.07 (t, J 7 Hz, Me)], 2.97 (d, J 8 Hz, OH, exchangeable), 3.1—3.55 (m, AB of ABX_3 system, $\text{O}\cdot\text{CH}_2\text{Me}$), 4.07 (q, J 7 Hz, $\text{CO}_2\cdot\text{CH}_2\text{Me}$), 5.14 (d, J 8 Hz, CHOH), and 7.29 (m, $2 \times \text{Ph}$) (Found: C, 72.7; H, 7.1. $\text{C}_{18}\text{H}_{22}\text{O}_4$ requires C, 72.9; H, 7.0%).

Ethyl 3-Ethoxy-2-oxo-3,3-diphenylpropenoate.—Ethyl 3-ethoxy-2-hydroxy-3,3-diphenylpropenoate (6.24 g, 0.02 mol) in dichloromethane (20 ml) was added with stirring during 15 min to a solution of chromium(vi) oxide (12.0 g, 0.12 mol) and pyridine (19.0 g, 0.24 mol) in dichloromethane (300 ml). Stirring was continued for a further 15 min. The liquid portion was decanted, and the residue washed with ether (100 ml). The combined organic solutions were washed with aqueous 5% sodium hydroxide (150 ml) and saturated aqueous sodium hydrogen carbonate (50 ml) and dried. Evaporation left a mixture, from which ethyl 3-ethoxy-2-oxo-3,3-diphenylpropenoate (4.9 g, 78%), δ 0.99 (t, J 7 Hz, $\text{CO}_2\cdot\text{CH}_2\text{Me}$), 1.06 (t, J 7 Hz, $\text{O}\cdot\text{CH}_2\text{Me}$), 3.03 (q, J 7 Hz, $\text{O}\cdot\text{CH}_2\text{Me}$), 4.03 (q, J 7 Hz, $\text{CO}_2\cdot\text{CH}_2\text{Me}$), and 7.20 (m, $2 \times \text{Ph}$) (Found: C, 72.75; H, 6.4. $\text{C}_{19}\text{H}_{20}\text{O}_4$ requires C, 73.1; H, 6.4%).

Ethyl 2-[Ethoxy(diphenyl)methyl]prop-2-enoate.—Methyltriphenylphosphonium bromide (3.4 g, 9.0 mmol) in dimethyl sulphoxide (30 ml) was added to sodium methylsulphinylmethanide [from sodium hydride (0.24 g, 0.01 g atom) in dimethyl sulphoxide (30 ml)] and the mixture was stirred for 2 h at room temperature. The resultant solution was then added, under nitrogen, to ethyl 3-ethoxy-2-oxo-3,3-diphenylpropenoate (3.1 g, 0.01 mol) in dimethyl sulphoxide (25 ml). Subsequently the mixture was stirred for 3 h at room temperature and then heated at 120 °C for 6 h, cooled, and poured into cold water (100 ml). The organic layer was separated, the aqueous layer was extracted with ether (100 ml), and the combined organic solutions were washed with water (100 ml) and dried. Evaporation, and filtration of the residue, in light petroleum, through a short alumina column, gave an oil (2.3 g). Preparative t.l.c. on silica plates, developed with benzene, gave the ether (3; $\text{R}^1 = \text{CO}_2\text{Et}$, $\text{R}^2 = \text{Et}$) (0.15 g, 5%) as an oil, δ 1.03 (t, J 7 Hz, $\text{CO}_2\cdot\text{CH}_2\text{Me}$), 1.15 (t, J 7 Hz, $\text{O}\cdot\text{CH}_2\text{Me}$), 3.09 (q, J 7 Hz, $\text{O}\cdot\text{CH}_2\text{Me}$), 3.97 (q, J 7 Hz, $\text{CO}_2\cdot\text{CH}_2\text{Me}$), 6.24 (d, J 2 Hz, HCH), 6.43 (d, J 2 Hz, HCH), and 7.30 (m, $2 \times \text{Ph}$) (Found: C, 77.6; H, 7.4. $\text{C}_{20}\text{H}_{22}\text{O}_3$ requires C, 77.4; H, 7.1%).

