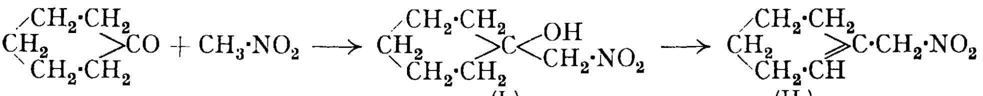
126. *The Effect of the Nitro-group in Three-carbon Tautomerism.*

By H. B. Fraser and G. A. R. Kon.

As tautomerism in a three-carbon system is favoured by the presence of a negative group on one of the terminal carbon atoms, the effect of the nitro-group in nitro-olefins and nitro-esters on this property has been examined.

The nitro-hydrocarbons were prepared from nitromethane or a homologue and cyclic ketones; *e.g.*, *cyclo*hexanone yields (I) only with sodium ethoxide as condensing agent,



$$CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}CO + CH_3{\cdot}NO_2 \longrightarrow CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}C{<}\begin{matrix}OH\\CH_2{\cdot}NO_2\end{matrix} \longrightarrow CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH\end{matrix}{\geqslant}C{\cdot}CH_2{\cdot}NO_2$$

(I.) (II.)

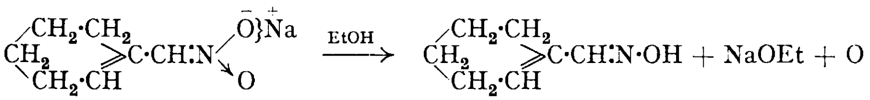
and (I) and (II) with piperidine. The *hydroxy*-compound is readily dehydrated to 1-*nitromethyl*cyclo*hexene* (II).

Methyl ethyl, diethyl, and methyl propyl ketones condense with nitromethane (2 mols.) to form products of the type $RR'C(CH_2{\cdot}NO_2)_2$.

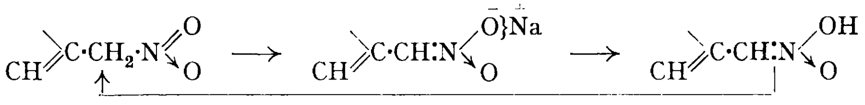
The nitro-olefin (II) was shown to have a $\beta\gamma$-unsaturated structure by oxidation to adipic acid both with permanganate and with ozone, and by a comparison of its molecular refraction with that of related compounds; the corresponding *cyclo*pentane derivative also has a similar structure.

The nitro-olefin (II) in dilute aqueous solution is acid to litmus; alcoholic solutions can be fairly rapidly titrated with alkali, although the end-point is not sharp. Freshly prepared solutions do not give a colour with ferric chloride. The sodio-derivative, formed with great ease, gives in water an alkaline solution which develops a purple colour with ferric chloride, and from which the solid *aci*-form is precipitated on cautious acidification. The *aci*-form is characterised by its immediate solubility in alkali and even in aqueous sodium bicarbonate, and by the deep colour it gives with ferric chloride. It is slightly more reactive towards iodine chloride than the parent nitro-olefin. It is unstable and reverts completely to the liquid form in an evacuated desiccator after an hour, as is shown by the disappearance of the reaction with ferric chloride: the nitro-form thus produced does not differ in any way from the initial material, and there appears to be no tendency to produce the Δ^{α}-isomeride.

