11β-oxido-Δ^4-pregnene-17α,21-diol-3,20-dione 21-acetate (II) show R_f 0.33 and 0.50, respectively. Fractions amounting to 2.04 g., rich in product were rechromatographed on neutral alumina to yield 0.667 g. of purified compound, m.p. 195–215° dec. Treatment with decolorizing charcoal and three crystallizations from acetone–hexane yielded analytical material, m.p. 213–216° dec., $[\alpha]^{24}\text{D}$ +219° (1.0), $\lambda_{\max}$ 238 mμ (ε 16,400); $\lambda\lambda_{\max}^{\text{Nujol}}$ 2.82, 2.89, 5.81, 6.00 and 6.19 μ.

Anal. Calcd. for $C_{23}H_{30}O_6$: C, 68.69; H, 7.51. Found: C, 68.65; H, 7.58.

$\Delta^{4,8(9)}$-Pregnadiene-11β,17α,21-triol-3,20-dione 11β,21-Diacetate (XXIVa).—A solution consisting of 102.5 mg. (0.255 millimole) of $\Delta^{4,8(9)}$-pregnadiene-11β,17α,21-triol-3,20-dione 21-acetate (XXIV), 1 ml. of pyridine and 1 ml. (10.6 millimoles) of acetic anhydride was allowed to stand for 1 week at room temperature (24°). The mixture was diluted with 20 ml. of water, filtered and the residue washed with water. The precipitate amounting to 81.5 mg. (71.4%) was recrystallized from acetone–hexane to yield 65.4 mg. (57.3%) of product, m.p. 201–204°, $[\alpha]^{25}\text{D}$ +224° (1.0), $\lambda_{\max}$ 237 mμ (ε 16,000); $\lambda\lambda_{\max}^{\text{Nujol}}$ 2.96, 5.79, 5.97 and 6.13 μ.

Anal. Calcd. for $C_{25}H_{32}O_7$: C, 67.55; H, 7.26. Found: C, 67.52; H, 7.51.

$\Delta^{4,7,9(11)}$-Pregnatriene-17α,21-diol-3,20-dione 21-Acetate (XXV).—To a solution of 304 mg. (0.756 millimole) of 17α-hydroxy-$\Delta^{8(9)}$-dehydrocorticosterone 21-acetate (XXIV) and 3.75 ml. of pyridine cooled to 0° was added dropwise with cooling 0.75 ml. (10 millimoles) of methanesulfonyl chloride. The mixture was allowed to stand at 0° for 24 hours. To the mixture was added 10 g. of ice and after 15 minutes the product was extracted with ethyl acetate. Concentration of the washed, dried extract yielded 189 mg. (64.9%) of crude triene. The crude material was treated with decolorizing charcoal and crystallized twice from acetone–hexane to yield 85 mg. (29%) of pale yellow needles, m.p. 199–203°, $[\alpha]^{27}\text{D}$ +236° (1.0); $\lambda\lambda_{\max}$ 242.5 mμ (ε 26,200), 237.5(sh) and 250(sh) mμ (ε 24,900 and 22,100), $\lambda\lambda_{\max}^{\text{CHCl}_3}$ 2.9, 5.74(sh), 5.78, 6.0 and 6.12 μ.

Anal. Calcd. for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found: C, 71.53; H, 7.31.

Reduction of XXV with lithium aluminum hydride in tetrahydrofuran yielded an amorphous product; $\lambda\lambda_{\max}$ 237, 244 mμ (ε 7,780, 8,510), 251(sh) mμ (ε 6,130).

Acknowledgment.—The authors are indebted to R. W. Walker for infrared measurements and R. N. Boos for analytical determinations.

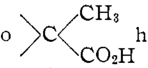
RAHWAY, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE]

Synthetic Studies in Resin Acids. II[1]

BY USHARANJAN GHATAK, NARENDRA NATH SAHA[2] AND PHANINDRA CHANDRA DUTTA[3]

RECEIVED FEBRUARY 18, 1957

The conversion of $>C{=}O$ to  $>C(CH_3)(CO_2H)$ has been studied for the case of cyclohexanone and 10-methyldecalone. Two successful methods were achieved for cyclohexanone and one of these was also effective for the decalone system. The second procedure, involving action of methylmagnesium iodide on ethyl 10-methyldecalidene-1-cyanoacetate, failed because reduction rather than addition occurred. The significance of the above syntheses for the preparation of diterpenoid resin acids is noted.

In the synthesis of compounds related to diterpenoid resin acids, the conversion of the tricyclic ketones[1,4] to the corresponding *gem*-methylcarboxylic acids, is of considerable importance. The purpose of the present investigation was to seek suitable means for this conversion, using cyclohexanone and 10-methyldecalone as model compounds. In this communication the essential steps for two procedures, which were successful for the synthesis of 1-methyl-1-carboxy-cyclohexane VII are described. A recent publication,[5] which appeared subsequent to our preliminary communication[6] embodying these methods, has also supported these results.

