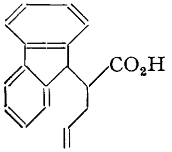
467. *Some Derivatives of* 1-*Benzyl*-n-*but*-3-*ene*-1-*carboxylic Acids.*

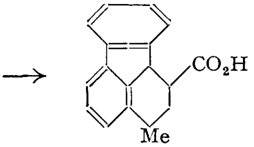
By Neil Campbell and H. Wang.

Three acids related to 1-benzyl-*n*-but-3-ene-1-carboxylic acid have been prepared. Two were found not to undergo ring-closure by the Darzens method (*Compt. rend.*, 1926, **183**, 748, 1110), but the acid (III; R_1 = Me, R_2 = H), although not isolated in a pure state, was cyclised to 4 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid.

1-Benzyl-*n*-but-3-ene-1-carboxylic acid is readily converted into a tetralin derivative by sulphuric acid, and the general application of the reaction was realised by Darzens (see Linstead, *Ann. Reports*, 1936, **33**, 326). Since the tetralins are readily dehydrogenated by chloranil to derivatives which are easily decarboxylated, the Darzens method constitutes a good method for synthesising substituted naphthalenes. We have attempted to extend the method by preparing 1-9′-*fluorenyl*-n-*but*-3-*ene*-1-*carboxylic acid* (I) and converting it into 4-methyl-1 : 2 : 3 : 4-tetrahydrofluoranthene-2-carboxylic acid (II). All attempts to effect ring closure of the acid (I), however, were unsuccessful, the products being either unchanged material or sulphonic acids. This failure was quite unexpected since the 1-position in the fluorene molecule, though less susceptible to electrophilic substitution, readily participates in ring closure (see, *e.g.*, France, Tucker, and Forrest, *J.*, 1945, **7**, and subsequent papers).



(I.)



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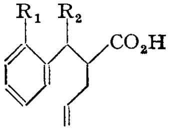

(III.)

The simplest explanation would be the formation of a γ-lactone which would be only slowly converted into the cyclic acid (II) (cf. Darzens, *Compt. rend.*, **1930**, **190**, 305), but against this is the fact that unchanged material was often obtained under conditions in which 1-benzyl-*n*-but-3-ene-1-carboxylic acid or the corresponding lactone is cyclised. A similar failure in ring closure was obtained with 1-*benzhydryl*-n-*but*-3-*ene*-1-*carboxylic acid* (III; R_1 = H, R_2 = Ph), but 1-2′-methylbenzyl-*n*-but-3-ene-1-carboxylic acid (III; R_1 = Me, R_2 = H) was cyclised to yield finally 1 : 5-dimethylnaphthalene. Attempts to prepare 1-2′-phenylbenzyl-*n*-but-3-ene-1-carboxylic acid (III; R_1 = Ph, R_2 = H) failed.

An attempt was made to cyclise 9-*hydroxy*-9-*epoxyallylfluorene* (cf. Bradsher, *Chem. Reviews*, 1946, **38**, 474), but the only products were resins.

Experimental.

(All analyses were by Drs. Weiler and Strauss, Oxford.)

Preparation of 1-9′-*Fluorenyl*-n-*but*-3-*ene*-1-*carboxylic Acid.*—Fluorenone [2 : 4-*dinitrophenylhydrazone*, orange needles, m. p. 299—301° (Found : N, 15·3. $C_{19}H_{12}O_4N_4$ requires N, 15·55%)] was converted into fluoren-9-ol by the modified method of Werner and Grob (Campbell and Fairfull, this vol., p. 1239), and the fluorenol (25 g.) suspended in glacial acetic acid (150 c.c.). Dry hydrogen bromide was passed through until saturation was reached, and the solution was then heated at its b. p. for 3 minutes with the hydrogen bromide still passing. The cold solution with water gave 9-bromofluorene, crystallising in needles from light petroleum (b. p. 80—100°), m. p. 103—104°; yield, 22 g. (66%). Sodium (1·55 g.) was dissolved in absolute ethanol (45 c.c.), and ethyl allylmalonate (13·2 g.) and then 9-bromofluorene (16·4 g.) were gradually added to the warm solution. The mixture was boiled under reflux until it was no longer alkaline (about 6 hours). Most of the ethanol was removed by distillation, the semi-solid residue shaken with warm water, and the resulting oil extracted with ether. The ethereal layer was washed 4 times with water, dried (Na_2SO_4), and on evaporation gave crude ethyl α-9-fluorenyl-α-allylmalonate (15 g., 62%), which did not solidify and could not be distilled under reduced pressure without decomposition. The substance was also obtained from allyl bromide and *ethyl* 9-*fluorenylmalonate*, needles (from aqueous ethanol), m. p. 68—69° (Found : C, 73·95; H, 6·2. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%). The latter compound was prepared but not isolated by Bachmann and Sheehan (*J. Amer. Chem. Soc.*, 1940, **62**, 2687). Ethyl 9-fluorenylallylmalonate (15 g.) was hydrolysed by heating it under reflux for 2 hours with 10% alcoholic sodium hydroxide (50 c.c.). A salt-like solid was obtained which, when dissolved in water and acidified with dilute hydrochloric acid, gave a little effervescence of carbon dioxide and a brown oil which solidified on cooling. The solid was heated at 170—180° until evolution of carbon dioxide ceased. The oil on cooling solidified and when crystallised twice from light petroleum (b. p. 100—120°) gave colourless needles of 1-9′-*fluorenyl*-n-*but*-3-*ene*-1-*carboxylic acid*, m. p. 128—129° (4·25 g., 39%) (Found : C, 81·3; H, 6·3. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%). The acid in ethanol decolorised aqueous potassium permanganate. Efforts to effect ring closure of the acid with concentrated sulphuric or phosphoric acid or both were unsuccessful.