All attempts to alkylate the nitro-olefin were unsuccessful: no reaction takes place between the sodio-derivative and alkyl iodides in neutral solvents, and in alcoholic solution Δ^1-tetrahydrobenzaldoxime is produced (compare Kohler and Stone, *J. Amer. Chem. Soc.*, 1930, **52**, 761):



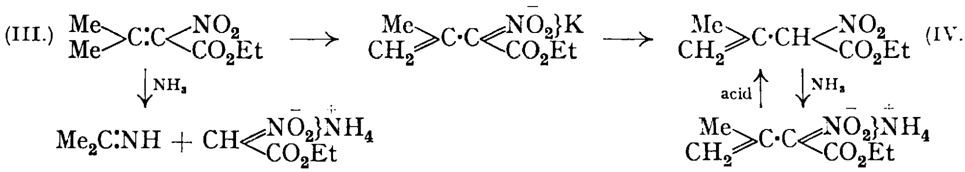
This shows that the anionic charge in the nitrolate ion remains throughout on oxygen and that there is no tendency for its redistribution even to the α-carbon of the three-carbon system, otherwise the formation of an α-alkyl derivative would be expected. The formation of the *aci*-form is also due to this cause; the gradual reconversion of the *aci*-form into the nitro-form shows that equilibrium is eventually established in the system, but this does not involve the three-carbon system and can be formulated as follows:



Although α-alkyl derivatives cannot be obtained from the nitro-olefin (II) by alkylation, they are readily formed by the condensation of *cyclo*hexanone with nitroethane or nitropropane; they are in every way similar to the compound (II).

It might be inferred from these results that the nitro-group does not confer mobility on a three-carbon system. Actually, owing to the existence of the nitro-olefins solely in their Δ^{β}-modifications, the mobility is not apparent and only becomes so in the related nitro-esters. The overwhelming predominance of the Δ^{β}-form in the nitro-olefins can be attributed to the inductive effect of the nitro-group, which increases the toleration of the adjacent carbon for covalent union with hydrogen.

By the nitration of ethyl ββ-dimethylacrylate Bouveault and Wahl (*Compt. rend.*, 1900, **131**, 687, 748; *Bull. Soc. chim.*, 1901, **25**, 808) obtained an α-nitro-Δ^{α}-ester (III), which gave a potassio-derivative (of undetermined structure) from which the isomeric Δ^{β}-ester (IV) was produced on acidification. The structures assigned to the two esters were based on the facts that (III) undergoes fission with ammonia, giving the ammonium compound of ethyl nitroacetate, and (IV) forms an unstable ammonium compound, from which it can be regenerated.



We have confirmed the structures of the two esters by oxidation and by an examination of their physical properties. Neither ester gives a colour with ferric chloride, but in aqueous solution acquires this property on keeping; such solutions are faintly acid. The Δ^{β}-ester (IV) has a pleasant odour and is characterised by the rapidity with which its alcoholic solution can be titrated with alkali. The ester produced on acidification of the potassio-derivative does not contain any measurable amount of the *aci*-form and, unlike the potassio-derivative, does not give a colour with ferric chloride; it can be concluded that equilibrium between the nitro- and the *aci*-nitro-form is very rapidly established, doubtless owing to the additional activation due to the carbethoxy-group. In addition, the Δ^{β}-ester always contains a small amount of the Δ^{α}-isomeride, which increases if the regeneration is carried out without special precautions; this result was observed on one occasion when benzoic acid was used to liberate the Δ^{β}-ester, probably because the reaction required some days for completion. It can therefore be concluded that there is a definite tendency in these compounds for a redistribution of the anionic charge in the three-carbon system, a tendency not observed in the nitro-olefins and also attributable to the effect of the carbethoxy-group; the formation of a potassio-derivative from a Δ^{α}-ester must, of course, likewise involve a rearrangement within the three-carbon system. The latter change is slow compared with the rapid equilibration of the nitro–*aci*-nitro-system, because the Δ^{α}-ester can be titrated with alkali but the process takes about an hour to complete.

Ethyl *cyclo*hexylideneacetate is readily nitrated, giving an *α-nitro*-Δ^{α}-ester convertible through the potassio-derivative into the Δ^{β}-*isomeride*, which is not obtainable by the nitration of ethyl *cyclo*hexenylacetate. The two esters are entirely analogous to those discussed above. Their physical properties show the expected differences and furnish a welcome standard of comparison with those of the corresponding nitro-olefins. The esters could not be alkylated : no reaction took place in neutral solvents, and in alcoholic solution the *oxime* of ethyl Δ^{1}-*cyclo*hexenylpyruvate was formed (compare p. 605).