In procedure I, ethyl cyclohexane-1-carbethoxy-1-acetate obtained from the dicyano-ester[7] was the starting material. The silver salt of the monoester IV afforded the bromoester V on treatment with bromine. Hunsdiecker degradation promised to be a useful route to rather inaccessible bromides of the neopentyl type and hence it has been utilized successfully to build up the quaternary methyl group. The bromide V on reduction with zinc and acetic acid yielded VI, from which VII was obtained on alkaline hydrolysis. VII was further characterized by conversion to its amide.[8] In procedure II, VIII was obtained through the conjugate addition[9] of methyl Grignard reagent to III in the presence of cuprous iodide.[10] The controlled hydrolysis of VIII and pyrolysis of the acidic product yielded the nitrile IX. Attempts at acidic or alkaline hydrolysis of the nitrile were unsuccessful. The nitrile IX was then allowed to react with phenylmagnesium bromide leading to X, which on further reaction with the same reagent gave a mixture of the corresponding carbinol and the dehydrated product. This mixture was directly oxidized to VII.

With the idea that these two procedures in the case of unsymmetrical ketones should lead to dif-

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(1) (a) For a preliminary communication *cf. Chemistry & Industry*, 51 (1957); (b) Part I, N. N. Saha, P. N. Bagchi and P. C. Dutta, THIS JOURNAL, **77**, 3408 (1955).

(2) Post-doctoral Fellow, Department of Chemistry, University of Southern California.

(3) Communications regarding this paper may be sent to this author.

(4) G. Stork and A. W. Burgstahler, THIS JOURNAL, **73**, 3544 (1951).

(5) W. Parker and R. A. Raphael, *J. Chem. Soc.*, 1723 (1955).

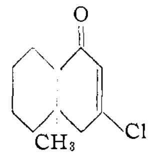
(6) N. N. Saha, P. Bagchi and P. C. Dutta, *Chemistry & Industry*, 1143 (1954).

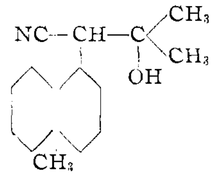
(7) A. Lapworth and J. A. McRae, *J. Chem. Soc.*, **121**, 2754 (1922).

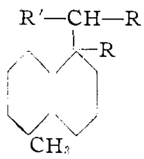
(8) J. Gutt. *Ber.*, **40**, 2067 (1907).

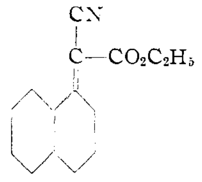
(9) (a) A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1943); (b) E. R. Alexander, J. D. McCollum and D. E. Paul, THIS JOURNAL, **72**, 4791 (1950).

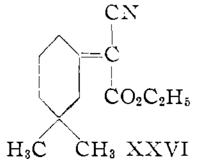
(10) M. S. Kharasch and P. O. Tawney, THIS JOURNAL, **63**, 2308 (1941); *cf.* R. M. Keefer, L. J. Andrews and R. E. Kepner, *ibid.*, **71**, 2381 (1949).

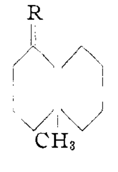

XII

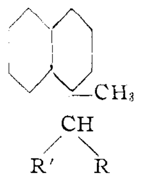

XXII

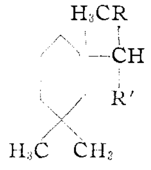

XIV, R = R' = CN; R'' = $CO_2C_2H_5$
XV, R = CO_2H; R'' = H; R' = CO_2H
XVI, R = CO_2CH_3; R'' = H, R' = CO_2H
XVII, R = CO_2CH_3; R'' = H, R' = Br
XVIII, R = CO_2CH_3; R' = R'' = H
XIX, R = H, R' = CN; R'' = CO_2CH_3
XX, R = R' = H; R'' = CN
XXI, R = R' = H; R'' = COC_6H_5
XXIII, R = H, R' = CN; R'' = $CO_2C_2H_5$
XXX, R = R' = H; R'' = CO_2CH_3


XXIV

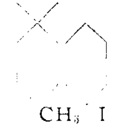

XXVI

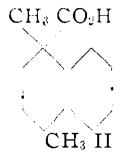

XI, R = O
XIII, R = $=C\begin{matrix}CN\\CO_2C_2H_5\end{matrix}$

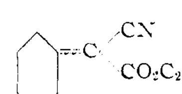

XXV, R = CN; R' = $CO_2C_2H_5$
XXVIII, R = H; R' = $COCH_3$

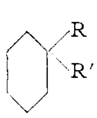

XXVII, R = CN; R' = $CO_2C_2H_5$
XXIX, R = H; R' = $COCH_3$

ferent epimers[11] and also for the reasons stated before,[1b] 10-methyldecalone (XI) was selected as the second starting ketone. In this case the stereochemistry of the final products, which were expected to result by the above routes, was of special interest in connection with the synthesis of the natural resin-acids, represented by abietic acid and podocarpic acid or their congeners. It was believed that the conjugate addition to the unsaturated cyano-ester XIII, of ions or components of Grignard complex probably through ions and/or radicals,[12] might be markedly influenced stereochemically[13] by the presence of the angular methyl group (*e.g.*, in XI). The degree of stereospecificity may not be the same in both cases and one of the reasons might be that the general pattern of homolytic reactions is singularly free from powerful electrostatic forces, which operate in ionic reactions in addition to steric factors. The first of the above routes proved successful and led to 1,10-dimethyldecalin-1-carboxylic acid, the stereochemistry of which may be either as shown in I or II.


