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Conjugate Additions of Grignard Reagents to alpha, beta-Unsaturated Esters

XIV. Studies on the High-Boiling By-Products from the Conjugate Addition

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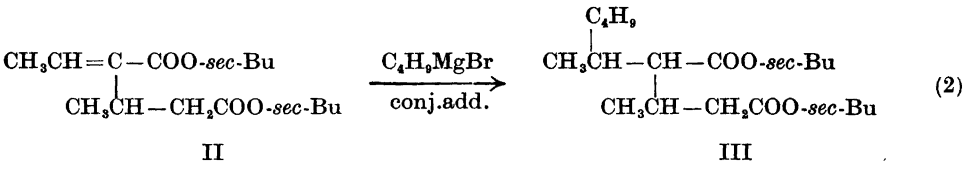
The chief by-product from the reaction with tiglic ester has been found to be a substituted glutaric ester analogous to the by-product from the reaction with crotonic ester. Contrary to previous belief, these compounds are presumably produced by the Michael addition of the simple conjugate addition product to another molecule of unsaturated ester, this route originally being proposed by E. P. Kohler. Experiments relating to the elucidation of structure and mode of formation of these products from tiglic and crotonic ester are described.

The product from tiglic ester has been transformed into the corresponding cyclobutanone. *sec*-Butyl tiglate has, in moderate yield, been dimerized by an intermolecular conjugate Michael condensation.

In continuation of the work described in the preceding paper [1] we have investigated the higher-boiling product, which, besides the simple conjugate addition product, is obtained by the reaction between butylmagnesium bromide and *sec*-butyl tiglate and angelate.

These products, which are actually mixtures of a great number of compounds, consist of essentially the same components, although the relative amounts of these, formed from the two *cis*, *trans*-isomeric esters, are different. The main component of the product from tiglic ester has been considered [2] to be a substituted glutaric ester: di-*sec*-butyl α-(1-methylpentyl)-α,β,γ-trimethylglutarate (V, below). The corresponding compound obtained from *sec*-butyl crotonate, III (di-*sec*-butyl α-(1-methylpentyl)-β-methylglutarate), was believed to be formed by a preliminary intermolecular Michael condensation, followed by a conjugate addition of the Grignard reagent to the double bond of the dimerization product, an ethylideneglutaric ester II [2]:

$$\begin{matrix} CH_3CH{=}CH{-}COO\text{-}sec\text{-}Bu \\ CH_3CH{=}CH{-}COO\text{-}sec\text{-}Bu \\ \text{I} \end{matrix} \xrightarrow[(RMgX)]{\text{Michael}} \begin{matrix} CH_3CH{=}C{-}COO\text{-}sec\text{-}Bu \\ \quad\quad\quad | \\ CH_3CH{-}CH_2COO\text{-}sec\text{-}Bu \\ \text{II} \end{matrix} \qquad (1)$$

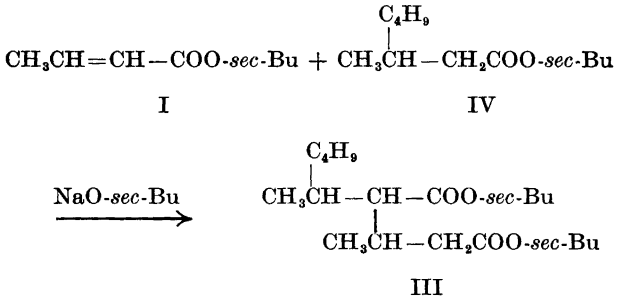


II III (2)

Certain analogous compounds have previously been encountered in conjugate addition reactions by other workers,[3] in particular by Kohler,[4] who, however, on the basis of apparently conclusive evidence, proposed the reverse order of reactions for the case of the reaction between phenylmagnesium bromide and benzylideneacetophenone.

Recently Owens, Meyers and Zimmerman [5] have reported the thorough investigation of the products obtained from methacrylic and acrylic esters by reactions with certain organomagnesium compounds. The major part of these products consists of compounds believed to result from one conjugate addition followed by one or more Michael additions, *i.e.* according to the Kohler sequence [4].