Ethyl ββ-diethylacrylate and ethyl β-methyl-β-propylacrylate also give *α-nitro*-Δ^{α}-esters, convertible into their Δ^{β}-*isomerides* through their potassio-derivatives. They do not call for any special remark, except that the Δ^{β}-ester derived from the methylpropyl compound appears to give acetaldehyde in place of propaldehyde on ozonisation; the compound is still under investigation.

EXPERIMENTAL.

Condensation of cyclo*Hexanone with Nitromethane.*—17 C.c. of nitromethane and 30 c.c. of *cyclo*hexanone (excess) were treated with 2—3 c.c. of a solution of 1 g. of sodium in 15 c.c. of alcohol. After 12 hours, the mixture was treated with dilute acid and extracted with ether, the extract washed with water, aqueous sodium bicarbonate, and water, dried, and evaporated, and the residue distilled. A 45% yield of 1-*nitromethyl*cyclo*hexanol* (I) was obtained, b. p. 125—130°/17 mm.; this on redistillation had $d_{4^{\circ}}^{20\cdot8^{\circ}}$ 1·1506, n_D 1·4855, $[R_L]_D$ 39·88 (Found : C, 53·0; H, 8·4; N, 9·0. $C_7H_{13}O_3N$ requires C, 52·8; H, 8·2; N, 8·8%). When 1·5 c.c. of piperidine were used in place of sodium ethoxide in the above condensation, a 40% yield of condensation product was obtained; about 75% of this boiled at 112—116°/17 mm., had $d_{4^{\circ}}^{20\cdot0^{\circ}}$ 1·0699, n_D 1·4853, $[R_L]_D$ 37·82 (calc., 37·49), and consisted of 1-*nitromethyl*cyclo*hexene* (II) (Found : C, 59·3; H, 7·7; N, 10·0. $C_7H_{11}O_2N$ requires C, 59·5; H, 7·9; N, 10·0%). A higher-boiling fraction consisted of the hydroxy-compound (Found : C, 53·1; H, 8·1; N, 8·7%). Other bases gave poorer yields of condensation product : methylamine or ethylamine in alcohol (30% yield), concentrated aqueous ammonia (20% yield), 10% aqueous sodium or potassium hydroxide (10% yield); pyridine and diethylamine appeared to bring about the formation of compounds of high molecular weight.

Dehydration of 1-*Nitromethyl*cyclo*hexanol* (I).—(i) Dehydration with phosphoric oxide or hot acetic anhydride was unsatisfactory. (ii) The hydroxy-compound (25 g.) was heated for 1·5 hours with 40 g. of phosphorus oxychloride in 150 c.c. of benzene, cooled, and treated with ice-water, and the benzene solution washed with sodium bicarbonate, water, dried, and distilled under reduced pressure; the yield of the olefin was 55%; b. p. 106—108°/17 mm., $d_{4^{\circ}}^{20\cdot0^{\circ}}$ 1·0733, n_D 1·4856, $[R_L]_D$ 37·74. (iii) A 70—75% yield of the same material was obtained by adding 20 g. of thionyl chloride drop by drop to 25 g. of the hydroxy-compound in 25 g. of pyridine cooled in a freezing mixture, and working up the mixture as above after 2 hours (at room temperature); this method was adopted as standard.

Oxidation of 1-*Nitromethyl*cyclo*hexene* (II).—(i) 8 G. of the olefin, emulsified with ice-water, were shaken with ice-cold 3·16% potassium permanganate solution until the colour persisted (5O were used). The filtered liquid was shaken with ether, concentrated, acidified, and extracted with ether. The extract was evaporated, nitrous fumes finally escaping; the residue was adipic acid (good yield). No trace of *cyclo*hexanone was isolated; a control experiment showed that it is stable under the conditions used.