I


II


III


IV, R = CH_2CO_2H; R' = $CO_2C_2H_5$
V, R = CH_2Br; R' = $CO_2C_2H_5$
VI, R = CH_3; R' = $CO_2C_2H_5$
VII, R = CH_3; R' = CO_2H
VIII, R = CH_3; R' = $CH(CN)CO_2C_2H_5$
IX, R = CH_3; R' = CH_2CN
X, R = CH_3; R' = $CH_2CO{\cdot}C_6H_5$

From consideration of the steric courses of reactions and results in a closely related work,[14] it can be concluded with confidence that the product obtained is II. That the synthetic acid did not belong to the podocarpic acid series (*e.g.*, I) was also apparent from the comparatively less drastic conditions,[15] that were required for the isolation of the acid II.

The ketone XI was obtained from 10-methyldecalin-1,3-dione.[16] This was converted to the chloro-ketone XII which in its turn was reduced catalytically with or without the addition of pyridine. The formation of the isomeric 3-ketone appeared less likely from steric considerations, and structure XI was confirmed through the isolation of 1-methylnaphthalene by action of methylmagnesium iodide and subsequent dehydrogenation. The desired ketone XI condensed[17] with ethyl cyanoacetate to afford XIII. The dicyano-ester XIV was obtained in an excellent yield by addition of hydrocyanic acid[18] to XIII. The dibasic acid XV was isolated in a highly crystalline form and the partial hydrolysis of the diester led to the half-ester XVI. Hunsdiecker degradation of the latter yielded XVII, which was reduced to XVIII. Finally acid II was obtained by hydrolyzing the ester with methanolic potassium hydroxide.

During the course of this investigation, the remote possibility of the formation of XXX in place of XVIII was considered and discarded on the basis of hydrolytic experiments. Attempts at hydrolysis under mild conditions led to the re-

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(11) N. N. Saha, Thesis, 1953, Calcutta University.

(12) M. S. Kharasch and O. Reinmuth, "Grignard Reaction of Nonmetallic Substances," Constable & Co., London, 1954, Chapter V.

(13) (a) D. H. Hey, *J. Chem. Soc.*, 1974 (1952); (b) H. Heusser, P. Th. Herzig, A. Fürst and Pl. A. Plattner, *Helv. Chim. Acta*, **33**, 1093 (1950).

(14) N. N. Saha, B. K. Ganguli and P. C. Dutta, *Chemistry & Industry*, 412 (1956).

(15) (a) I. R. Sherwood and W. F. Short, *J. Chem. Soc.*, 1006 (1938); (b) W. P. Campbell and D. Todd, THIS JOURNAL, **64**, 928 (1942).

(16) C. R. Clemo and H. G. Dickenson, *J. Chem. Soc.*, 735 (1935).

(17) E. J. Cragoe, C. M. Robb and J. M. Sprague, *J. Org. Chem.*, **15**, 381 (1950).

(18) E. Hope and W. Sheldon, *J. Chem. Soc.*, **121**, 2223 (1922).

covery of the ester thereby ruling out the structure XXX.

In the second route which was expected to lead to acid I, reaction of XIII with methylmagnesium iodide in the presence of cuprous iodide did not proceed as anticipated on the basis of reaction in the cyclohexane series; the product isolated was a complex mixture as revealed by infrared studies and was characterized by a strong hydroxyl band (3 μ) and a doublet (7.25 and 7.3μ) of a *gem*-dimethyl group. The neutral material was subjected to controlled alkaline hydrolysis. The acid from the base-soluble portion, was decarboxylated and the nitrile so obtained was converted into the corresponding phenyl ketone. The analytical values of it and of the related dinitrophenylhydrazone indicated that the ketone should be represented by XXI. This was further confirmed by the mixed melting point determination of this derivative, prepared from an authentic sample of the ketone XXI (*vide infra*). It is now apparent that the major product of the Grignard reaction is XXIII, resulting from the reduction of the double bond. Consequently XX represents the structure of the nitrile. This observation parallels action of Grignard reagents on azo-compounds[19] or hindered ketones.[20] There are recorded[21] some cases of reduction of alkalidene cyano-acetates with Grignard reagents from higher aliphatic as well as aromatic halides. In the original reaction mixture some amount of the compound XXII, quite analogous to that isolated in the case of the tricyclic ketone,[14] was most probably present but the isolation of the same or of the corresponding dehydration product in a pure state could not be accomplished.

To prepare an authentic dinitrophenylhydrazone of XXI, the unsaturated cyano-ester XIII was reduced with aluminum amalgam to XXIII which through the same series of reactions as described before, yielded the corresponding ketone. Fractional crystallization of the dinitrophenylhydrazones revealed that this ketone was a mixture of stereoisomers, one of which was identical with the ketone XXI described above.