The above sequence was suggested to us by the fact that the attempted Michael addition of the simple conjugate addition product, *sec*-butyl 3-methylheptanoate, IV, to *sec*-butyl crotonate under the influence of sodium *sec*-butoxide:

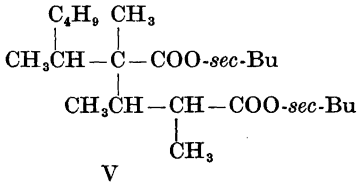


I IV (3)

III

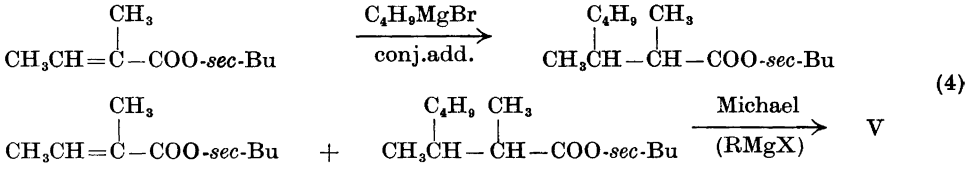
resulted in the almost quantitative recovery of *sec*-butyl 3-methylheptanoate, IV, and the dimerization of the crotonic ester, I, to a high yield of II. Furthermore, experiments attempting to find the optimum conditions for the simple conjugate addition,[2] likewise pointed to the sequence (1)—(2) outlined above.

No proof, however, for the actual mode of formation of the compound III during the Grignard reaction was given, and obviously, the corresponding compound from *sec*-butyl tiglate (and angelate):



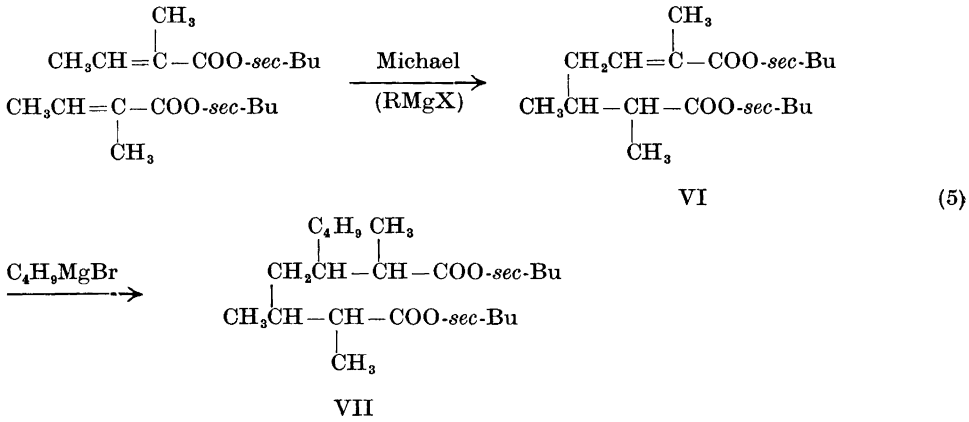
V

could not be formed by (1)—(2) since the tiglic ester contains no α-hydrogen atom, and therefore cannot form a dimerization product analogous to II. Ester V is, therefore, presumably formed according to the Kohler route:



(4)

Another possibility was that the product was not V at all, but rather VII, formed by the participation of the active β-methyl group of the tiglic ester, by way of a dimer Michael condensation product (VI):



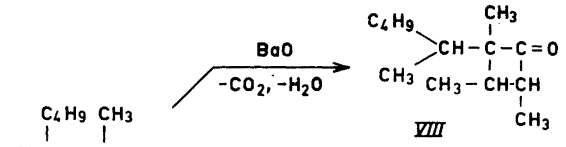
(5)

We believe that we have now proved that the main component of the high-boiling products from tiglic and angelic esters is V, rather than VII *. After saponification, the acid formed could be transformed into a cyclic ketone as well as into an intramolecular anhydride:

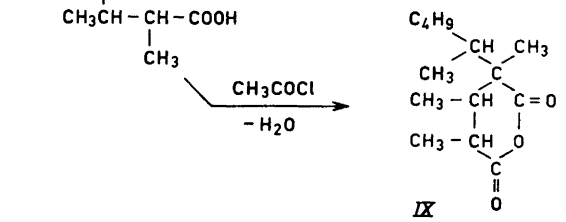
* It should be noted, that whereas the high-boiling residue from *sec*-butyl crotonate to an extent of 90 % consists of III, the residues from *sec*-butyl tiglate and angelate are mixtures of a great number of compounds. Compound V constitute the major part in the case of tiglic ester, but another component is also present in a large quantity, probably some 1,2-addition product (ketone, tertiary alcohol, lactone) corresponding to V. In the case of the uncatalyzed reaction with angelic ester the amount of this other unidentified compound is almost equal to the amount of V, and in the case of the catalyzed reaction with angelic ester this compound forms the greater part of the residue.

In general, all the high-boiling components appear on the gas-chromatograms as double peaks, presumably because they are mixtures of diastereomers.

Although the simple conjugate addition product from tiglic and angelic esters (*cf.* eqn. (4)), as well as other low-boiling reaction products (*cf.* the preceding paper [1]), might also be expected be mixtures of stereoisomers, no evidence for this has yet been obtained. However, no attempts have been made, so far, neither to ascertain whether or not these products are mixtures of diastereomers, nor to determine the stereochemical configuration of any product.

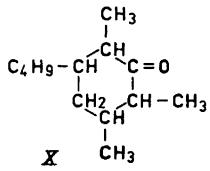


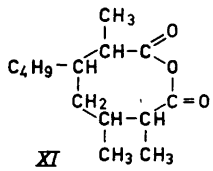
(6)



(7)

The infra-red spectra of these two compounds strongly indicate that they are a cyclobutanone (VIII) * and a glutaric anhydride (IX), respectively, rather than a cyclohexanone (X) and a pimelic anhydride (XI), respectively:





As outlined above this result means that the Kohler sequence must be the one followed in the case of tiglic and angelic esters.

Our earlier assumption concerning the formation of the high-boiling products might, therefore, be erroneous also for the case of crotonic ester. As stated above, our evidence for the reverse sequence of reactions was not at all decisive. On the other hand, this sequence could not be entirely ruled out for the crotonic ester case, and it might well be that the Kohler sequence is followed by tiglic ester only because the other is here precluded.

However, some new results obtained makes it highly probable that the Kohler route is the correct one also for the case of crotonic ester.

Since one reason for our failure to effect the addition of 3-methylheptanoic ester to crotonic ester might have been the use of a much weaker base (sodium *sec*-butoxide) than the Grignard reagent, we have now tried to bring about this Michael addition using butylmagnesium bromide as the condensing reagent, as in the actual process. We have run the reaction between *sec*-butyl crotonate and butylmagnesium bromide in the presence of two equivalents of *sec*-butyl 3-methylheptanoate. If the Grignard reagent could effect the Michael addition, the yield of the high-boiling product should be greatly increased. The yield found was actually lower than when the reaction was run without added 3-methylheptanoic ester.

* To our knowledge a cyclo-ketonization of a glutaric acid into a cyclobutanone has not previously been reported.

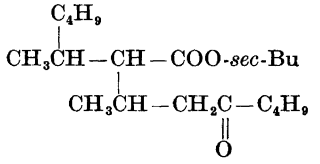
Although the amount of this ester, recovered from the experiment was lower than the sum of the amount of ester added and the amount of ester which should have been formed by conjugate addition, this discrepancy could be accounted for by the attack of the Grignard reagent on the carbonyl group of the added 3-methylheptanoic ester, a tertiary alcohol being formed in 20 % yield. This was determined by a blind experiment in which no crotonic ester was added. In the two runs with mixtures of crotonic and 3-methylheptanoic esters being added to butylmagnesium bromide, we obtained exactly the amount of 3-methylheptanoic ester calculated from the "blind" experiments with no crotonic ester and with no 3-methylheptanoic ester. Thus even in presence of butylmagnesium bromide the Michael addition does not occur.