Syntheses of Ethyl α-2-*Methylbenzyl*-α-*allylmalonate and* 1 : 5-*Dimethylnaphthalene*.—2-Methylbenzyl bromide (18 g.), ethyl allylmalonate (20 g.), sodium (2·3 g.), and absolute ethanol (40 c.c.) were condensed as above to give *ethyl* α-2-*methylbenzyl*-α-*allylmalonate*, b. p. 199—203°/15 mm. (10 g., 34%) (Found : C, 70·15; H, 8·1. $C_{18}H_{24}O_4$ requires C, 71·0; H, 7·95%). The ester (6 g.) was hydrolysed by heating it under reflux with potassium hydroxide (8 g.) in 50% aqueous ethanol (25 c.c.), and the solution was acidified with dilute hydrochloric acid. The mixture was extracted with ether and the ether evaporated; the resulting oil on distillation gave off carbon dioxide and yielded 1-2′-methylbenzyl-*n*-but-3-ene-1-carboxylic acid, b. p. 195—200°/25 mm. This acid could not be prepared in the pure state since distillation was accompanied by slight decarboxylation. The impure acid (6 g.) was shaken with 80% sulphuric acid (18 g.) in the cold, and a solid gradually separated. After 5 hours the solution was neutralised with 12% sodium carbonate and extracted with ether. The aqueous layer on acidification gave 4 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, which was crystallised from 50% ethanol, m. p. 141—142°; yield, 2·0 g. (33%) (Found : C, 76·5; H, 8·0. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%). The acid (1 g.), chloranil (2·5 g.), and xylene (10 c.c.) were heated under reflux for 48 hours, the solution was filtered, and an equal volume of ether added to the filtrate. Extraction with 4% potassium hydroxide followed by acidification yielded a brown product which on repeated extraction with hot water gave 4 : 8-dimethyl-2-naphthoic acid; colourless plates (water), m. p. 186—188° (0·2 g., 20%). The acid was decarboxylated by heating it in an oil-bath at 215—220° with quinoline and copper and subsequent acidification with dilute hydrochloric acid. 1 : 5-Dimethylnaphthalene separated and was crystallised from aqueous ethanol; m. p. 79—80° (lit., 80°); picrate, yellow-orange needles, m. p. 137—138° (lit., 138—139°). An attempt to decarboxylate the dimethyltetrahydronaphthoic acid under the same conditions gave only unchanged acid.

1-*Benzhydryl*-n-*but*-3-*ene*-1-*carboxylic Acid*.—Benzhydryl bromide (22·0 g.), ethyl allylmalonate (18·0 g.), sodium (2·12 g.), and absolute ethanol (60 c.c.) gave *ethyl* α-*benzhydryl*-α-*allylmalonate*, a colourless oil, b. p. 237—239°/26 mm. (12·1 g., 37%) (Found : C, 75·85; H, 7·2. $C_{23}H_{26}O_4$ requires C, 75·4; H, 7·15%). The ester was also prepared in 39% yield by condensing allyl bromide with *ethyl benzhydrylmalonate*, which in turn was obtained from benzhydryl bromide and ethyl malonate as an oil, b. p. 233—235°/27 mm., which solidified on storage; m. p. 43—45°; yield, 49% (Found : C, 73·7; H, 6·9. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·8%). Ethyl benzhydrylmalonate was identified by hydrolysis with 30% sodium hydroxide to the acid which when heated at 170—180° yielded ββ-diphenylpropionic acid, m. p. 151—153° (lit., 155°) (anilide, m. p. 175—177°; lit., 177—178°). Ethyl benzhydrylallylmalonate (12 g.) was heated under reflux with 10% sodium hydroxide (50 c.c.) for 3 hours, and on acidification plates of the acid were deposited, m. p. 165—170° with evolution of carbon dioxide. The solid was heated at 180° until evolution of gas was complete, and the resulting oil crystallised from benzene. 1-*Benzhydryl*-n-*but*-3-*ene*-1-*carboxylic acid* separated in prisms, and more was obtained by the addition of light petroleum (b. p. 60—80°); m. p. 156—157°; yield, 1·2 g. (14%) (Found : C, 79·8; H, 6·2. $C_{18}H_{18}O_2$ requires C, 81·15; H, 6·8%). Attempts at ring-closure with concentrated sulphuric acid, phosphoric acid, and mixtures of these acids under a variety of conditions failed, the only products being unchanged material or a charred mass.