Finally to trace the origin of this abnormal type of reaction induced by the Grignard reagent and to evaluate the steric effect of the angular methyl group, α-decalone was converted to XXIV, which led to the normal addition product XXV and the corresponding ketone XXVIII in good yields. Similarly XXVI from 3,3-dimethylcyclohexanone behaved in a normal way leading to XXVII, which yielded XXIX. In both cases the ketones were characterized through well-defined semicarbazones.

Evidently the powerful non-bonded interaction between the angular methyl group and the axially oriented intermediate complex,[22] incorporating the cyanoacetic ester residue in the normal addition product, was responsible for this abnormal reaction-path, indicating once more the importance of steric factors in the abnormalities of Grignard reactions.

Acknowledgments.—We are indebted to Prof. Norman Kharasch, Department of Chemistry, University of Southern California, for kindly reading this manuscript. Our grateful thanks are also due to Dr. R. Schwyzer, Basle, Switzerland, and to Mrs. Chhabi Dutta, University College of Science, Calcutta, for micro-analyses.

Experimental[23]

Ethyl 1-Bromomethylcyclohexane-1-carboxylate (V).—Ethyl cyclohexane-1-carbethoxy-1-acetate (15 g., 0.062 mole) was hydrolyzed with a solution of potassium hydroxide (4.5 g., 0.08 mole), water (4.5 ml.) and ethanol (81 ml.). The crude half-ester (11.1 g.) in alcohol (20 ml.) was neutralized (phenolphthalein) with 1 *N* sodium hydroxide solution and converted into the silver salt. It was dried at 50–60° and finally under vacuum at 110° for 15 hours. The salt (11 g.) was suspended in dry carbon tetrachloride (50 ml.) and gradually treated with a solution of bromine (2 ml.) in the same solvent (10 ml.) at the reflux temperature. Silver bromide was collected and the carbon tetrachloride layer was washed with 5% sodium carbonate solution. Distillation afforded 6.9 g. (43%), b.p. 105–107° (4 mm.).

Anal. Calcd. for $C_{10}H_{17}O_2Br$: C, 48.2; H, 6.8. Found: C, 48.2; H, 6.8.

Ethyl 1-Methylcyclohexane-1-carboxylate (VI).—A mixture of the bromide (3.75 g., 0.0145 mole), zinc dust (7.2 g., 0.11 g. atom) and glacial acetic acid (24 ml.) was refluxed for 8 hours. The reaction mixture was poured into water, neutralized with sodium carbonate and finally extracted with ether. The pleasant-smelling ester, 1.5 g. (61%), distilled at 62–63° (4 mm.).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.6. Found: C, 70.3; H, 10.5.

On hydrolysis with methanolic potassium hydroxide (20%), the free acid was obtained; m.p. 36° (lit.[6] 38°). The corresponding **amide** melted at 67–68° (lit.[6] 68–69°).

Ethyl 1-Methylcyclohexylcyanacetate (VIII).—To the Grignard reagent prepared from magnesium (3.7 g., 0.152 g. atom), methyl iodide (27.7 g., 0.195 mole) in ether (60 ml.) cuprous iodide (1 g., 0.0026 mole) was added, followed by the slow addition of the unsaturated cyano-ester (25 g., 0.129 mole) in ether (50 ml.). On refluxing for 2 hours the reaction mixture was worked up and purified by treating with a solution of sodium cyanide (7.2 g.) in aqueous alcoholic solution. The colorless ester, 19.6 g. (72.7%), boiled at 157° (12 mm.), $n^{35}D$ 1.4613.

Anal. Calcd. for $C_{12}H_{19}NO_2$: C, 68.9; H, 9.1. Found: C, 69.3; H, 9.4.

Methylcyclohexylacetonitrile (IX).—The cyano-ester VIII (15 g., 0.071 mole) was hydrolyzed with a solution of potassium hydroxide (5.25 g., 0.093 mole) in water (3.7 ml.) and ethanol (120 ml.). The acidic product (10 g.) was decarboxylated at 200° for a half-hour and the nitrile was obtained as a colorless mobile liquid; 5 g. (51.4%), b.p. 80° (3 mm.).

Anal. Calcd. for $C_9H_{15}N$: C, 78.8; H, 10.9. Found: C, 79.1; H, 10.8.

ω-(Methylcyclohexyl)-acetophenone (X).—To a solution of phenylmagnesium bromide, from magnesium (5.2 g., 0.219 mole) and bromobenzene (34 g., 0.216 mole), in ether (100 ml.) was added the nitrile (14.7 g., 0.107 mole) in ether (20 ml.). The reaction mixture was refluxed for one hour and after removal of most of the ether, it was again heated on the water-bath for another hour. On decomposition of the complex the ketone was isolated as a pale-yellow mobile liquid, b.p. 150–155° (6 mm.), 21.3 g. (92.2%).

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.3; H, 9.2. Found: C, 83.1; H, 9.05.

The 2,4-dinitrophenylhydrazone crystallized as orange needles from ethyl acetate, m.p. 215°.