This result, however, does not disprove the Kohler route either, since under the actual conditions for the conjugate addition reaction, the free 3-methylheptanoic ester is not present, but is formed *in situ* as the magnesium enolate, which is just the form necessary for it to be able to react in the Michael addition. This magnesium enolate may not form at all from the free ester and a Grignard reagent.

It was, therefore, investigated whether the magnesium enolate of 3-methylheptanoic ester would add to crotonic ester. This was tried by producing the magnesium enolate by a normal conjugate addition reaction between crotonic ester and butylmagnesium bromide under optimum conditions,[6] destroying the excess of Grignard reagent, and finally adding another equivalent of crotonic ester with which the preformed magnesium enolate could react. Although the Michael addition product III under these conditions was indeed obtained in relatively high yield, these experiments did not contribute to the elucidation of the reaction path.

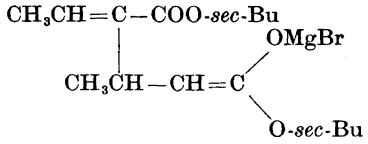
Evidence for the Kohler route was, however, gained from the following results: When, in the reaction between *sec*-butyl crotonate and butylmagnesium bromide, an actual excess of crotonic ester relative to Grignard reagent was used, no 3-methylheptanoic ester was obtained; crotonic ester was recovered, whereas no trace of crotonic ester dimer (II) could be detected. The Michael addition product (III) was obtained in quantitative yield calculated from the amount of crotonic ester consumed. This result indicates that II is not an intermediate in the formation of III, since, if this was the case, II rather than crotonic ester should be found besides III. In fact, the crotonic ester dimer (II) has never been found in the product from any conjugate addition reaction with crotonic ester.

Finally, compound III was not formed by an attempted conjugate addition of butylmagnesium bromide to compound II. Instead another compound was obtained. This was not pure, but, on the basis of infra-red spectrum, analysis and other evidence, we tentatively assign to it the structure of a ketonic ester (*sec*-butyl 2-(1′-methylpentyl)-3-methyl-5-oxononanoate):



XII

One cannot, however, expect that this reaction should necessarily give III, since, again, in the proposed formation of III during the conjugate addition process, the crotonic ester dimer is not occurring as such, but as a magnesium enolate:



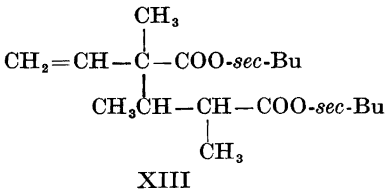
which cannot, like the free ester, undergo carbonyl addition of Grignard reagents in the non-conjugated ester group.

Some similar *experiments related to the tiglic ester* problem were also carried out. First the attempted Michael addition of *sec*-butyl 2,3-dimethylheptanoate to *sec*-butyl tiglate was tried. (The former of the two esters is the simple conjugate addition product from tiglic ester and butylmagnesium bromide). As the condensing agent were used sodium amide and potassium amide. As in the corresponding experiments with crotonic ester, referred to above, no addition was accomplished.

Most of the 2,3-dimethylheptanoic ester was recovered, partially in the form of the amide. Some of the tiglic ester was dimerized, but to a much smaller extent than was the case with crotonic ester in the corresponding experiments using sodium *sec*-butoxide. This latter observation is consistent with the result of the experiment described below.

Secondly, an attempt was made to find out whether tiglic ester would at all undergo intermolecular Michael condensation, in the presence of a basic reagent, to form a dimer. Apparently, a dimer was indeed formed, but the yields were so low and the necessary conditions so drastic that it appears unlikely, that a reaction of this kind could be involved in the facile formation, in considerable quantities, of the high-boiling by-product from the conjugate addition of butylmagnesium bromide to tiglic ester.

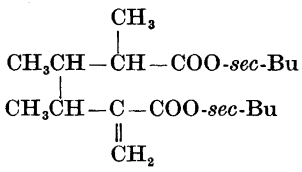
As mentioned above, the dimer must necessarily have the structure VI (above), which for the high-boiling product should give the pimelic ester structure VII. (This has, as mentioned above, been disproved in favour of V). The other possibility for the dimer to have the structure:



XIII

was excluded because of the absence in the infra-red spectrum of any absorption band for the vinyl group. In fact, both infra-red and nuclear magnetic resonance spectra are consistent with the assumed structure VI.

