# Synthesis of 2-Benzylcyclobuta[a]naphthalene-1-carboxylic Acid

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Syntheses of 3-benzyl-2,3-dihydrobenz[e]inden-1-one and the title compound are described, but attempts to convert the latter into a derivative of dibenzo[a,h]biphenylene were unsuccessful. The dehydration of 3-hydroxy-3-(2-naphthyl)-4-phenylbutanoate yields both the expected unsaturated acid and 2-(2-naphthyl)-1-phenylpropene, the latter possibly by a fragmentation reaction. Some statements in the literature about benzyl 1-naphthyl ketone have been corrected.

BENZYL 2-NAPHTHYL KETONE, prepared from naphthalene and phenylacetyl chloride in nitrobenzene with aluminium trichloride, underwent the Reformatsky reaction with ethyl bromoacetate to give ethyl 3-hydroxy-3-(2-naphthyl)-4-phenylbutanoate (I; R = Et), m.p. 79°, dehydration of which afforded the unsaturated ester (II; R = Et). The position of the double bond in (II; R = Et) was established by preparing the ester by the Wittig reaction between benzyl 2-naphthyl ketone and diethyl (ethoxycarbonylmethyl)phosphonate anion. It is known that the Wittig reaction yields unsaturated products without migration of the double bond.

(I)   (II)

(III)
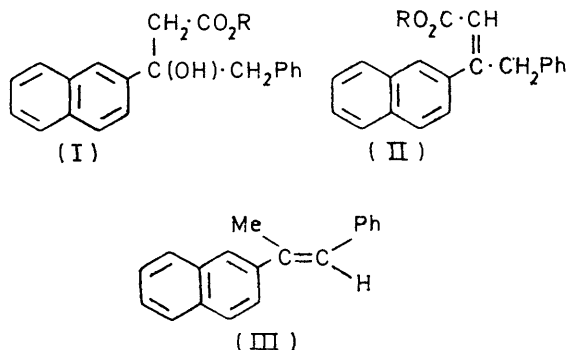
The Z-configuration of the ester (II; R = Et) was indicated by further study of the products of the foregoing Wittig reaction, carried out in 1,2-dimethoxyethane. The crystalline ester, m.p. 79°, was obtained along with an oil whose n.m.r. spectrum showed that it was probably a mixture of Z- and E-isomers. Whereas the crystalline compound showed a methylene signal at τ 6·2 the oily mixture showed two singlets at τ 6·2 and 5·4. In the E-isomer the ethoxycarbonyl and benzylic groups are cis to one another and a deshielding effect of the carbonyl group on the methylene group is to be expected.[1]

Treatment of the hydroxy-acid (I; R = H) with 50% sulphuric acid gave a low yield of the unsaturated acid (II; R = H) and a high yield of (E)-2-(2-naphthyl)-1-phenylpropene (III); with formic acid only the hydrocarbon resulted. The structure (III) was established mainly by the n.m.r. spectrum, which showed three

methyl protons at τ 7·69 and an olefinic proton at 3·06. Expansion of the spectrum showed the former signal to be a doublet and the latter a quartet, the result of allylic coupling of the methyl group and the olefinic proton,[3] the bulky aryl groups as expected lying trans to one another. The constitution (III) of the hydrocarbon was confirmed by its formation from 2-acetylnaphthalene and benzylidenetriphenylphosphorane, and from dehydration of the product obtained by the interaction of benzyl 2-naphthyl ketone and methylmagnesium iodide. The configurational assignment was supported by the stability of the hydrocarbon in acetic acid containing a trace of hydrobromic acid.[3]

The m.p. of the hydrocarbon (III) is the same as that reported for the corresponding 1-naphthyl compound, stated to be obtained by dehydration of the product from benzyl 1-naphthyl ketone and methylmagnesium iodide.[4] Repetition of this preparation was attempted, care being taken to use pure benzyl 1-naphthyl ketone,[5] but in spite of many attempts no reaction took place and it is probable that the previous workers[4] used a mixture of benzyl 1- and 2-naphthyl ketones in which only the latter reacted to give the hydrocarbon (III). The steric hindrance already noted is reflected in the inertness of 1-acetylnaphthalene towards benzylmagnesium bromide and towards triphenylbenzylidenephosphorane, although it undergoes the Reformatsky reaction.