(ii) 6 G. of the olefin in 50 c.c. of ethyl acetate were treated with ozonised oxygen until the latter escaped freely; the absorption was rapid, and on removal of the solvent under reduced pressure a stable crystalline *ozonide* remained, m. p. 105° after crystallisation from ethyl acetate (Found: C, 44·3; H, 6·1; N, 7·6. $C_7H_{11}O_5N$ requires C, 44·4; H, 5·9; N, 7·4%); it was unchanged by cold water after some days. The ozonide was decomposed by warm 10% aqueous sodium bicarbonate, dissolving almost completely. The alkaline solution was shaken with ether and acidified; ether then extracted adipic acid as the sole product.

Sodio-derivative and aci-*Form of* (II).—The sodio-derivative was immediately precipitated when the nitro-olefin was added to sodium ethoxide suspended in ether; after being washed with ether and with petroleum, it was a yellow powder, which could be kept in a desiccator for some time. When an aqueous solution was acidified with a very small excess of acetic or 10% hydrochloric acid, the solid *aci*-form of the nitro-olefin was precipitated, m. p. 63—65°. A similar product was obtained by carrying out the regeneration with dry benzoic acid in anhydrous ether and removing the sodium benzoate formed after 3 days, or by passing dry hydrogen chloride into an ethereal suspension of the sodio-derivative. Oxidation of the product showed that the pure Δ^{β}-compound was formed in every case.

Ammonium derivative. When dry ammonia was passed into an ethereal solution of the nitro-olefin, a yellow ammonium salt was precipitated after some time; it decomposed in a vacuum desiccator, or on treatment with dilute acid, regenerating the original olefin, $d_{4°}^{20·0°}$ 1·0721, n_D 1·4845. A brilliant green colour developed when an ethereal suspension of the ammonium compound was treated with dilute hydrochloric acid (compare Steinkopf and Jürgens, *J. pr. Chem.*, 1911, **84**, 686).

Attempted alkylation. The sodio-derivative of (II) was unchanged by methyl or ethyl iodide in boiling benzene or ether solution. If alcohol was added to such a mixture, the solid dissolved on heating over-night and sodium iodide was precipitated. Water was then added, and the ethereal solution washed with sodium sulphite, water, dried, and evaporated. On distillation the main fraction, b. p. 100—110°/12 mm., partly solidified; the solid was washed with light petroleum and recrystallised from petroleum (b. p. 60—80°), forming long needles m. p. 98°, of Δ^1-tetrahydrobenzaldoxime (Wallach, *Annalen*, 1908, **359**, 252) (Found: C, 67·5; H, 8·8; N, 11·4. Calc.: C, 67·2; H, 8·9; N, 11·2%), from which the aldehyde could be produced by warming with dilute sulphuric acid.

Effect of mineral acids. The nitro-olefin was unchanged after prolonged boiling with 10 or 30% hydrochloric acid or with 25% sulphuric acid.

Condensation of cyclo*Hexanone with Nitroethane.*—The reactants and piperidine were left together for a week, and the product was worked up as described on p. 606; sodium ethoxide was a less satisfactory catalyst. A 30% yield of 1-α-*nitroethyl*cyclo*hexanol* was obtained as a viscous colourless oil, b. p. 122—125°/14 mm., $d_{4°}^{20·0°}$ 1·1122, n_D 1·4852, $[R_L]_D$ 44·65 (Found: C, 55·4; H, 8·4; N, 8·1. $C_8H_{15}O_3N$ requires C, 55·6; H, 8·7; N, 8·1%). No unsaturated fraction appeared to be formed.