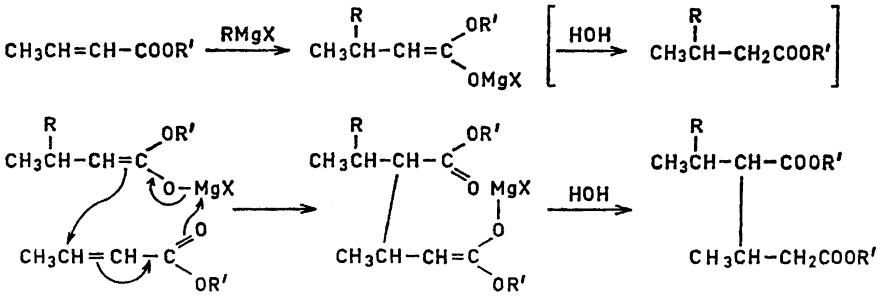
The following adipic ester structure for the dimer was likewise excluded because of the spectra:



XIV

This type of dimer (dimethyl α-methylene-δ-methyladipate) was obtained by England *et al.*[6a] from methyl methacrylate by heating it in autoclave at 225° for 12 hours.

Considering the evidence discussed above, one must conclude that the high-boiling product which, besides the simple conjugate addition product, is obtained from the reaction between an α,β-unsaturated ester (*e.g.* crotonic ester) and a Grignard reagent is a substituted glutaric ester formed according to the general route put forward by Kohler:



The magnesium enolate, primarily produced by the simple conjugate addition of the Grignard reagent to the unsaturated ester, undergoes a subsequent Michael addition to another molecule of unsaturated ester to form a magnesium enolate of a substituted glutaric ester.

EXPERIMENTAL

Microanalyses are by Mr. Preben Hansen, Microanalytical Division, The Chemical Laboratory, The University of Copenhagen.

When nothing else is specified, distillations were through a simple 45 cm × 8 mm Podbielniak type column with a tantalum wire spiral, a heated jacket and a partial reflux head as described by Cason and Rapoport.[7] For certain distillations were used either the 5 cm × 10 mm Widmer type column packed with 1/16 in. Dixon gauze rings, designed by Clauson-Kaas and Limborg[8] (in the following abbreviated: C—K), or a small scale distilling apparatus as described by Lieb and Schöninger[9] (L and S).

All products were analyzed by gas chromatography and infra-red spectroscopy, using a Perkin-Elmer fractometer, No. 116E, and a Perkin-Elmer Infracord, model 137, with sodium chloride optics, respectively.

The nuclear magnetic resonance spectra were recorded at The Chemical Laboratory, The University of Copenhagen, on a Varian A-60 Analytical NMR spectrometer. The spectra were measured and interpreted by Miss Regitze Rosenørn, lic.techn., of this Laboratory *.

Investigations related to the high-boiling product from *sec*-butyl tiglate and butylmagnesium bromide: di-*sec*-butyl α-(1-methylpentyl)-α,β,γ-trimethylglutarate (V)

Preparation and analyses. The product was obtained from the conjugate addition reactions between *sec*-butyl tiglate and butylmagnesium bromide as previously described.[2,6] It was a mixture of several compounds. About half the quantity was one single compound, which after two distillations, the final one in C—K [8] (above), was obtained pure, b.p. 135—137°/0.4 mm, n_D^{20} 1.4514 (reported [2] 158°/1.5 mm, n_D^{25} 1.4520). (Found: C 71.60; H 11.30. Calc. for $C_{22}H_{42}O_4$ (370.56): C 71.30; H 11.43).