The formation of the hydrocarbon (III) presents points of interest. It is known that αβ- and βγ-unsaturated carboxylic acids undergo decarboxylation,[6] but our αβ-unsaturated acid (II; R = H), on treatment with formic acid, underwent no change. The formation of the hydrocarbon could be the result of fragmentation,[7] in which formation of a carbonium ion is accompanied by decarboxylation[8] (see Scheme). The formation of the stilbene derivative instead of a styrene derivative involves rearrangement; similar rearrangements are known.[2] The dehydration by formic acid of 3-hydroxy-3,4-diphenylbutanoic acid (IV) and of 3-hydroxy-3,3-diphenyl-propionic acid (V) likewise gives (E)-α-methylstilbene (VI) and 1,1-diphenylethylene (VIII), respectively, in good yield.
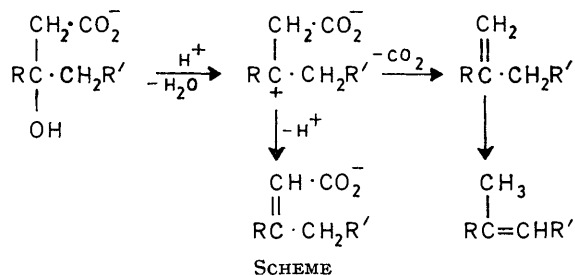
[1] H. J. Tumlinson, R. C. Gueldner, D. D. Hardee, A. C. Thomson, P. A. Hedin, and J. P. Minyard, J. Org. Chem., 1971, 36, 2616.

[2] Cf. I. Ho and J. G. Smith, Tetrahedron, 1970, 26, 4277.

[3] Cf. E. Ellingboe and R. C. Fuson, J. Amer. Chem. Soc., 1933, 55, 2964.

[4] J. W. Cook and R. A. F. Galley, J. Chem. Soc., 1931, 2012.

[5] J. W. Cook and C. L. Hewett, J. Chem. Soc., 1934, 376; G. Lock, Monatsh., 1943, 74, 77.

[6] D. S. Noyce, P. A. King, and G. L. Woo, J. Org. Chem., 1961, 26, 632.

[7] C. A. Grob and P. W. Schiess, Angew. Chem. Internat. Edn., 1967, 6, 1.

[8] Cf. D. S. Noyce and R. A. Heller, J. Amer. Chem. Soc., 1965, 87, 4325.

Reduction of the unsaturated acid (II; R = H) followed by ring closure gave 3-benzyl-2,3-dihydrobenzo[e]inden-1-one (VIII), the structure of which was

$$CH_2 \cdot CO_2^-$$
$$RC \cdot CH_2R' \xrightarrow[-H_2O]{H^+} RC \cdot CH_2R' \xrightarrow{-CO_2} RC \cdot CH_2R'$$
$$OH$$

$$\downarrow -H^+$$

$$CH \cdot CO_2^-$$
$$RC \cdot CH_2R'$$

$$CH_3$$
$$RC=CHR'$$

SCHEME

established by its mass spectral fragmentation pattern. The most abundant ions in addition to the molecular ion (m/e 272) were readily accounted for by loss of a benzyl (i.e. tropylium) ion giving a peak at 181 (M^+ −91) as well

$$PhCH_2 \cdot C(OH) \cdot CH_2 CO_2H \longrightarrow$$
$$Ph$$

$$\begin{matrix} Ph & Me \\ C=C \\ H & Ph \end{matrix}$$

(IV)   (VI)

$$Ph_2C(OH) \cdot CH_2 \cdot CO_2H \longrightarrow Ph_2C=CH_2$$

(V)   (VII)
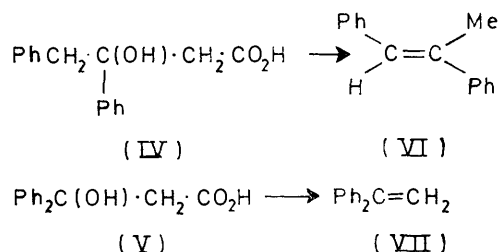
as peaks at 152 [M^+ −91 − 29(CHO)] and 91 (M^+ −181). This was confirmed by the i.r. spectrum, which showed the characteristics of a 1,2-disubstituted naphthalene,

(VIII)   (IX)