Anal. Calcd. for $C_{21}H_{24}N_4O_4$: C, 63.6; H, 6.0. Found: C, 63.3; H, 5.8.

Methylcyclohexylcarboxylic Acid (VII).—The above ketone (15 g., 0.069 mole) was again treated with the Grignard reagent from magnesium (3.3 g., 0.136 mole) and bromobenzene (21.67 g., 0.138 mole) in the usual way. A

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(19) H. Franzen and W. Deibel, *Ber.*, **38**, 2716 (1905).

(20) C. G. Swain and H. B. Boyles, THIS JOURNAL, **73**, 870 (1951).

(21) F. S. Prout, *ibid.*, **74**, 5915 (1952), and subsequent publications.

(22) H. J. Shine, *J. Chem. Soc.*, 8 (1951).

(23) All boiling points and melting points are uncorrected.

viscous liquid (14 g.) was finally obtained, b.p. 197–200° (2 mm.).

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.7; H, 8.8. Calcd. for $C_{21}H_{24}$: C, 91.3; H, 8.7. Found: C, 89.3; H, 8.2.

The above compound (10 g.) was oxidized with chromic anhydride (9 g.) in water (6 ml.) and acetic acid (56 ml.) at room temperature and finally on the boiling water-bath for 2 hours. The reaction mixture was subjected to steam distillation and from the distillate the cyclohexane acid, m.p. 36°, was isolated. The amide melted at 66–67° alone or mixed with the previous sample.

1-Keto-3-chloro-10-methyl-Δ^2-octalin (XII).—10-Methyldecalin-1,3-dione was prepared from 2-methylacetylcyclohexene[24] with a slight modification. The diketone (27 g., 0.15 mole) in chloroform (50 ml.) was refluxed on the water-bath for 3 hours with phosphorus trichloride (7.5 g., 0.055 mole). The solvent was distilled off under reduced pressure. It was cooled and treated with an excess of ice-cold water. The ethereal extract was washed with cold sodium hydroxide solution (2%). On removal of the solvent, the residue distilled at 126–128° (6 mm.) as a colorless liquid; 17 g. (57.1%).

Anal. Calcd. for $C_{11}H_{15}OCl$: C, 66.4; H, 7.5. Found: C, 66.4; H, 7.5.

1-Keto-10-methyldecalin (XI).—The enol-chloride (14.2 g.) in ethanol (40 ml.) was hydrogenated with palladium-carbon (2 g., 5%) at room temperature. The hydrogenated product was worked up and the ketone, 10 g. (84%), boiled at 130–132° (12 mm.) as a sweet-smelling colorless liquid.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.5; H, 10.8. Found: C, 79.4; H, 10.8.

The semicarbazone was obtained in a quantitative yield, m.p. 204–205°, and crystallized from dilute ethanol in shining flakes, m.p. 206–207°.

Anal. Calcd. for $C_{12}H_{21}N_3O$: N, 18.8. Found: N, 18.8.

1-Methylnaphthalene.—The ketone (3 g., 0.018 mole) was allowed to react with methylmagnesium iodide, prepared from magnesium (2.4 g., 0.098 g. atom). The carbinol was dehydrated by distillation (85 mm.) in the presence of a crystal of iodine. The hydrocarbon (2.4 g.) distilled at 140–142° (85 mm.). To a solution of the hydrocarbon (1.4 g.) in carbon tetrachloride (6 ml.) was added bromine (1.4 g.). The residue, on removal of the solvent, was mixed with collidine (4 ml.) and refluxed for 15 minutes in an atmosphere of nitrogen. The reaction mixture was poured into ice-cold 6 *N* hydrochloric acid and extracted with ether. The diene (0.4 g., b.p. 130–140° (85 mm.)), was dehydrogenated in a sealed tube at 300–325° for 50 hours with selenium (1.6 g.). The hydrocarbon was purified by distillation over sodium and converted into a picrate. On crystallization from ethanol, this melted at 139–140° (lit.[25] 140–141°) alone or mixed with an authentic sample.

Ethyl 10-Methyldecalidene-1-cyanoacetate (XIII).—The ketone XI (2.5 g., 0.015 mole) was condensed with ethyl cyanoacetate (3.4 g., 0.03 mole) in benzene (6 ml.) and acetic acid (1.5 ml.) in the presence of ammonium acetate (0.4 g. added in 4 lots) by refluxing for 36 hours in a flask fitted with a constant water-separator. The product was extracted with benzene and thoroughly washed with water. On removal of the solvent and low boiling products, the unsaturated ester, 2.6 g. (66.4%), was collected at 175–180° (4 mm.).

Anal. Calcd. for $C_{16}H_{23}NO_2$: C, 73.5; H, 8.8. Found: C, 73.5; H, 8.4.