Dehydration. This was carried out with thionyl chloride (p. 606); 1-*nitroethyl*cyclo*hexene* had b. p. 120—123°/24 mm., $d_{4°}^{20·0°}$ 1·0529, n_D 1·4835, $[R_L]_D$ 41·71 (Found: C, 62·2; H, 8·5; N, 8·9. $C_8H_{13}O_2N$ requires C, 61·9; H, 8·4; N, 9·0%). It was a pale yellow, mobile oil of pleasant odour.

Oxidation of 1-α-*Nitroethyl*cyclo*hexene.*—The olefin was oxidised with potassium permanganate in neutral solution as described on p. 606. The acid fraction contained adipic acid and some acetic acid, which was identified as its *p*-bromophenacyl ester, m. p. 85° (yield of the mixed acids, 60%). The same products were also obtained on ozonisation; the ozonide was not obtained as a solid, but was again very stable.

Sodio-derivative. A yellow sodio-derivative was formed from 1-α-nitroethyl*cyclo*hexene with the aid of sodium ethoxide. On treatment with ice-cold dilute hydrochloric acid, or with dry benzoic acid in ether, it gave a liquid *aci*-form, which developed a purple colour with ferric chloride, and could be kept about 1·5 hours before being converted into the initial nitro-form, $d_{4°}^{20·0°}$ 1·0536, n_D 1·4842.

Ammonium derivative. A yellow ammonium derivative was slowly formed by the method described above; the original nitro-olefin was obtained from it on keeping.

Condensation of cyclo*Hexanone with* α-*Nitropropane.*—This was carried out with the aid of piperidine. The 1-α-*nitropropyl*cyclo*hexanol* obtained (yield, 10%) had b. p. 140—145°/12 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0922, n_D 1·4794, $[R_L]_D$ 48·60 (Found : C, 57·9; H, 9·0; N, 7·6. $C_9H_{17}O_3N$ requires C, 57·7; H, 9·2; N, 7·5%). Dehydration with thionyl chloride gave an 80% yield of 1-α-nitropropyl*cyclo*hexene, b. p. 117—118°/11 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0302, n_D 1·4813, $[R_L]_D$ 46·76.

Oxidation.—(i) Oxidation of the above nitro-olefin with permanganate as described on p. 606 gave a small amount of neutral fraction, in which propaldehyde was identified in the form of its condensation product with dimethyldihydroresorcinol, m. p. 153°, mixed m. p. 154°. The acid products (60% yield) were adipic acid and propionic acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 62°). (ii) The ozonide was obtained as a crystalline solid; it was decomposed by warm aqueous sodium bicarbonate, yielding adipic and propionic acids as the sole products.

Sodio-derivative. This and the ammonium derivative were formed exactly as described on p. 607; the *aci*-form of the nitro-olefin was also obtained in the same way and had similar properties and stability and the nitro-olefin re-formed from it was identical with the initial material.

Condensation of cyclo*Pentanone with Nitromethane.*—This was carried out with the aid of piperidine. The product, obtained in poor yield, consisted chiefly of 1-*nitromethyl*cyclo*pentene*, b. p. 89—91°/14 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0810, n_D 1·4783, $[R_L]_D$ 33·29 (Found : C, 57·0; H, 6·9; N, 10·6. $C_6H_9O_2N$ requires C, 56·7; H, 7·1; N, 11·0%). Oxidation of this with permanganate gave glutaric acid.

The sodio-derivative, which was readily formed, gave, on treatment with ice-cold dilute hydrochloric or acetic acid, the *aci*-form as an oil, which developed a green colour with ferric chloride and was converted after 1½ hours into the original nitro-form, $d_{4^\circ}^{20\cdot0^\circ}$ 1·0826, n_D 1·4788.