(X)
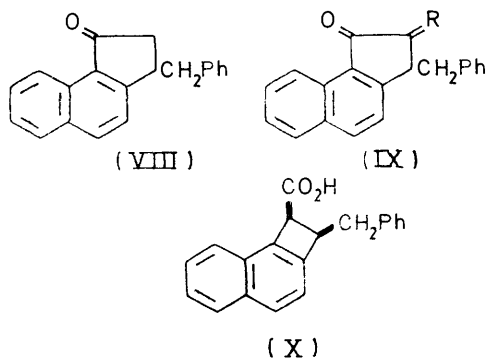
particularly in the finger-print region with the highly characteristic 830 cm^{-1} CH bending of the adjacent hydrogen C-4 and C-5 atoms, and by the n.m.r. spectrum with a signal at τ 0·85 characteristic of the deshielded 9-proton in the *peri*-position.[9]

Treatment of the ketone (VIII) with nitrous acid gave the hydroxyimino-ketone (IX; R = N·OH), which was converted by alkaline chloramine into the diazoketone (IX; R = N$_2$). It is known that such α-diazoketones undergo a Wolff rearrangement and concomitant ring contraction when subjected in aqueous media to u.v. irradiation,[10] and it was expected that the diazo-

ketone (IX; R = N$_2$) would thus yield the cyclobutanaphthalenecarboxylic acid (X). However, irradiation of the diazo-ketone in aqueous tetrahydrofuran gave only a low yield of the cyclobutanaphthalene (X), the structure of which was confirmed by a weak i.r. cyclobutene band at 1000 cm^{-1}. Efforts to ring-close the acid with hydrogen fluoride were unsuccessful, the resulting mixture of products containing none of the desired ketone as shown by the lack of a peak at m/e 270 in the mass spectrum. This was disappointing since the cis-configuration of the cyclobutene ring necessary for ring closure is indicated by the coupling constant of the methine protons (2·3 Hz).[11]

The n.m.r. spectra of the hydroxyimino-ketone and the diazo-ketone present points of interest. In [$^2H_6$]acetone the methine and methylene protons of the former gave an AB$_2$ pattern [τ 5·38 (1H, t, CH) and 6·4 (2H, d, CH$_2$)]. The diazo-ketone, on the other hand, showed an ABX spectrum of three unsymmetrical quartets [H$_X$ τ 4·5, H$_A$ τ 6·5, H$_B$ τ 7·1 (J_{AX} 5·4, J_{BX} 9·2, J_{AB} 13·5 Hz)]. Clearly the two methylene protons are non-equivalent, showing a geminal coupling constant larger than the vicinal constants, which are themselves unequal. This non-equivalence of the methylene protons can be attributed to the differential deshielding provided by the highly polar diazo-group. The hydroxyimino-group exerts no such influence.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and chromatographic purification was effected on alumina (Spence grade H). I.r. spectra were measured for Nujol suspensions unless otherwise indicated, u.v. spectra for solutions in ethanol. ^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R10 (60 MHz) or a Varian HA 100 spectrometer for solutions in deuteriochloroform unless otherwise indicated. Molecular weights were obtained with an A.E.I.-G.E.C. MS 902 mass spectrometer. Photochemical reactions were carried out with a Hanovia 1L photochemical reactor (medium-pressure mercury vapour arc, emitting mainly at 254, 265, 297, 313, and 366 nm). Quartz arc tubes gave 80% transmission down to 185 nm through a thickness of 1 mm of quartz.

3-Hydroxy-3-(2-naphthyl)-4-phenylbutanoic Acid (I; R = H).—Benzyl 2-naphthyl ketone [12] (123 g) in sodium-dried benzene (2 l) was added to ethyl bromoacetate (83·5 g) in benzene (500 ml). A portion (100 ml) of this solution was boiled, and zinc wool (35·0 g) and iodine (trace) were added. A vigorous reaction set in and the remainder of the ketonic solution was added at a rate sufficient to maintain boiling; otherwise a good yield was not obtained. After further boiling (2 h) the solution was cooled and decomposed with 2N-sulphuric acid. The dried (MgSO$_4$) layer was evaporated to give *ethyl 3-hydroxy-3-(2-naphthyl)-4-phenylbutanoate* (I; R = Et), needles (from ethanol) (131 g), m.p. 79° (Found: C, 79·05; H, 6·7%; M, 334. C$_{22}$H$_{22}$O$_3$ requires C, 79·0; H, 6·6%; M, 334), $\nu_{max.}$ 3500m (OH), 1705s (ester CO), and 1040m cm^{-1} (ester

[9] G. O. Dudek, *Spectrochim. Acta*, 1963, **19**, 691.
[10] L. Horner, W. Kirmse, and K. Muth, *Chem. Ber.*, 1958, **91**, 430.
[11] G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Gava, *Tetrahedron*, 1964, **20**, 1179.
[12] N. P. Buu-Hoï, N. Hoan, and P. Jacquignon, *J. Chem. Soc.*, 1951, 1381.