Ethyl 10-Methyldecalin-1-cyano-1-cyanoacetate (XIV).—To a cold solution of the unsaturated ester XIII (8.5 g., 0.033 mole) in ethanol (130 ml.) was added sodium cyanide (4.8 g., 0.098 mole), dissolved in the minimum quantity of water and subsequently diluted with ethanol (30 ml.). The temperature of the reaction mixture was raised to 38° whereupon the solution turned pale red. It was cooled and acidified with concentrated hydrochloric acid (5.4 ml.). On allowing the solution to stand for one hour at room temperature, it was poured into an excess of ice-cold dilute hydrochloric acid. The chloroform extract afforded a thick yellowish liquid, 8 g. (85.4%) at 180–185° (0.3 mm.).

Anal. Calcd. for $C_{17}H_{24}N_2O_2$: C, 70.8; H, 8.3. Found: C, 70.8; H, 8.2.

10-Methyldecalin-1-succinic Acid (XV).—A solution of the dicyano-ester XIV (10 g., 0.035 mole) in acetic acid (20 ml.) was treated with a mixture of concentrated sulfuric acid (20 ml.) and water (20 ml.) and the mixture was refluxed slowly on an oil-bath for 25 hours. The mixture was cooled and diluted with ice-cold water (40 ml.). A crystalline solid separated out. The solid was filtered and washed with petroleum ether (b.p. 40–60°) to remove the adhering oil. A white crystalline solid (3.8 g.) was obtained, m.p. 173–174°. The filtrate was diluted with an excess of water and extracted with ether. The ethereal layer was mixed with petroleum ether washings. The crude mixture (4 g.), left after the removal of the solvents, was again hydrolyzed as before. On working up the reaction mixture a colored solid was obtained and this on crystallization from ethyl acetate–acetic acid after boiling with charcoal, yielded a further lot of the crystalline acid (0.6 g., m.p. 172–174°). The total yield was 4.4 g. (50%). This was recrystallized from acetic acid containing a little water and it melted at 175°.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.1; H, 8.6. Found: C, 65.9; H, 8.5.

The acid (2.5 g.) in methanol (25 ml.) was esterified with an excess of an ethereal solution of diazomethane. After removal of the solvent, the residue afforded a colorless liquid, 2.55 g. (92%), boiling at 147° (0.15 mm.).

Anal. Calcd. for $C_{16}H_{26}O_4$: C, 68.1; H, 9.2. Found: C, 68.5; H, 9.2.

10-Methyldecalin-1-carbomethoxy-1-acetic Acid (XVI).—To a solution of the diester (2.3 g.) in methanol (13 ml.) was added a solution of potassium hydroxide (0.6 g.) in water (1 ml.). The solution was allowed to stand at room temperature for 3 hours and finally refluxed for 3 hours on the water-bath. The reaction mixture was cooled and excess alkali neutralized with acetic acid. After removal of methanol under suction, the residue was diluted with water and extracted with ether to remove neutral materials. The alkaline solution was acidified whereupon a crystalline solid, 1.8 g. (82.3%), separated out. This on crystallization from ethyl acetate separated as shining needles and melted at 161–162°.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.2; H, 8.9. Found: C, 67.4; H, 9.0.

Methyl 10-Methyl-1-bromomethyldecalin-1-carboxylate (XVII).—The half-ester (1.3 g.) in methanol (50 ml.) was neutralized with 1 *N* sodium hydroxide solution. A little more than the calculated quantity of silver nitrate solution was added with stirring and the white silver-salt precipitated out. The mixture was filtered and the precipitate was thoroughly washed with water and finally dried at 110–120° for 15 hours in vacuum. The silver salt (1.8 g.) was suspended in carbon tetrachloride (35 ml.) and treated with a solution of bromine (0.92 g.) in the same solvent (5 ml.) and worked up as before. The bromo-ester, 1.25 g. (85%), boiled at 135–140° (0.2 mm.).

Anal. Calcd. for $C_{14}H_{23}O_2Br$: C, 55.4; H, 7.5. Found: C, 55.2; H, 7.6.

Methyl 1,10-Dimethyldecalin-1-carboxylate (XVIII).—A mixture of the bromo-ester (1.0 g.), zinc dust (2.0 g.) and acetic acid (17 ml.) was refluxed for 15 hours. The reaction was poured into water while hot and thoroughly extracted with ether. It afforded 0.35 g. (47.4%) which boiled at 120–122° (4 mm.).

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 75.0; H, 10.7. Found: C, 75.1; H, 10.7.

1,10-Dimethyldecalin-1-carboxylic Acid (II).—The ester (*ca.* 0.25 g.), recovered from an unsuccessful attempt at hydrolysis with 10% methanolic potassium hydroxide, was again refluxed for 32 hours with potassium hydroxide (1.5 g.) in methanol (5 ml.). The reaction mixture was diluted with water, and methanol was removed by passing in steam. The alkaline solution was extracted with ether to remove any neutral matter. On acidification with cold hydrochloric acid, it afforded a crystalline acid (*ca.* 0.1 g.). On crystallization from aqueous acetone it afforded small cubes, m.p. 120°.

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.2; H, 10.4. Found: C, 74.2; H, 10.5.

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(24) N. C. Deno and H. Chafetz, THIS JOURNAL, **74**, 3940 (1952).

(25) G. Darzens and M. Moureu, *Compt. rend.*, **183**, 748 (1926).