Diethyl 2,5-Bisdiphenylmethylenhexanedioate.¹⁶—A stirred solution of ethyl 2-bromomethyl-3,3-diphenylpropenoate (3.45 g, 10 mmol) in 1,2-dimethoxyethane (50 ml) at 50 °C under argon was treated over 25 min with tetracarbonylnickel (2.34 g, 14 mmol). The mixture was kept at 50 °C for a further 6 h and then diluted with ether (100 ml). The excess of tetracarbonylnickel and ether were distilled off at water-pump pressure. The residue was shaken with ether (100 ml) and the undissolved solid collected on a filter and

¹⁵ F. F. Blicke and J. A. Faust, *J. Amer. Chem. Soc.*, 1954, **76**, 316.

¹⁶ Cf. M. F. Semmelhack, Ph.D. Thesis, Harvard University, 1967, p. 96.

then washed with trichloromethane (100 ml). The ether and trichloromethane solutions were combined and evaporated. Extraction of the solid residue with hot light petroleum removed unchanged bromo-derivative. Crystallisation of the remaining material from trichloromethane-light petroleum gave the *diester* (1.1 g, 80%), m.p. 201–203°, δ 0.84 (t, J 7 Hz, $2 \times \text{Me}$), 2.58 (s, $2 \times \text{CH}_2$), 3.88 (q, J 7 Hz, $2 \times \text{CH}_2\text{Me}$), and 7.29 (m, $4 \times \text{Ph}$) (Found: C, 81.3; H, 6.4. $\text{C}_{36}\text{H}_{34}\text{O}_4$ requires C, 81.5; H, 6.7%).

Electrolysis of 1-Ethyl Hydrogen 2-Diphenylmethylene-succinate.—The half-ester (9.3 g, 0.03 mol) was neutralised with ethanolic 0.075M-sodium ethoxide (400 ml, 0.03 mol) and the solution was electrolysed for 2.4 h at 23 °C. The undivided cell⁵ had a platinum anode (10 cm² in area) and a mercury pool cathode. The applied potential was 100 V and the current, initially 2.5 A, had fallen to a low steady value at the end of the electrolysis. The solution was then neutralised with acetic acid, and the ethanol removed at water-pump pressure and room temperature. The residue was diluted with water (100 ml) and extracted with ether (200 ml). The ethereal solution was extracted with aqueous 2M-sodium hydroxide, which removed the starting half-ester (5.4 g). The ethereal solution was washed with water (100 ml), dried, and evaporated, to give the neutral products (4.9 g), from which a solid slowly separated. Further material was precipitated by addition of ether. The solid (0.29 g) was collected and crystallised from trichloromethane-light petroleum, to give diethyl 2,5-bis-diphenylmethylenehexanedioate, m.p. 200–203°, identical (i.r. and n.m.r. data) with an authentic sample. The two major products from the remaining material were isolated by preparative t.l.c. (silica plates; benzene) of a part (1.20 g) of the material. The ethers (2; $\text{R}^1 = \text{CO}_2\text{Et}$, $\text{R}^2 = \text{Et}$) (810 mg, 69%) and (3; $\text{R}^1 = \text{CO}_2\text{Et}$, $\text{R}^2 = \text{Et}$) (140 mg, 12%) were isolated in this way and identified (t.l.c. and i.r. and n.m.r. data) by comparison with authentic samples.

Electrolysis of 4,4-Diphenylbut-3-enoic Acid.—4,4-Diphenylbut-3-enoic acid (17.85 g, 0.075 mol) was neutralised with methanolic 0.188M-sodium methoxide (400 ml, 0.075 mol) and the solution was then electrolysed for 3.7 h in the cell described above. A work-up similar to that described for the previous electrolysis recovered 4,4-diphenylbut-3-enoic acid (5.2 g) and gave a mixture (12.4 g) of neutral products. A part of this (9.7 g) was distilled, and a fraction (6.6 g), b.p. 128–150° at 0.4 mmHg, was collected; the residue was retained. The distillate (1.0 g) was then separated into 3-methoxy-1,1-diphenylpropene (0.72 g) and 3-methoxy-3,3-diphenylpropene (0.27 g) by chromatography in benzene on an alumina column; the ethers were identified by comparison (t.l.c. and i.r. and n.m.r. data) with authentic samples. Repeated preparative t.l.c. (silica plates; benzene) of the residue from the distillation gave samples of 1,1,6,6-tetraphenylhexa-1,5-diene and 3,3-diphenylprop-2-enyl 4,4-diphenylbut-3-enoate which were identical (t.l.c. and i.r. and n.m.r. data) with authentic samples.