Condensation of Aliphatic Ketones with Nitromethane.—With sodium ethoxide, piperidine, pyridine, methylamine, or " molecular " sodium as condensing agent, the yield of the product was 15—25%. Acetone gave a *product*, b. p. about 135°/19 mm., m. p. 89—90° (Found : C, 37·2; H, 6·4; N, 17·3. $C_5H_{10}O_4N_2$ requires C, 37·0; H, 6·2; N, 17·3%). Methyl ethyl ketone gave a pale yellow *oil* of unpleasant odour, b. p. 135—138°/9 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·1886, n_D 1·4662 (Found : C, 41·1; H, 7·1; N, 16·2. $C_6H_{12}O_4N_2$ requires C, 40·9; H, 6·9; N, 15·9%). Diethyl ketone gave an *oil*, b. p. 135—138°/10 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·1713, n_D 1·4660 (Found : C, 44·0; H, 7·2; N, 15·0. $C_7H_{14}O_4N_2$ requires C, 44·2; H, 7·4; N, 14·7%). Methyl propyl ketone gave an *oil*, b. p. 144°/11 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·1498, n_D 1·4980 (Found : C, 44·5; H, 7·4; N, 15·0. $C_7H_{14}O_4N_2$ requires C, 44·2; H, 7·4; N, 14·7%).

Ethyl α-Nitro-β-methyl-Δ^{α}-butenoate (III).—This ester was prepared essentially as described by Bouveault and Wahl (*Compt. rend.*, 1900, **131**, 687); the nitration was performed in a wide-necked flask cooled in a freezing mixture, air being passed through the reaction mixture to ensure thorough mixing; the temperature was 0—5°. The pure ester had $d_{4^\circ}^{22\cdot0^\circ}$ 1·1149, n_D 1·4598, $[R_L]_D$ 42·49 (Found : C, 48·4; H, 6·3; N, 8·2. Calc. : C, 48·5; H, 6·4; N, 8·1%). Titration in alcoholic solution with standard alkali required an hour for completion.

Oxidation. (i) The ester was oxidised with permanganate as described on p. 606 (3O/g.-mol.). The filtered solution, which gave a positive iodoform reaction in the cold, was distilled in steam; treatment of the first 20 c.c. of distillate with semicarbazide gave an abundant precipitate of acetonesemicarbazone. The remaining solution, acidified and concentrated, deposited oxalic acid. (ii) Ozonisation of the ester (5 g.) required 7 days' continuous treatment in ethyl acetate solution. The ozonide, decomposed by shaking with water for 12 hours, gave a very small amount of formaldehyde (detected by means of dimethyldihydroresorcinol) and also acetone and oxalic acid.

Action of ammonia. Bouveault and Wahl's results were confirmed, except that the ammonium derivative of ethyl nitroacetate was found to melt at 131° after crystallisation from methyl alcohol (Found : C, 32·4; H, 6·5; N, 18·9. Calc. : C, 32·0; H, 6·7; N, 18·7%). The ester obtained on acidification had b. p. 88—91°/12 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·2085, n_D 1·4247 (Found : C, 36·4; H, 5·2; N, 10·8. Calc. : C, 36·1; H, 6·3; N, 10·5%).

Ethyl α-Nitro-β-methyl-Δ^{β}-butenoate (IV).—The potassio-derivative prepared from the Δ^{α}-ester was treated with a very slight excess of cold dilute hydrochloric acid. The oil precipitated, which gave no colour with ferric chloride immediately after formation, was extracted with ether; it had b. p. 100—104°/13 mm., $d_{4^\circ}^{22\cdot0^\circ}$ 1·0507, n_D 1·4440, $[R_L]_D$ 41·60 (Found : C, 48·3; H, 6·5; N, 8·4. Calc. : C, 48·5; H, 6·4; N, 8·1%).

A similar product was obtained by passing somewhat less than the calculated amount of dry hydrogen chloride into a suspension of the potassio-derivative in ether at 0°. The ester regenerated by means of benzoic acid in ether after 5 days was evidently a mixture of the two isomerides. A fraction, b. p. 106—107°/12 mm., had $d_{4^\circ}^{19\cdot0^\circ}$ 1·1120, n_D 1·4528, $[R_L]_D$ 42·06; another, b. p. 110—112°/12 mm., had $d_{4^\circ}^{19\cdot0^\circ}$ 1·1143, n_D 1·4560, $[R_L]_D$ 42·23.

