

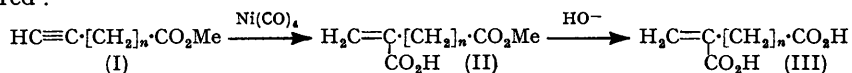
*Researches on Acetylenic Compounds. Part XLIV.\* The Reaction between Nickel Carbonyl and Some Esters of  $\omega$ -Acetylenic Acids.*

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Reaction of esters of  $\omega$ -acetylenic acids with nickel carbonyl provides a simple route to half-esters of  $\alpha$ -methylenedicarboxylic acids.

THE interaction of esters of  $\omega$ -acetylenic acids (Eglinton and Whiting, *J.*, 1953, 3052) has now been studied, and a simple route to certain otherwise inaccessible half-esters thereby discovered :



Compounds of type (II) have previously been obtained only from the corresponding dicarboxylic acids. In contrast to these earlier methods, that now described yields only one of the two possible half-esters of (III), its structure being known without doubt.

The esters (I;  $n = 1, 2, 3,$  and  $4$ ) reacted smoothly with nickel carbonyl under the standard conditions (Jones, Shen, and Whiting, *J.*, 1950, 230) to give the products (II) in yields of 28–46%; on a larger scale the yields would probably approach 50%, since these were typical exothermal "Type A" reactions (*idem*, *J.*, 1951, 48). Hydrolysis converted the half-esters into the dicarboxylic acids (III), the first two members of which series were already known. Pent-4-ynoic acid itself, under the usual conditions, did not undergo exothermal reaction ("Type B"), though a small (5%) yield of the expected dicarboxylic acid was obtained. Hex-5-ynonitrile, on the other hand, underwent a normal exothermal reaction and gave the expected half-nitrile of (III;  $n = 3$ ) in 40% yield; its infra-red spectrum indicated that the possible cyclisation to a glutarimide derivative had not taken place.

In the alkaline hydrolysis of (II;  $n = 1$ ) under vigorous conditions, the itaconic acid formed was rearranged to mesaconic acid.

Nickel carbonyl did not react with ethyl propiolate under the usual conditions, a result in accordance with the empirical rules of Jones, Shen, and Whiting (*loc. cit.*, 1951). It might be expected that replacement of the ethoxycarbonyl group by the carbamoyl or  $\cdot\text{CO}_2^-$  groupings, in which internal conjugation more effectively reduces the tautomeric effect of the carbonyl linkage, might permit reaction. With propiolamide no exothermal reaction occurred and no recognisable product was isolated; but when propiolic acid, in the presence of acetic acid and excess of sodium acetate (the dissociation constants of acetic and propiolic acids are  $1.8 \times 10^{-5}$  and  $1.4 \times 10^{-2}$ , respectively) was treated with nickel carbonyl a quite unexpected product, *trans-trans*-muconic acid, was obtained in small yield. No precedent is known for a reductive coupling reaction of this type.

*Light-absorption Properties.*—The ultra-violet absorption spectra of the acids (III) are

\* Part XLIII, preceding paper.

illustrated, together with that of mesaconic acid, in the Figure. Since simple  $\alpha$ -alkyl-acrylic acids are difficult to purify, these results may be useful for comparison purposes; 95% ethanol was used in every case. Unfortunately the only recent and fairly extensive study of the absorption spectra of ethylenic acids (Ungnade and Ortega, *J. Amer. Chem. Soc.*, 1951, **73**, 1565) is, as the authors have recently pointed out (*idem*, 1952, **74**, 6313), largely invalidated as a result of scattered-light errors (cf. Eglinton, Jones, and Whiting, *J.*, 1952, 2873). The results reported confirm a general impression that, as with the corresponding ketones, an  $\alpha$ -alkyl group displaces the maximum of acrylic acid less than a  $\beta$ -alkyl group, and are consistent with the present observation that the spectra of acids (III) show no maximum above 2060 Å; crotonic acid has  $\lambda_{\text{max}}$ . 2035 Å,  $\epsilon = 14,600$ . The well-defined inflection at 2400 Å is noteworthy (it seems to be general for  $\alpha\beta$ -ethylenic acids and esters), as is the much flatter curve found with mesaconic acid.