Ethyl 2,3-Epoxy-2-methyl-3,3-diphenylpropanoate.—A mixture of benzophenone (18.2 g, 0.1 mol) and ethyl 2-chloropropanoate (27 g, 0.2 mol) in dry ether (50 ml) was

added to sodium ethoxide (13.6 g, 0.2 mol) at 0–5 °C at such a rate as to keep the temperature below 5 °C. The mixture was then stirred at room temperature under nitrogen for 12 h. The solvent was distilled off and the residue was heated at 100 °C for 6 h with stirring. The material was then cooled to 0 °C and poured into ether (100 ml) and ice-cold water (100 ml). The ether layer was separated, and the aqueous layer was extracted with ether (2×100 ml). The combined ethereal solutions were washed with aqueous 5% sodium hydrogen carbonate (2×100 ml) and dried. Evaporation left an oil which solidified on cooling in liquid nitrogen. Crystallisation gave *ethyl 2,3-epoxy-2-methyl-3,3-diphenylpropanoate* (22.3 g, 79%), m.p. 45–46°, δ 0.84 (t, J 7 Hz, $\text{CO}_2\text{CH}_2\text{Me}$), 1.41 (s, tert. Me), 3.87 (q, J 7 Hz, $\text{CO}_2\text{CH}_2\text{Me}$), and 7.29 (m, $2 \times \text{Ph}$) (Found: C, 76.4, H, 6.2. $\text{C}_{18}\text{H}_{18}\text{O}_3$ requires C, 76.6; H, 6.4%).

Ethyl 3-Ethoxy-2-hydroxy-2-methyl-3,3-diphenylpropanoate.—Ethyl 2,3-epoxy-2-methyl-3,3-diphenylpropanoate (10 g) was dissolved in ethanol (100 ml) containing concentrated sulphuric acid (0.5 ml). The solution was refluxed for 18 h, then concentrated to ca. 25 ml under reduced pressure at room temperature, and diluted with water (100 ml). The organic phase was separated, and the aqueous layer extracted with ether (2×100 ml). The combined organic material was washed with saturated aqueous sodium hydrogen carbonate (50 ml) and water (100 ml) and dried. Evaporation gave a solid, which on crystallisation from light petroleum afforded *ethyl 3-ethoxy-2-hydroxy-2-methyl-3,3-diphenylpropanoate*, m.p. 82–83°, δ 0.90 (t, J 7 Hz, OCH_2Me), 1.12 (t, J 7 Hz, $\text{CO}_2\text{CH}_2\text{Me}$), 1.54 [s, $\text{C}(\text{OH})\text{Me}$], 2.6–3.4 (m, AB of ABX_3 system, OCH_2Me), 3.4–4.2 (m, AB of ABX_3 system, $\text{CO}_2\text{CH}_2\text{Me}$), 4.56 (s, OH, exchangeable), and 7.29 (m, $2 \times \text{Ph}$) (Found: C, 73.4; H, 7.4. $\text{C}_{20}\text{H}_{24}\text{O}_2$ requires C, 73.1; H, 7.3%).

Ethyl 2-Oxo-3,3-diphenylbutanoate.—Ethyl 2,3-epoxy-2-methyl-2,3-diphenylpropanoate (5 g) was dissolved in ethanol (100 ml) containing concentrated sulphuric acid (0.5 ml) and the solution was refluxed for 2 h. The solution was evaporated under reduced pressure at 80 °C and the residue, on cooling, dissolved in ether (200 ml). The ethereal solution was washed with saturated aqueous sodium hydrogen carbonate (50 ml) and water (100 ml) and dried. Distillation gave ethyl 2-oxo-3,3-diphenylbutanoate¹⁷ (4.0 g, 79%), b.p. 120–124° at 0.005 mmHg, δ 1.14 (t, J 7 Hz, $\text{CO}_2\text{CH}_2\text{Me}$), 2.12 (s, Ph_2CMe), 4.19 (q, J 7 Hz, $\text{CO}_2\text{CH}_2\text{Me}$), and 7.27 (m, $2 \times \text{Ph}$) (Found: C, 76.95; H, 6.6. Calc. for $\text{C}_{18}\text{H}_{18}\text{O}_4$: C, 76.6; H, 6.4%).

We thank Mr. J. A. Gunn for some preliminary experiments, the Commonwealth Scholarship and Fellowship Plan for a maintenance award (to F. M. B.), and Professor E. J. Corey for supplying some experimental details concerning the coupling of allylic halides with tetracarbonylnickel.

[7/276 Received, 15th February, 1977]

¹⁷ J. Kagan and D. A. Agdeppa, jun., *Helv. Chim. Acta*, 1972, 55, 2255.