Oxidation. The ozonide of the ester (the first specimen described above) was readily decomposed by shaking with water. The aqueous solution gave a positive iodoform reaction, but acetone could not be isolated as semicarbazone. Formaldehyde was isolated in quantity by means of dimethyldihydroresorcinol; oxalic acid and acetic acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 85°) were also identified.

Ammonium compound. Bouveault and Wahl's results were confirmed; the Δ^{β}-ester was obtained on acidification, b. p. 112—115°/21 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·1056, n_D 1·4440, $[R_L]_D$ 41·58 (Found: C, 48·6; H, 6·2; N, 8·0%).

*Ethyl α-Nitro*cyclo*hexylideneacetate.*—Attempts to condense ethyl nitroacetate (Bouveault and Wahl, *Bull. Soc. chim.*, 1904, **31**, 847, 929) with *cyclo*hexanone were unsuccessful. Ethyl *cyclo*hexylideneacetate was nitrated as described on p. 608, but the best results were obtained when the nitration product was poured into ice-water as soon as all the ester had been introduced. The *ester* (yield, 50%) had b. p. 130—134°/4 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·1330, n_D 1·4918, $[R_L]_D$ 54·55 (Found: C, 56·2; H, 7·1; N, 6·8. $C_{10}H_{15}O_4N$ requires C, 56·3; H, 7·1; N, 6·6%). It was a viscous yellow oil with a pungent odour and gave a colour with ferric chloride only after a long time.

Oxidation. Oxidation with permanganate (equivalent to 3 atoms of oxygen) as described on p. 606 gave an 85% yield of *cyclo*hexanone, identified in the form of semicarbazone; the acid fraction consisted of oxalic acid, but no adipic acid was detected. The same products were also formed on ozonisation.

Action of ammonia. An ethereal solution of the ester was treated with dry ammonia, and the precipitated salt, and also the filtrate from it, were treated with dilute acid. The products were ethyl nitroacetate and *cyclo*hexanone, respectively.

Potassio-derivative. This was obtained in 40% yield by leaving the ester with an ethereal suspension of potassium ethoxide over-night; it gave a deep purple colour with ferric chloride.

*Ethyl α-Nitro-Δ^1-*cyclo*hexenylacetate.*—The above potassio-derivative gave on cautious acidification with cold dilute hydrochloric acid the Δ^{β}-*ester*, b. p. 124—126°/3 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·1332, n_D 1·4806, $[R_L]_D$ 53·40 (Found: C, 56·1; H, 6·9; N, 6·9. $C_{10}H_{15}O_4N$ requires C, 56·3; H, 7·1; N, 6·6%). The ester is immediately soluble in cold sodium hydroxide solution.

Oxidation. The Δ^{β}-ester required permanganate equivalent to 5 atoms of oxygen for oxidation. The neutral fraction consisted of a small amount of unattacked ester. Oxalic and adipic acids were obtained in quantity.

Action of ammonia. On treatment with gaseous ammonia, the Δ^{β}-ester formed an unstable ammonium compound, from which it was recovered unchanged on acidification, $d_{4^\circ}^{20\cdot0^\circ}$ 1·1329, n_D 1·4800, $[R_L]_D$ 53·46.

Attempted alkylation. The potassio-derivative was unchanged after prolonged boiling with ethyl iodide in benzene or ether solution. In alcoholic solution, it slowly dissolved, and potassium iodide was precipitated. The product solidified after distillation under reduced pressure, m. p. 98° after crystallisation from petroleum (b. p. 60—80°), and probably consisted of the *oxime* of ethyl Δ^1-*cyclo*hexenylpyruvate (Found: C, 61·2; H, 7·5; N, 7·2. $C_{10}H_{15}O_3N$ requires C, 60·9; H, 7·7; N, 6·9%).