It has been pointed out recently (Freeman, *J. Amer. Chem. Soc.*, 1953, **75**, 1859) that  $\alpha$ -methylene-acids do not show the strong absorption band at ca. 880  $\text{cm}^{-1}$  associated with the simple  $>\text{C}=\text{CH}_2$  grouping, but do absorb at 935–950  $\text{cm}^{-1}$ . The acid (III;  $n = 3$ ) (in Nujol) and its dimethyl ester (in carbon disulphide) did show fairly strong bands at 959  $\text{cm}^{-1}$  and 950  $\text{cm}^{-1}$ , respectively, but confirmation of its structure by ozonolysis (36% yield of formaldehyde) was considered necessary.

#### EXPERIMENTAL

*Ethyl 3-Carboxybut-3-enoate*.—Ethyl but-3-ynoate (6.5 g.), ethanol (30 c.c.), glacial acetic acid (3 c.c.), and water (1 c.c.) were stirred at 70°. A solution of nickel carbonyl (2 c.c.) in ethanol (15 c.c.) was added dropwise; an exothermal reaction began after a short induction period, and the temperature was maintained at 75° by controlling the rate of addition. After the solution had cooled, ether (50 c.c.) was added and all volatile material (b. p. <50°) was distilled off, the remaining solution was poured into dilute sulphuric acid, and the acid fraction was isolated with ether. Evaporation of the dried extract gave an oil which soon solidified; crystallisation from light petroleum (b. p. 30–40°)—ether gave the *half-ester* (2.8 g., 28%) as stout needles, m. p. 58–59° (Found: C, 52.75; H, 6.2.  $\text{C}_7\text{H}_{10}\text{O}_4$  requires C, 53.15; H, 6.35%).

*Itaconic Acid*.—A solution of ethyl 3-carboxybut-3-enoate (0.5 g.), potassium hydroxide (1.0 g.), and water (20 c.c.) was set aside at 20° for 5 days. After evaporation of the ethanol and acidification the acid fraction was isolated by continuous extraction with ether; crystallisation from nitromethane gave needles (0.29 g., 71%), m. p. 167–168° (Delisle, *Annalen*, 1893, **269**, 87, gives m. p. 162–164°).

*Mesaconic Acid*.—Ethyl 3-carboxybut-3-enoate (1.0 g.) was heated under reflux with 50% potassium hydroxide (10 c.c.) for 30 min. Isolation of the acid fraction followed by recrystallisation from nitromethane gave the acid as small prisms, m. p. 199–200° (Fittig, *Annalen*, 1877, **188**, 73, gives m. p. 200°).

*Ethyl 4-Carboxypent-4-enoate*.—The reaction was carried out as above at 70° with ethyl pent-4-ynoate (12.6 g.), ethanol (30 c.c.), glacial acetic acid (6 c.c.), water (1.5 c.c.), and a solution of nickel carbonyl (5 c.c.) in ethanol (15 c.c.). Isolation of the acid fraction with ether followed by distillation gave the *half-ester* (7.85 g., 46%), b. p. 100–102°/0.01 mm.,  $n_D^{20}$  1.4575 (Found: C, 55.1; H, 7.05.  $\text{C}_8\text{H}_{12}\text{O}_4$  requires C, 55.8; H, 7.0%), which solidified to a mass of needles, m. p. ca. 5°.

*$\alpha$ -Methyleneglutaric Acid*.—(i) Ethyl 4-carboxypent-4-enoate (2.6 g.) was hydrolysed by heating it under reflux with 50% aqueous potassium hydroxide (20 c.c.) for 30 min. Acidification followed by isolation with ether gave the acid (1.7 g., 81%), which crystallised from acetone–benzene as small prisms, m. p. 131–132° (von Pechmann, *Ber.*, 1903, **36**, 1202, gives m. p. 130–131°).

