

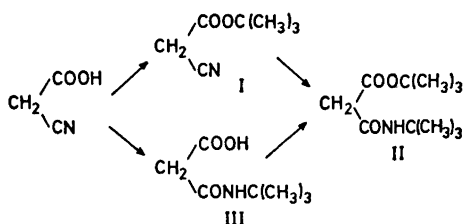
The Acid-catalyzed Reaction between Cyanoacetic Acid and Isobutene

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In a well-known procedure¹ for the preparation of tertiary butyl esters, a carboxylic acid is treated with an excess of isobutene and a small amount of concentrated sulphuric acid. In Ref. 1, no mention is made of cyanoacetic acid. The tertiary butyl ester of this acid is a valuable synthetic intermediate,² which is usually prepared *via* the acid chloride,³ or by treatment of *tert*-butyl bromoacetate with cyanide ion.⁴

Since the preparation described in Ref. 3 is technically rather disagreeable, particularly on a large scale, and the one in Ref. 4 has other disadvantages (low overall yield, expensive starting material), the direct addition of isobutene to cyanoacetic acid was attempted. The main difficulty one expects is that a Ritter type carbonium ion attack on the nitrile group will compete with ester formation. This was actually found to be the case, since the resulting compounds were formed in comparable amounts. Also, a small amount of the compound resulting from addition of one molecule of isobutene at each position was isolated. The reactions are depicted in Scheme 1.



Scheme 1. Products formed from cyanoacetic acid and isobutene.

The final product (II in Scheme 1) can be formed in two ways, neither of which needs to be excluded on the basis of the present evidence. For comparison,

it should be mentioned that the Ritter reaction between ethyl cyanoacetate and isobutene, yielding *N-tert*-butylmalonamic acid ethyl ester, has been described in the literature.⁵

Table 1. Product yields in the reaction of cyanoacetic acid and isobutene.

Mole ratio acid/olefin	Per cent yield		
	I ^a	II ^a	III ^a
1:1	8	— ^b	— ^b
1:1.5	13	6	10 ^c
1:2	22	8	— ^b

^a Designations from Scheme 1.

^b Not determined.

^c Lower limit.

The influence of the molar ratio of reactants upon the yields can be seen in Table 1. No quantitative work-up of the water-soluble product(s), *N-tert*-butylmalonamic acid and, possibly, unreacted cyanoacetic acid, was carried out. In the one case where the yield of the former is stated, it, therefore, represents a lower limit.

Experimental. In a 500 ml Parr bottle, 43 g (0.5 mol) of cyanoacetic acid was dissolved in 100 ml of dry ether and 5 ml of conc. sulphuric acid. The bottle was chilled in Dry Ice-acetone, 56 g (1 mol) of liquid isobutene was added, and the bottle was connected to a low-pressure Parr apparatus. The bottle was shaken for a few hours, until all solid material had disappeared, and then allowed to stand overnight. The pressure never exceeded 15 psi. After venting the bottle, its contents were poured onto 200 g of ice and 200 ml of water. The pH value was adjusted to 8 by the addition of solid sodium carbonate, and the phases were separated. The ethereal phase was washed with saturated sodium chloride solution and dried over anhydrous potassium carbonate. After filtration and flash evaporation of the solvent, the remainder was distilled *in vacuo*, using a 15 cm Vigreux column. As a precaution against decomposition, a trace of potassium carbonate was present in the distillation flask. A fraction boiling at 62–63°/4 mm, weighing 15.2 g, was identified as *tert*-butyl cyanoacetate, yield

22 %. NMR signals at 60 MHz: 9 H at $\delta=1.51$ (s), and 2 H at $\delta=3.37$ (s), solvent deuteriochloroform, internal reference tetramethylsilane. A second fraction, boiling at $104^\circ/4$ mm, weighing 8.7 g, was identified as *N-tert-butylmalonic acid tert-butyl ester*, yield 8 %. The latter fraction was obtained as a very viscous oil which solidified when kept at 5° . NMR signals at 60 MHz: 9 H at $\delta=1.37$ (s), 9 H at $\delta=1.48$ (s), 2 H at $\delta=3.15$ (s), and 1 H at $\delta=6.95$ (broad), same solvent and reference as above. The IR spectrum was also in agreement with the proposed structure.

Experiments with less than twice the amount of isobutene as cyanoacetic acid were performed in the same manner. In the one using a mole ratio 1.5:1 for the reactants, the aqueous phase from the work-up was also investigated. After addition of excess aqueous hydrochloric acid, it was extracted three times with 100 ml portions of ether. The combined ethereal extracts were flash evaporated, and the residue dried by azeotropic distillation with benzene. A viscous oil, weighing 8 g, remained. This was only sparingly soluble in water and could not, therefore, consist of unchanged cyanoacetic acid. An NMR spectrum at 60 MHz of the potassium salt (prepared *in situ* in deuterium oxide by the addition of potassium carbonate) displayed, in addition to the water peak, two peaks at the relative positions expected for *tert-butyl* and "acidic" methylene, respectively, and in the ratio of about 12:1. Since the protons of the methylene group may exchange with the solvent, no quantitative significance can be given to this ratio, but one can nevertheless conclude that the aqueous phase contained *N-tert-butylmalonic acid*.

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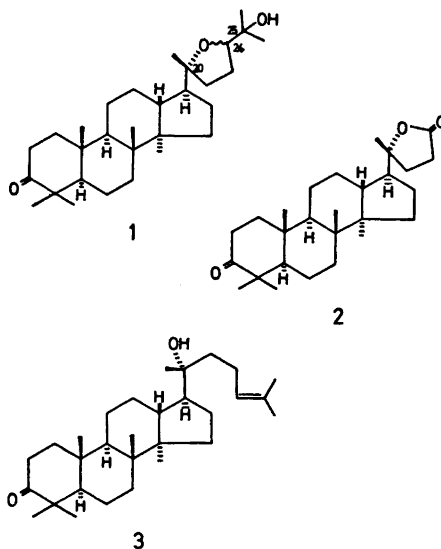
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20R,24 ξ ,-Ocotillone, a Triterpenoid from Commercial Tolu Balsam

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In continuation of an investigation of tolu balsam,^{1,2} a commercially available bled resin from *Myroxylon balsamum* (L.) Harms (Leguminosae), the constituents of the hexane soluble neutral fraction have been studied.³ The non-volatile part of this fraction consists of a complex mixture of triterpenoids of which one, obtained in a pure state by repeated chromatography and subsequent recrystallisations, is found to be a compound previously not encountered in Nature. The present paper gives the evidence on which structure I has been assigned to this compound.



The mass spectrum of compound I gives valuable structural information. It exhibits important peaks at m/e 443 ($M-15$), 440 ($M-18$), 425 ($M-15-18$), 399 ($M-59$), 381 ($M-59-18$), 357, 313,

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