Ethyl α-Nitro-β-ethyl-Δ^{α}-pentenoate.—Ethyl ββ-diethylacrylate (Kon and Nargund, J., 1932, 2461) was nitrated as described on p. 608 and gave a 25% yield of the *nitro*-ester, b. p. 119—122°/13 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0724, n_D 1·4608, $[R_L]_D$ 51·48. (Found: C, 54·0; H, 7·5; N, 7·3. $C_9H_{15}O_4N$ requires C, 53·7; H, 7·5; N, 7·0%). This was a yellow oil with a sharp odour. On oxidation with permanganate (3O) it gave diethyl ketone and oxalic acid; with ammonia it gave the ammonium salt of ethyl nitroacetate, and the mother-liquor on acidification was found to contain diethyl ketone.

Ethyl α-Nitro-β-ethyl-Δ^{β}-pentenoate.—The above Δ^{α}-ester gave a poor yield of potassio-derivative, which developed a purple colour with ferric chloride and on acidification with 10% hydrochloric acid gave the Δ^{β}-*ester*, b. p. 117—120°/14 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0652, n_D 1·4499, $[R_L]_D$ 50·73. This ester did not give a colour with ferric chloride even immediately after formation, but at once dissolved in alkali and could be rapidly titrated (Found: C, 54·1; H, 7·4; N, 6·9. $C_9H_{15}O_4N$ requires C, 53·7; H, 7·5; N, 7·0%). The products of decomposition of its ozonide were acetaldehyde (identified as the dimethyldihydroresorcinol derivative, m. p. and mixed m. p. 138—139°) and acetic and propionic acids (identified as *p*-bromophenacyl esters). With ammonia the Δ^{β}-ester formed an unstable ammonium compound, from which it could be regenerated on acidification, b. p. 117—120°/15 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0659, n_D 1·4504, $[R_L]_D$ 50·73. An attempt to prepare the Δ^{β}-ester by nitration of ethyl β-ethyl-Δ^{β}-pentenoate was unsuccessful.

Ethyl α-Nitro-β-methyl-Δ^{α}-hexenoate.—Ethyl β-methyl-β-propylacrylate, prepared from the mixture of the two stereoisomeric acids (Kon, Leton, Linstead, and Parsons, J., 1931, 1411), was nitrated, giving a 25% yield of the *nitro*-ester, b. p. 119—122°/13 mm., $d_{4°}^{20·0°}$ 1·0703, n_D 1·4600, $[R_L]_D$ 51·48 (Found : C, 53·9; H, 7·6; N, 7·0. $C_9H_{15}O_4N$ requires C, 53·7; H, 7·5; N, 7·0%). This ester gave methyl propyl ketone and oxalic acid on oxidation (permanganate or ozone) and was converted by dry ammonia into methyl propyl ketone and ethyl nitroacetate.

Ethyl α-Nitro-β-methyl-Δ^β-hexenoate.—The Δ^α-ester was converted into a yellow potassio-derivative, which gave a purple colour with ferric chloride and on acidification with 10% hydrochloric acid gave the Δ^β-*ester*, b. p. 118—120°/14 mm., $d_{4°}^{20·0°}$ 1·0665, n_D 1·4505, $[R_L]_D$ 50·71 (Found : C, 54·0; H, 7·2; N, 7·1. $C_9H_{15}O_4N$ requires C, 53·7; H, 7·5; N, 7·0%); it was characterised by its immediate solubility in cold 10% sodium hydroxide solution. Oxidation (ozone) gave a considerable quantity of acetaldehyde (dimethyldihydroresorcinol compound, m. p. and mixed m. p. 138—139°) and also oxalic acid and butyric acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 62°), but no propaldehyde could be found. The structure of the ester is therefore uncertain.

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