Methyl 10-Methyldecalin-1-cyanoacetate (XIX).—To the Grignard reagent prepared from magnesium (4.7 g., 0.193 g. atom) and methyl iodide (12.5 ml., 0.201 mole) in ether (50 ml.), pure benzene (70 ml.) was added. To the hot solution, left after removal of ether from the water-bath, was added cuprous iodide (1.0 g.). The reagent was cooled in ice and the unsaturated cyano-ester XIII (11.8 g., 0.045 mole) in benzene (10 ml.) was added dropwise. The mixture was allowed to stand in an ice-bath for 30 minutes and finally refluxed for 2 hours. The complex was decomposed and the benzene layer was washed with water and 2% sodium bisulfite solution. On removal of the solvent, the residue was dissolved in alcohol (50 ml.) and purified by treatment with a solution of sodium cyanide (5 g.) in aqueous alcoholic solution. On working up the reaction mixture in the usual way, the product (8.5 g.) distilled at 120–170° (1.5 mm.). A high-boiling residue remained in the distillation flask. The distillate (8.5 g.) was hydrolyzed with a solution of potassium hydroxide (12.5 g.) in methanol (125 ml.) at room temperature for 6 hours and on reflux for one hour. On acidification, methanol was distilled off and a neutral material, 3.5 g. (31.1%), was isolated boiling at 135–145° (4 mm.). On acidification of the alkaline extract the cyano-acid (3.5 g.) was re-esterified with an excess of diazomethane. The cyano-ester, 3 g. (26.6%), boiled at 155–160° (1 mm.).

Anal. Calcd. for $C_{15}H_{23}NO_2$: C, 72.2; H, 9.2. $C_{16}H_{25}NO_2$: C, 73.0; H, 9.5. Found: C, 72.1; H, 9.0.

The neutral fraction on redistillation boiled at 138–140° (4 mm.).

Anal. Calcd. for $C_{16}H_{27}NO$: C, 77.1; H, 10.8. $C_{17}H_{29}NO$: C, 77.5; H, 11.0. Found: C, 76.7; H, 10.4.

In the infrared, the compound was characterized by strong bands at 3 μ (OH), 4.4 μ (CN) and a doublet at 7.25 and 7.3 μ (*gem*-dimethyl group). There was no absorption in the carbonyl or in the double-bond region.

Three grams of this product was mixed with *phosphorus pentoxide* (4.8 g.) under benzene (20 ml.) and the mixture was refluxed for 2 hours on the water-bath. A yellowish liquid (2 g.) was obtained boiling at 120–125° (3 mm.); $\lambda_{\max}^{\text{alc}}$ 220 mμ, log ϵ 3.8.

Anal. Calcd. for $C_{16}H_{25}N$: C, 83.1; H, 10.8; N, 6.0. $C_{17}H_{27}N$: C, 83.2; H, 11.0; N, 5.7. Found: C, 83.3, 82.9; H, 10.7, 10.7; N, 5.8.

10-Methyldecalin-1-acetonitrile (XX).—The cyano-acid (1.5 g.) was heated in an oil-bath at 200–205° for a half-hour until the evolution of carbon dioxide was over. A mobile liquid, 0.7 g. (57.6%), distilled at 128–130° (6 mm.).

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.7; H, 10.9. $C_{14}H_{23}N$: C, 81.9; H, 11.2. Found: C, 82.1; H, 10.5.

ω-(10-Methyldecalin-1)-acetophenone (XXI).—Phenylmagnesium bromide from magnesium (0.88 g., 0.0362 mole) and bromobenzene (5.7 g., 0.0363 mole) was diluted with benzene (15 ml.). On distilling off most of ether a solution of the nitrile (2.4 g., 0.0125 mole) in benzene (10 ml.) was added and the mixture was refluxed for 4 hours. The phenyl ketone, 2.8 g. (83%), was obtained, b.p. 165–170° (0.7 mm.). It formed a **2,4-dinitrophenylhydrazone**, which on crystallization from ethyl acetate afforded orange shining flakes, m.p. 207°.

Anal. Calcd. for $C_{25}H_{30}N_4O_4$: C, 66.6; H, 6.6; O, 14.2. $C_{26}H_{32}N_4O_4$: C, 67.2; H, 6.9; O, 13.8. Found: C, 66.7, 66.6; H, 6.5, 6.3; O, 14.5, 14.4.

The ketone was regenerated from this derivative on treatment with stannous chloride in aqueous acetone.[26]

Anal. Calcd. for $C_{19}H_{26}O$: C, 84.4; H, 9.6. $C_{20}H_{28}O$: C, 84.5; H, 9.8. Found: C, 84.2; H, 9.9.

Ethyl 10-Methyldecalin-1-cyanoacetate (XXIII).—To aluminum amalgam (5.0 g.) under moist ether (300 ml.) was added the unsaturated cyano-ester XIII (5.0 g.). The mixture was allowed to stand for 48 hours with occasional addition of water (5 ml., total 20 ml.). During this period, almost all the aluminum foil had disappeared. The ethereal layer was decanted off. The sludge was dissolved in ice-cold hydrochloric acid and the turbid solution was again extracted with ether. The combined ethereal extracts were worked up and the saturated ester, 4.4 g. (87.3%), was obtained boiling at 147–148° (0.3 mm.).