Saponification. The above product (V) (10 g) was dissolved in a solution of 12 g (0.2 mole) of potassium hydroxide in 95 ml of ethyleneglycol. The mixture was placed in a container (a tube) of stainless steel and boiled under reflux for 5 days. Heating was accomplished by immersion in a metal bath of 200°. The temperature of the condensing vapour was about 125°. After cooling, the mixture was diluted with an equal volume of water, the solution extracted with ether to remove non-saponified material. On acidification with hydrochloric acid the acid was precipitated as a viscous black oil. This was thoroughly extracted with ether, the ether solution washed with sodium chloride solution and dried over anhydrous sodium sulfate. After removal of the solvent by distillation, the residue (6.7 g) was a viscous light brown oil.

Cyclo-ketonization (eqn. (6)). The procedure of Schäppi and Seidel for the transformation of α,α,β-trimethylpimelic acid into 2,2,3-trimethylcyclohexanone [10] was largely followed. The above acid (2.1 g) was mixed with barium hydroxide ($Ba(OH)_2$,8 H_2O; 100 mg) and rapidly distilled (L and S,[9] above). The distillate was dissolved in ether (10 ml), the solution washed with 5 ml of 2 N sodium hydroxide, then with 5 ml of water. After removal of the ether, the residue on distillation (L and S,[9] above) gave a product, b.p. 112—116°/10 mm, with very little fore- and after-run. The main fraction gave the correct analysis for the cyclic ketone: 2,3,6-trimethyl-5-butylcyclohexanone (X) or 2,3,4-trimethyl-2-(1'-methylpentyl)cyclobutanone (VIII). (Found: C 79.80; H 11.94. Calc. for $C_{13}H_{24}O$ (196.32): C 79.53; H 12.32). The infra-red spectrum had a carbonyl band at 1765 cm^{-1} (5.67 μ), which is consistent with a cyclobutanone and excludes the possibility of a cyclohexanone (1725—1705 cm^{-1}).[11] The gas-chromatographic analysis showed the presence of two compounds, presumably stereoisomers, the ratio of which was about 5:1.

Intramolecular dehydration to cyclic anhydride (eqn. (7)). The above acid (1 g) was boiled under reflux with 2 ml of acetyl chloride for 2 h. After standing overnight, another 1 ml of acetyl chloride was added, and the mixture was boiled under reflux again for 2 h. After standing for 3 days the mixture was distilled (L and S,[9] above). After a fore-run, the main fraction, b.p. 110—115°/0.3 mm was obtained. (Found: C 70.10; H 9.68. Calc. for $C_{14}H_{24}O_3$ (240.33): C 69.96; H 10.07). The infra-red spectrum showed two carbonyl absorptions at 1803 and 1757 cm^{-1}, resp. (5.55 and 5.70 μ, resp.). The ratio between the intensities of these was about 1/2.4, consistent with that reported for a glutaric anhydride (1812 and 1764 cm^{-1}, ratio 1/2.7).[12] Thus, the compound is presumably α-(1-methylpentyl)-α,β,γ-trimethylglutaric anhydride (IX). The gas-chromatogram showed the presence of two compounds, presumably stereo-isomers.

Attempted Michael addition of sec-*butyl 2,3-dimethylheptanoate to* sec-*butyl tiglate.* To a stirred and refluxed suspension of sodium amide (0.1 mole) in ether [13] was added, during 10 min, a solution of *sec*-butyl 2,3-dimethylheptanoate (25.7 g, 0.12 mole) in ether (50 ml). After another 20 min of reflux, *sec*-butyl tiglate (15.6 g, 0.1 mole) was added during 10 min. The mixture was boiled under reflux for 1 ¼ h, poured onto ice and water,

* The authors wish to express their sincere thanks to Professor Børge Bak, The Chemical Laboratory, The University of Copenhagen, and to Miss Regitze Rosenørn for this valuable help.

extracted with ether, dried over sodium sulfate and distilled. Similarly, potassium amide was employed, and also sodium amide in liquid ammonia [14] was tried. The result was nearly the same in all these experiments: The 2,3-dimethylheptanoic ester was almost quantitatively recovered, the tiglic ester was, to a degree of about 30 %, converted into the dimer described below, while part of it was found unchanged. In the runs with potassium amide in ether and with sodium amide in liquid ammonia the amount of recovered 2,3-dimethylheptanoic ester was smaller and some solid compound was formed, probably 2,3-dimethylheptamide.