(ii) Pent-4-ynoic acid (4.9 g.), ethanol (30 c.c.), glacial acetic acid (3 c.c.), and water (1.5 c.c.) were heated at 70° while a solution of nickel carbonyl (3 c.c.) in ethanol (10 c.c.) was added in small portions during 15 min. No exothermal reaction took place; isolation of the acidic fraction with ether followed by crystallisation from acetone–benzene gave the acid (0.4 g., 5.5%) as small prisms, m. p. 132–133° undepressed on admixture with a specimen prepared by method (i).

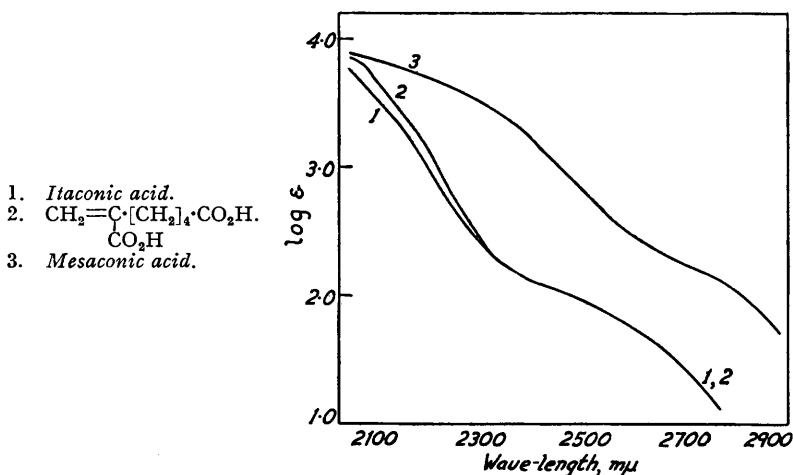
*Ethyl 5-Carboxyhex-5-enoate*.—Ethyl hex-5-ynoate (10 g.), ethanol (30 c.c.), glacial acetic acid (5 c.c.), and water (1.5 c.c.) were treated at 70° with nickel carbonyl (3 c.c.) in ethanol (10 c.c.). Isolation of the acid fraction with ether followed by distillation gave the *half-ester*

(5.3 g., 40%), b. p. 101—103°/0.01 mm.,  $n_D^{27}$  1.4608, which solidified to a mass of needles, m. p. 25—27° after crystallisation from light petroleum (b. p. 40—60°) (Found: C, 57.3; H, 7.3.  $C_9H_{14}O_4$  requires C, 58.2; H, 7.6%).

*α-Methyleneadipic Acid.*—(i) Ethyl 5-carboxyhex-5-enoate (1.9 g.) was heated under reflux with 20% aqueous potassium hydroxide (20 c.c.) for 30 min. Acidification and isolation of the acid fraction with ether, followed by crystallisation from water, gave the *acid* (1.55 g., 96%) as minute prisms, m. p. 127—128.5° (Found: C, 52.6; H, 5.9.  $C_7H_{10}O_4$  requires C, 53.1; H, 6.4%).

(ii) 1-Cyanopent-4-ene-4-carboxylic acid (1.35 g.; see below) was heated under reflux with 10% aqueous potassium hydroxide (20 c.c.) until evolution of ammonia ceased (4 hr.). Isolation of the acid fraction after acidification gave the *acid* (1.0 g., 65%), m. p. 127.5—128° after three crystallisations from water; the melting-point was undepressed on admixture with a specimen obtained from (i).