Ethyl α-(2-*Phenylbenzyl*)-α-*allylmalonate*.—To magnesium (7·5 g.) and dry ether (30 c.c.), *o*-bromotoluene (55 g.) in ether (190 c.c.) was gradually added, the reaction being started by addition of a few drops of methyl iodide. The solution was then heated under reflux for 1½ hours until all the magnesium had dissolved. *cyclo*Hexanone (31 g.) was slowly added, and the solution heated under reflux for 24 hours. The product was worked up in the usual way and 1-*o*-tolyl*cyclo*hexanol was obtained as a liquid, b. p. 154—156°/25 mm. (lit., 149—151°/14 mm.), yield 38 g. (63%). The carbinol (25 g.) was shaken in the cold with 90% formic acid (25 c.c.), and after ½ hour *o*-tolyl*cyclo*hex-1-ene separated in 97% yield. The *cyclo*hexene (20 g.) was heated under reflux for 24 hours with chloranil (57·5 g.) in xylene (150 c.c.). The cold solution was filtered, and an equal volume of ether added to the filtrate, which was then washed twice with 4% potassium hydroxide solution, water, and finally distilled. 2-Methyldiphenyl (12 g., 61·5%) distilled at 134—141°/25 mm. (lit., 130—136°/27 mm.). 2-Methyldiphenyl (3·5 g.) was heated under reflux with *N*-bromosuccinimide (4·5 g.) and carbon tetrachloride (20 c.c.) for 3 hours, and the cold mixture filtered and distilled under reduced pressure. *o*-Phenylbenzyl bromide (4·13 g., 80%) distilled at 168—172°/18 mm. (lit., 166°/12 mm.). The bromide (5·75 g.) was condensed with ethyl allylmalonate (4·60 g.), sodium (0·54 g.), and absolute alcohol (10 c.c.) as above, and gave *ethyl* α-2-*phenylbenzyl*-α-*allylmalonate*, b. p. 240—265°/23 mm., which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 68—69° (3·53 g., 41%) (Found : C, 75·3; H, 7·4. $C_{23}H_{26}O_4$ requires C, 75·4; H, 7·15%). The ester was hydrolysed by 10% alcoholic sodium hydroxide or 50% sulphuric acid, but the resulting oil could be neither solidified nor distilled under reduced pressure without decomposition.

Attempted Preparation of 2-*Methyl*-2′-*chloromethyldiphenyl*.—2 : 2′-Dimethyldiphenyl was prepared by Ullmann's method (*Annalen*, 1904, **332**, 38), but under his conditions, *i.e.*, 230° for 3 hours, very little of the diphenyl compound was obtained from *o*-iodotoluene. At 280° for 6 hours, however, 2 : 2′-

dimethyldiphenyl was obtained as an oil, b. p. 251—258°/747 mm., which solidified in a freezing mixture; m. p. 13—18° (lit., 18°); yield, 62%. Under these conditions *o*-bromotoluene reacted only slightly, even when the time was increased to 15 hours. Attempts to prepare the monochloromethyl compound with sulphuryl chloride and benzoyl peroxide failed.

9-*Hydroxy*-9-*epoxyallylfluorene*.—Efforts to prepare 9-hydroxy-9-allylfluorene by the action of allylmagnesium bromide on fluorenone (Backer and Strating, *Rec. Trav. chim.*, 1941, **60**, 391) were unsuccessful, probably owing to the coarse magnesium available which resulted in formation of a considerable quantity of diallyl. With allylmagnesium chloride (Kharasch and Fuch, *J. Org. Chem.*, 1944, **9**, 359), however, 9-hydroxy-9-allylfluorene was obtained in 39% yield as pale yellow prisms (light petroleum), m. p. 114° (lit., 119·5—120°) (Found: C, 86·0; H, 6·3. Calc. for $C_{16}H_{14}O$: C, 86·4; H, 6·35%). 9-Hydroxy-9-allylfluorene (2·22 g.) was dissolved in chloroform containing perbenzoic acid (1·65 g.) and kept in a stoppered bottle in the refrigerator for 24 hours. The solution was shaken with sodium carbonate solution, and the chloroform layer washed with water. The dried chloroform extract on evaporation gave a yellowish solid which was twice purified by dissolving it in the minimum quantity of benzene and adding twice the volume of light petroleum (b. p. 60—80°). 9-*Hydroxy*-9-*epoxyallylfluorene* slowly separated in prisms, m. p. 127—128° (1·82 g., 76·5%) (Found: C, 80·2; H, 6·0. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%). Cyclisation of the epoxide was attempted under conditions similar to those used by Bradsher and Amore (*J. Amer. Chem. Soc.*, 1943, **65**, 2016), but the only product isolated was a black resin.

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