*Preparation and identification of tiglic ester dimer: di-*sec*-butyl 1,4,5-trimethylpent-1-ene-1,5-dicarboxylate, VI, cf.* eqn. (5). An attempt to bring about the self-condensation of tiglic ester by means of sodium *sec*-butoxide, similar to the self-condensation of *sec*-butyl crotonate,[2] mentioned above, failed, as no reaction took place. By the use 1 or ½ molar equivalent of sodium amide in ether (reflux for 2 h) a 20—30 % yield of product was obtained, but the major part of the tiglic ester was lost as a non-distillable residue. In the presence of only catalytic amounts of sodium amide, most of the tiglic ester was recovered and only a 12 % yield of dimer was obtained. A 20 % yield of crude product was eventually obtained on a 0.8 mole scale, ½ equiv. of sodium amide to 1 equiv. of ester being applied.* The product had the b.p. 125—126°/0.3 mm, n_D^{20} 1.4532. (Found: C 69.40; H 10.30. Calc. for $C_{18}H_{32}O_4$ (312.44): C 69.19; H 10.32). The infra-red spectrum was entirely consistent with the structure VI. A band at 1645 cm^{-1} (6.07 μ), as well as one at 970 cm^{-1} (10.3 μ), indicated the presence of a carbon-carbon double bond in conjugation with an ester carbonyl group,[15] and the carbonyl absorption was split into two bands at 1730 and 1710 cm^{-1} (5.78 and 5.85 μ). The absorption around 1110 cm^{-1} (9 μ) for *sec*-butyl ester [16] was likewise found. Also because of the absence of any absorption at 3100—3000, 1420 or 915 cm^{-1} [17], characteristic of the vinyl group, the structure XIII could be excluded.

The NMR spectrum exhibits an absorption peak at $\tau = 3.32$ p.p.m. (carbon tetrachloride solution, tetramethylsilane the internal reference). This indicates the presence of one proton attached to a doubly bonded carbon atom. The structure of the peak (a triplet with the coupling constant $J = 7$ cycles/sec and further unresolved fine structure) was consistent with the presence of a methylene group at the proton-carrying ethylenic carbon atom and a methyl group at the other: $-CH_2CH=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-$. Ester VI is the only conceivable isomer containing this grouping, and the rest of the NMR spectrum was not incompatible with this formula.

Investigations related to the high-boiling product from *sec*-butyl crotonate and butylmagnesium bromide: di-*sec*-butyl α-(1-methylpentyl)-β-methylglutarate (III)

This product, which had previously been obtained in varying yields by conjugate addition reaction,[2,6] was to about 90 % one single substance (III), b.p. 135—138°/0.9 mm, n_D^{20} 1.4449 (reported [2] 136°/0.8 mm, n_D^{25} 1.4400). According to the gas-chromatographic analysis the main compound consists of two isomers, presumably diastereomers.

Attempted Michael addition of sec*-butyl 3-methylheptanoate to* sec*-butyl crotonate in the presence of butylmagnesium bromide.* The reaction between *sec*-butyl crotonate (0.1 mole) and butylmagnesium bromide (0.25 mole) was carried out according to the standard procedure for the preparation of 3-methylheptanoic ester,[6] except that a large amount (0.2 mole) of *sec*-butyl 3-methylheptanoate was present during the reaction. Two experiments were run; in one the 3-methylheptanoic ester was added to the ether solution of crotonic ester, so that a mixture of the two esters was added to the Grignard reagent. In the other experiment the 3-methylheptanoic ester was added to the Grignard reagent during 10 min prior to the addition of the crotonic ester. The products

* The total amount of VI formed, determined by means of gas chromatography, was about 36 %.

obtained were almost exactly the same and formed in the same amounts in the two experiments. The result was equal to that which could be calculated from a normal conjugate addition without extra 3-methylheptanoic ester and a "blind" reaction between 3-methylheptanoic ester and butylmagnesium bromide (without crotonic ester). The 3-methylheptanoic ester apparently reacted to some extent with the Grignard reagent to form a tertiary alcohol, but did not add to the crotonic ester.