*Ozonolysis of α-Methyleneadipic Acid.*—A slow stream of ozonised oxygen was passed through a solution of the acid (0.38 g.) in acetic acid (40 c.c.) during 1 hr. The issuing gases were passed through water (30 c.c.). At the end of the reaction the aqueous and acetic acid solutions



were mixed, saturated aqueous dimedone solution (100 c.c.) was added, and the solution was set aside at 0° for 48 hr. The formaldehyde derivative of dimedone was obtained as needles (0.26 g., 36%), m. p. 188—190° undepressed on admixture with an authentic specimen.

*Ethyl Hex-5-ynoate.*—This was prepared from hex-5-ynoic acid (Eglinton and Whiting, *loc. cit.*), ethanol, and sulphuric acid and had b. p. 67.5°/10 mm.,  $n_D^{25}$  1.4359 (Found: C, 68.6; H, 8.5;  $C\equiv CH$ , 17.55.  $C_8H_{12}O_2$  requires C, 68.5; H, 8.65;  $C\equiv CH$ , 17.85%).

*Ethyl 6-Carboxyhept-6-enoate* (II,  $n = 4$ ).—A mixture of ethyl hept-6-ynoate (5.1 g.), ethanol (30 c.c.), glacial acetic acid (2.5 c.c.), and water (1 c.c.) was treated with nickel carbonyl (2 c.c.) in ethanol (5 c.c.). Isolation of the acid fraction with ether followed by distillation gave the *half-ester* (2.4 g., 37%), b. p. 108—109°/0.02 mm.,  $n_D^{25}$  1.4602 (Found: C, 60.0; H, 8.05.  $C_{10}H_{16}O_4$  requires C, 60.0; H, 8.05%).

*α-Methylenepimelic Acid.*—Ethyl 6-carboxyhept-6-enoate (1.0 g.), potassium hydroxide (1 g.), and water (20 c.c.) were shaken at 20° for 16 hr., and the mixture was then acidified. The acid fraction was isolated with ether; crystallisation from water gave the *acid* as needles (0.45 g., 53%), m. p. 88.5—89.5° (Found: C, 55.45; H, 7.05.  $C_8H_{12}O_4$  requires C, 55.8; H, 7.05%).

*1-Cyanopent-4-ene-4-carboxylic Acid.*—A mixture of 1-cyanopent-4-yne (9.3 g.), ethanol (30 c.c.), glacial acetic acid (6 c.c.), and water (1.5 c.c.) was treated with a solution of nickel carbonyl (4 c.c.) in ethanol (15 c.c.). Isolation of the acid fraction with ether gave a pale yellow oil, and on distillation the fraction, b. p. 140—143°/1.5 mm., rapidly solidified. Crystallisation from carbon tetrachloride gave the *acid* as glistening plates (5.45 g., 39%), m. p. 58—61° (Found: C, 59.9; H, 6.45.  $C_7H_9O_2N$  requires C, 60.4; H, 6.5%).

*Reaction of Nickel Carbonyl and Sodium Propiolate.*—A solution of nickel carbonyl (4 c.c.) in ethanol (10 c.c.) was added during 30 min. to a mixture of sodium propiolate (from propiolic

acid, 7 g.), ethanol (50 c.c.), glacial acetic acid (4 c.c.), and water (2.4 c.c.), maintained at 70°. No exothermal reaction occurred; isolation of the acid fraction with ether gave a yellow pasty mass, which on trituration with ethyl acetate, followed by filtration and crystallisation of the residue from water, gave *trans-trans*-muconic acid (70 mg., 1%) as clusters of needles, m. p. 295—300° (Elvidge, Linstead, Sims, and Orkin, *J.*, 1950, 2239, give m. p. 301°). The acid was heated under reflux with methanol (15 c.c.) and sulphuric acid (1 drop) during 1 hr. After cooling, filtration of the crystalline precipitate, and recrystallisation from methanol the ester was obtained as needles, m. p. 157—158°, undepressed on admixture with an authentic specimen (*idem, ibid.*) (Found: C, 56.1; H, 6.1. Calc. for  $C_8H_{10}O_4$ : C, 56.5; H, 5.9%).

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