Anal. Calcd. for $C_{16}H_{25}NO_2$: C, 73.0; H, 9.5. Found: C, 73.2; H, 9.5.

The cyano-acid (2.8 g.) obtained from the alkaline hydrolysis of the cyano-ester XXIII (4 g.) afforded on pyrolysis the nitrile, 1.8 g. (79.4%), b.p. 130° (7 mm.).

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.7; H, 10.9. Found: C, 81.9; H, 10.9.

The nitrile (1.0 g.) yielded the phenyl ketone (1.1 g.), b.p. 150–160° (0.5 mm.). **The 2,4-dinitrophenylhydrazone** melted at 160–165°, which on repeated crystallization from ethyl acetate furnished shining orange flakes, m.p. 205–206°, alone or mixed with sample described before.

Anal. Calcd. for $C_{25}H_{30}N_4O_4$: C, 66.6; H, 6.6. Found: C, 67.0; H, 6.6.

Ethyl 3,3-Dimethylcyclohexylidenecyanoacetate (XXVI).—3,3-Dimethylcyclohexanone[27] (24 g., 0.190 mole) was condensed with ethyl cyanoacetate (46 g., 0.407 mole) as before. The product, 26 g. (62%), was collected at 130–132° (4 mm.).

Anal. Calcd. for $C_{13}H_{19}NO_2$: C, 70.6; H, 8.6. Found: C, 70.4; H, 8.9.

Ethyl 1,3,3-Trimethylcyclohexylcyanoacetate (XXVII).—Methylmagnesium iodide from magnesium (4.8 g., 0.197 g. atom) was added to the above ester (11.0 g., 0.049 mole) in the presence of cuprous iodide (1.0 g.) as a catalyst and the expected cyano-ester, 7.5 g. (64.6%), boiled at 138–140° (6 mm.).

Anal. Calcd. for $C_{14}H_{23}NO_2$: C, 70.9; H, 9.7. $C_{13}H_{21}NO_2$: C, 69.9; H, 9.4. Found: C, 71.1; H, 10.0.

(1,3,3-Trimethylcyclohexyl)-acetone (XXIX).—The nitrile (1.7 g., 0.0103 mole) from hydrolysis and decarboxylation of the above cyano-ester (5.0 g.) was converted into methyl ketone by allowing it to react with methylmagnesium iodide from magnesium (0.7 g., 0.0288 g. atom) and methyl iodide (5 g., 0.0352 mole). The ketone (1.3 g., 69.4%) was obtained as a sweet-smelling liquid boiling at 96° (6 mm.).

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.1; H, 12.0. $C_{11}H_{20}O$: C, 78.5; H, 11.9. Found: C, 78.7; H, 12.0.

The semicarbazone was obtained as silky white needles after recrystallization from dilute ethanol; m.p. 165–166°.

Anal. Calcd. for $C_{13}H_{25}N_3O$: C, 65.2; H, 10.4; N, 17.5. $C_{12}H_{23}N_3O$: C, 64.0; H, 10.2; N, 18.6. Found: C, 65.5; H, 10.2; N, 17.7.

Ethyl Decalidene-1-cyanoacetate (XXIV).—α-Decalone (15 g., 0.099 mole) was condensed with ethyl cyanoacetate (20 g., 0.177 mole) under identical conditions and the unsaturated ester, 17 g. (69.7%), was obtained, b.p. 170–172° (4 mm.).

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.8; H, 8.5. Found: C, 72.7; H, 8.5.

Ethyl 1-Methyldecalin-1-cyanoacetate (XXV).—Methylmagnesium iodide from magnesium (4.4 g., 0.181 g. atom) was added in the usual way to the above unsaturated cyano-ester (11.4 g., 0.046 mole). The purified product afforded a colorless mobile liquid; 6.5 g. (53.7%), b.p. 150–152° (0.6 mm.).

Anal. Calcd. for $C_{16}H_{25}NO_2$: C, 73.0; H, 9.5. $C_{15}H_{23}NO_2$: C, 72.3; H, 9.2. Found: C, 72.9; H, 9.8.

1-Methyldecalylacetone (XXVIII).—The nitrile (1.3 g.) obtained through controlled hydrolysis and decarboxylation of the ester XXV was converted to the methyl ketone, 1 g. (70.6%), as before, b.p. 100–105° (3 mm.).

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.7; H, 11.5. Found: C, 80.9; H, 11.4.

The semicarbazone, was obtained as shining needles after recrystallization from ethanol, m.p. 183–184°.

Anal. Calcd. for $C_{15}H_{27}N_3O$: C, 67.92; H, 10.2. Found: C, 67.98; H, 10.28.

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[26] J. Demaecker and R. H. Martin, *Nature*, **173**, 266 (1954), *cf.* R. Robinson, *ibid.*, **173**, 541 (1954).

[27] G. Büchi, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **31**, 245 (1948).