Additions of the magnesium enolate of sec*-butyl 3-methylheptanoate to* sec*-butyl crotonate.* The normal conjugate addition reaction between *sec*-butyl crotonate (0.1 mole) and butylmagnesium bromide (0.25 mole) was carried out,[6] except that the reaction mixture was not worked up. Instead it was again cooled down to 0°, and the excess of Grignard reagent was attempted destroyed by the addition during 10 min of an ether solution of varying amounts of a neutralizing agent, such as glacial acetic acid or butanol. Then another portion (0.1 mole) of crotonic ester was added during one hour. After further stirring at 0° for 1 h and at room temperature for another hour the following average yields were obtained. The high-boiling product III: 40 – 57 %, 3-methylheptanoic ester: 24 – 36 %, while 34 – 2 % of the crotonic ester was recovered.

Addition of sec*-butyl crotonate to a deficiency of butyl Grignard reagent.* This reaction was carried out as the standard conjugate addition reaction,[6] except that only 0.05 mole of Grignard reagent was used to 0.1 mole of crotonic ester. Of the crotonic ester 32 % was recovered; the rest was almost quantitatively transformed into the high-boiling product III, the yield being 61 %. The gas-chromatographic analysis showed that no crotonic ester dimer (II) was present in the reaction products.

Attempted addition of butylmagnesium bromide to crotonic ester dimer II. Di-*sec*-butyl α-ethylidene-β-methylglutarate, b.p. 102°/0.6 mm, n_D^{20} 1.4479 (reported [2] 120 – 121°/1.5 mm, n_D^{25} 1.4443), was obtained in 66 % yield as previously described [2] by the intermolecular Michael condensation in the presence of sodium *sec*-butoxide. The product was checked by infra-red spectroscopy and NMR spectroscopy. The infra-red spectrum [2] is entirely consistent with the proposed structure II. The NMR spectrum shows a signal for a vinylic proton with a fine structure showing spin-spin coupling to a methyl group, a feature which is possible only for the structure II among the different isomers. Furthermore, the ester was by conventional methods (*cf.* above) converted into the corresponding anhydride, the infra-red and NMR spectra of which were in complete agreement with α-ethylidene-β-methylglutaric anhydride, b.p. 89°/0.3 mm (Found: C 62.40; H 6.31. Calc. for $C_8H_{10}O_3$ (154.16): C 62.32; H 6.54).

The above ester II (28.4 g, 0.1 mole) dissolved in ether (100 ml), was added to a solution of butylmagnesium bromide (0.25 mole) as in the standard procedure for the conjugate addition reaction.[6] There was obtained about 19 g of product (about 80 % calculated on the basis of unrecovered starting material), b.p. 128 – 136°/0.5 mm, n_D^{25} 1.4568. It proved difficult to obtain a pure compound (Found: C 74.75; H 11.70. Calc. for XII, $C_{20}H_{38}O_3$ (326.50): C 73.57; H 11.73). The infra-red spectrum showed the presence of a *sec*-butyl ester group [16] and a ketone carbonyl group at 1715 cm^{-1} (5.83 μ) as well as a band at 1727 cm^{-1} (5.79 μ) considered as an ester carbonyl absorption. This compound (presumably *sec*-butyl 2-(1′-methylpentyl)-3-methyl-5-oxononanoate, XII) was converted into the corresponding methyl ester by way of saponification and esterification, b.p. 106 – 107°/0.3 mm, $n_D^{22.5}$ 1.4533. The analysis of this ester was even less correct than that of the *sec*-butyl ester (Found: C 73.60; H 11.27. Calc. for $C_{17}H_{32}O_3$ (284.43): C 71.78; H 11.34). The infra-red spectrum, on the other hand, was consistent with the structure of the methyl ester corresponding to XII, showing a ketonic and an ester carbonyl carbonyl absorption at 1712 cm^{-1} (5.84 μ) and 1739 cm^{-1} (5.75 μ), respectively. Corresponding to the poor elemental analyses for these products the gas-chromatographic analyses revealed the presence of rather large amounts of impurities.

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