C–O); τ 2·1—3·2 (12H, m, Ar), 5·4br (1H, OH, removed by shaking with D$_2$O), 6·1 (2H, q, O·CH$_2$), 6·5—7·4 (4H, m, 2CH$_2$), and 7·0 (3H, t, CH$_3$). Hydrolysis with sodium hydroxide followed by acidification gave the *acid*,^{f} crystals (from ethanol), m.p. 156° (Found: C, 78·5; H, 5·9%; *M*, 306. C$_{20}$H$_{18}$O$_3$ requires C, 78·4; H, 5·9%; *M*, 306), ν$_{max.}$ 3490m (OH) and 1690 cm^{-1} (carboxy CO); τ 2·0—3·1 (12H, m, Ar) and 6·5—7·4 (4H, m, 2CH$_2$); *methyl ester*, m.p. 104° (Found: C, 83·4; H, 5·9%; *M*, 302. C$_{21}$H$_{18}$O$_2$ requires C, 83·4; H, 6·0%; *M*, 302), ν$_{max.}$ 3500 (OH) and 1705s cm^{-1} (ester CO). Admixture with the unsaturated methyl ester described later resulted in a large m.p. depression. The analytical and molecular weight figures show that the hydroxy-ester when dried or volatilised is readily converted into the unsaturated ester.

3-(2-*Naphthyl*)-4-*phenylbut*-2-*enoic Acid* (II; R = Et).— The foregoing ethyl ester was boiled with formic acid (1 h); the acid was then removed by evaporation. The residue yielded *ethyl* 3-(2-*naphthyl*)-4-*phenylbut*-2-*enoate* (95%), needles (from ethanol), m.p. 79° (Found: C, 83·5; H, 6·2%; *M*, 316. C$_{22}$H$_{20}$O$_2$ requires C, 83·5; H, 6·4%; *M*, 316), ν$_{max.}$ 1715 cm^{-1} (αβ-unsaturated ester CO); τ 2·0—2·9 (12H, m, Ar and 1H, olefinic), 5·9 (2H, q, CH$_2$), 6·2 (2H, s, CH$_2$), and 8·8 (3H, t, CH$_3$). Hydrolysis yielded the *acid*, m.p. 157° (Found: C, 83·2; H, 5·6%; *M*, 288. C$_{20}$H$_{16}$O$_2$ requires C, 83·3; H, 5·6%; *M*, 288), ν$_{max.}$ 1695s cm^{-1} (unsat. carboxylic CO); λ$_{max.}$ 211, 225, 250, 265, and 298 nm (log ε 4·61, 4·64, 4·63, 4·53, and 4·43); τ 0·3 (1H, CO$_2$H), 2·1—3·0 (13H, m, Ar), and 6·2 (2H, s, CH$_2$); *methyl ester*, m.p. 107° (Found: C, 83·5; H, 5·9%; *M*, 302. C$_{21}$H$_{18}$O$_2$ requires C, 83·4; H, 6·0%; *M*, 302); λ$_{max.}$ 210, 224, 263, and 297 nm (log ε 4·53, 4·55, 4·56, and 4·34); ν$_{max.}$ 1715s cm^{-1} (ester CO); τ 2·0—2·9 (13H, m, Ar), 6·2 (2H, s, CH$_2$), and 6·4 (3H, s, CH$_3$).

The ethyl ester was also prepared by the interaction of diethyl (ethoxycarbonylmethyl)phosphonate anion, prepared from triethyl phosphite (16·6 g), ethyl bromoacetate (16·7 g), and sodium hydride (4·8 g, 50% oil suspension) in dimethylformamide (40 ml), and benzyl 2-naphthyl ketone (12·3 g) in dimethylformamide (50 ml). The mixture was kept overnight and when worked up yielded the ester, m.p. 79°. When the reaction was repeated in 1,1-dimethoxyethane as solvent, the crystalline ester was accompanied by an oil, hydrolysis of which yielded a mixture, presumably of the *cis*- and *trans*-unsaturated acids.

3-(2-*Naphthyl*)-4-*phenylbutanoic Acid*.—The unsaturated ester, m.p. 79°, or the oily ester mixture was hydrogenated in ethanol at room temperature and atmospheric pressure over 10% palladised charcoal to yield *ethyl* 3-(2-*naphthyl*)-4-*phenylbutanoate*, m.p. 38° (from ethanol) (Found: C, 82·6; H, 7·0. C$_{22}$H$_{22}$O$_2$ requires C, 83·0; H, 7·0%), ν$_{max.}$ 1735 cm^{-1} (ester CO). Hydrolysis yielded the *acid*, m.p. 143° (Found: C, 82·7; H, 6·6. C$_{20}$H$_{18}$O$_2$ requires C, 82·7; H, 6·25%); *methyl ester*, m.p. 73° (Found: C, 82·9; H, 6·6. C$_{21}$H$_{20}$O$_2$ requires C, 82·9; H, 6·6%), ν$_{max.}$ 1740 cm^{-1} (ester CO).

3-*Benzyl*-2,3-*dihydrobenz[e]inden*-1-*one* (VIII).—The foregoing acid (10 g) was kept for 4 h in hydrogen fluoride (150 ml), which was then allowed to evaporate. The residue was treated with sodium carbonate and extracted with chloroform. Evaporation of the extract gave the *benzindenone* (7·2 g), needles (from ether), m.p. 126·5° (Found: C, 87·9; H, 5·8%; *M*, 272. C$_{20}$H$_{16}$O requires C, 88·2; H, 5·9%; *M*, 272·3), λ$_{max.}$ 215, 220, 226, 232, 240, 248, 270, 295, 307, 315, and 329 nm (log ε 4·69, 4·65, 4·59, 4·55, 4·50,

4·42, 3·33, 3·85, 3·97, 3·92, and 3·74), ν$_{max.}$ 1685s (ketonic CO), 875, 830, 790, 740, and 670 cm^{-1}; τ 0·85 (1H, q, *peri*-H), 1·9—3·0 (10H, m, Ar), 6·3 (1H, m, CH), and 6·6— 7·8 (4H, m, 2CH$_2$). Inverse Friedel–Crafts and polyphosphoric acid cyclisations were much less effective. To the ketone (3·0 g) in warm ethanol (50 ml) and concentrated hydrochloric acid (2 ml), n-butyl nitrite (4·0 g) was added dropwise with stirring. After 1 h more nitrite (4·0 g) and acid (2 ml) were added. On cooling, 3-*benzyl*-2,3-*dihydro*-2-*hydroxyiminobenz[e]inden*-1-*one* (IX; R = N·OH) (2·75 g) separated; m.p. 210—211° (decomp.) (Found: C, 79·3; H, 4·8; N, 4·3%; *M*, 301. C$_{20}$H$_{15}$NO$_2$ requires C, 79·7; H, 5·0; N, 4·65%; *M*, 301), ν$_{max.}$ 3550w, 3250m (oxime OH), and 1690s cm^{-1} (CO), τ[(CD$_3$)$_2$CO] 1·0 (1H, s, *peri*-H), 1·8—3·07 (10H, m, Ar), 5·38 (1H, t, CH), and 6·4 (2H, d, CH$_2$).

2-*Benzylcyclobuta[a]naphthalene*-1-*carboxylic Acid* (X).— The finely powdered oxime (1·0 g) was added to 2N-sodium hydroxide (100 ml) at 0° containing sodium hypochlorite (12—14% w/v; 5·4 ml) and concentrated ammonia (1·3 ml). The suspension was stirred at 0° for 4 h and more sodium hypochlorite (5·4 ml) and ammonia (1·3 ml) were added. After 12 h the solid which had separated was washed with water and dissolved in ether. The dried (Na$_2$SO$_4$) solution on evaporation gave 3-*benzyl*-2-*diazo*-2,3-*dihydrobenz[e]inden*-1-*one* (IX; R = N$_2$), yellow plates (0·78 g) (from benzene–light petroleum), m.p. 159—160° (decomp.) (Found: C, 80·5; H, 4·5; N, 9·0. C$_{20}$H$_{24}$N$_2$O requires C, 80·5; H, 4·7; N, 9·4%), *m/e* 270 (loss of N$_2$); ν$_{max.}$ 2100s (C=N$_2$) and 1650s cm^{-1} (CO); λ$_{max.}$ 213, 216, 248, 255, 333, 342, and 352 nm (log ε 4·69, 4·68, 4·47, 4·41, 4·17, 4·21, and 4·14); τ 0·8 (1H, q, *peri*-H), 1·95—2·9 (10H, m, Ar), 4·5 (1H, dd CH), 6·5 (1H, dd, HC*H*), and 7·1 (1H, dd, *H*CH).

The diazo-ketone (1·0 g) was irradiated (15 h) in tetrahydrofuran (200 ml) to which had been added sodium carbonate (2·0 g) in water (40 ml). Water (25 ml) was added and the tetrahydrofuran was removed under reduced pressure. The oily product was dissolved in chloroform and shaken with sodium hydrogen carbonate (twice). Acidification and crystallisation of the product from benzene–light petroleum gave the *acid* as fine needles (0·1 g), m.p. 135° (Found: C, 83·1; H, 5·4%; *M*, 288. C$_{20}$H$_{16}$O$_2$ requires C, 83·3; H, 5·6%; *M*, 288), ν$_{max.}$ 3500w (sharp, free OH), 3000 (broad, bonded OH), and 1690s cm^{-1} (carboxylic CO); λ$_{max.}$ 210, 230, 270, 275, 279, 290, 301, 315, 323, and 333 nm (log ε 4·50, 4·88, 5·16, 5·15, 5·17, 5·07, 4·65, 4·60, 4·70, and 4·29); τ 0·4 (1H, CO$_2$H), 2·0—3·0 (11H, m, Ar), 5·3 (1H. d, CH), 5·8 (1H, m, CH), 6·6 (1H, dd, HC*H*), and 7·2 (1H, dd, HC*H*).

(E)-2-(2-*Naphthyl*)-1-*phenylpropene* (III).—3-Hydroxy-3-(2-naphthyl)-1-phenylbutanoic acid was boiled (1 h) in formic acid. Evaporation yielded a solid, which was dissolved in chloroform; the solution was shaken with sodium hydrogen carbonate, dried (MgSO$_4$), and evaporated to leave (E)-2-(2-*naphthyl*)-1-*phenylpropene* as needles (80%) (from ethanol), m.p. 139° (Found: C, 93·5; H, 6·65%; *M*, 244. C$_{19}$H$_{16}$ requires C, 93·4; H, 6·6%; *M*, 244); λ$_{max.}$ 215, 224, 266, and 329 nm (log ε 4·40, 4·42, 4·45, and 4·27).

Methylmagnesium iodide [from methyl iodide (7·1 g) and magnesium (1·22 g)] was added in ether to benzyl 2-naphthyl ketone (12·3 g) in ether (50 ml). After 5 h at room temperature the solution was decomposed with ice and ammonium chloride. Evaporation gave the expected

alcohol as an oil, $\nu_{max.}$ 3600 cm^{-1} (OH), which when boiled (1 h) in formic acid yielded the hydrocarbon (III) as plates, m.p. and mixed m.p. 139° (from benzene). Similar treatment of benzyl 1-naphthyl ketone left the ketone unchanged.

Triphenylbenzylphosphonium bromide (4·33 g) and potassium t-butoxide (11·2 g) were added under nitrogen to 2-acetylnaphthalene (1·7 g) in light petroleum (b.p. 40—60°; 200 ml), and the suspension was shaken for 48 h. The filtered solution was passed down an alumina column to give the unsaturated hydrocarbon (III), m.p. and mixed m.p. 139° (15%). No reaction was observed when the Wittig reagent was added to 1-acetylnaphthalene.

Action of Formic Acid on other Hydroxy-acids.—3-Hydroxy-3,4-diphenylbutanoic acid, when boiled (1 h) with formic acid, yielded (*E*)-1,2-diphenylprop-1-ene, m.p. and mixed m.p. with a sample prepared from 1,2-diphenylpropan-2-ol, 80° (lit.,[13a] 82°). 3-Hydroxy-3,3-diphenylpropionic acid likewise yielded 1,1-diphenylethylene as an oil which solidified in ice (lit.,[13b] m.p. 8°) and with chromic acid vielded benzophenone, identified as the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 246°. In neither instance was any unsaturated acid detected among the products.

[13] Heilbron's Dictionary of Organic Chemistry, 4th edn., vol. 3, (*a*) p. 1281; (*b*) p. 1293.