131. *Researches on Acetylenic Compounds. Part XVII. The Preparation of Substituted* 1-*Acetyl*cyclo*hexenes from* 4-*Benzoyloxy*cyclo*hexanone.*

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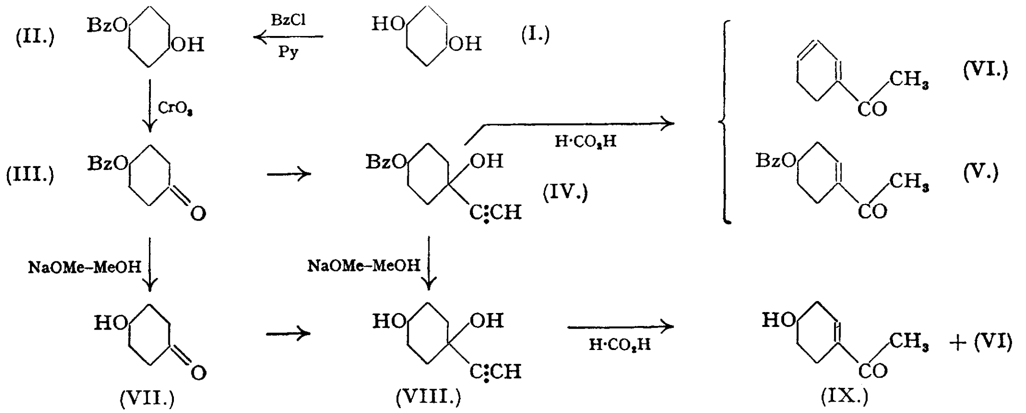
A method for the preparation of large quantities of 4-benzoyloxy*cyclo*hexanone (III) has been devised. Condensation with sodium acetylide in liquid ammonia furnishes the corresponding ethynylcarbinol (IV), and the rearrangement of this carbinol-ester with formic acid gives 4-benzoyloxy-1-acetyl*cyclo*hexene (V), together with some of the hitherto unknown 2 : 3-dihydroacetophenone (VI). Alcoholysis of the benzoate (IV) with methyl alcohol containing a little sodium methoxide yields the glycol (VIII) which can be converted into the hydroxy-derivative (IX).

These compounds should be useful intermediates for the synthesis of compounds related to the D provitamins, but preliminary attempts to effect Michael reactions with *cyclo*hexanone have not been promising.

In the preceding paper attempts to synthesise ketohydrophenanthrenes from 2 : 5-dihydroacetophenones, in order to obtain compounds related to provitamin D, were described. These 2 : 5-dihydroacetophenones were found to dehydrogenate too readily under the conditions of the Michael reaction and, as an alternative, the possibility of employing acetyl*cyclo*hexenes having hydroxyl or ester substituents in the 4 or 5 positions (type V or XII) has been explored. This paper describes the synthesis of several such substituted acetyl*cyclo*hexenes.

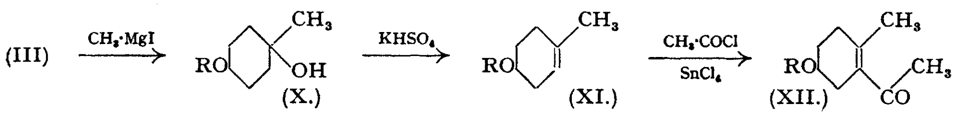
The key intermediate for syntheses of substances of the required type is 4-hydroxy*cyclo*hexanone (VII) or one of its esters; the esters can be prepared by oxidising a half-ester of *cyclo*hexane-1 : 4-diol (quinitol) (I), but no satisfactory method, which might be used for the production of considerable quantities of these esters in a pure state, has been described (cf. Dimroth, *Ber.*, 1939, **72**, 2043; Aldersley, Burkhardt, Gillam, and Hindley, *J.*, 1940, **10**; Dimroth, Schmeil, and Daake, *Ber.*, 1942, **75**, 317). However, it was found recently in these laboratories (Owen and Robins, this vol., p. 320), that both the *cis*- and the *trans*-isomers of quinitol could be converted directly into the mono-benzoates (II) with benzoyl chloride in chloroform and pyridine by working in the cold in dilute solutions. It has now been found that the same procedure can be used on the mixture of quinitol isomers obtained by hydrogenating quinol, although the monobenzoate (II) thus produced is also a mixture of isomers and therefore cannot be obtained crystalline. Moreover the yield is not affected by working in quite concentrated solutions. Oxidation of the monobenzoate mixture with chromium trioxide proceeds satisfactorily, so that large quantities of 4-benzoyloxy*cyclo*hexanone (III) can now be obtained in reasonable overall yield (*ca.* 50%) from quinitol by a two-stage process.



The ketone (III) was condensed with sodium acetylide in liquid ammonia, and an 87% yield of the *cis–trans*-mixture of 4-*benzoyloxy*-1-*ethynyl*cyclo*hexanol* (IV) was obtained. When this was heated under reflux with 85% formic acid, 4-*benzoyloxy*-1-*acetyl*cyclo*hexene* (V), m. p. 69°, was obtained in 36% yield (cf., *inter al.*, Fischer and Loewenberg, *Annalen*, 1929, **475**, 183; Hurd and Christ, *J. Amer. Chem. Soc.*, 1937, **59**, 118; Marvel and Walton, *J. Org. Chem.*, 1942, **7**, 88); the structure of the ketone was confirmed by its light-absorption properties. Some benzoic acid fission occurred under the conditions of the experiment, as 2 : 3-*dihydroacetophenone* (VI) (25% yield) could also be isolated. The structure of this compound was also confirmed by its light-absorption data which are nearly identical with those of the structurally analogous dihydro-*o*-tolualdehyde.

Preliminary experiments with (V) showed that benzoic acid was split off very easily under the conditions employed in Michael condensations. It was desirable therefore to prepare the corresponding acetate which would be expected to be more stable. When the keto-benzoate (III) was hydrolysed by 15 hours' refluxing with methanol containing a little sodium methoxide, a 70% yield of 4-hydroxy*cyclo*hexanone (VII) (Dimroth, *loc. cit.*; Aldersley, Burkhardt, Gillam, and Hindley, *loc. cit.*) was obtained. Condensation with sodium acetylide in liquid ammonia gave the *cis–trans*-mixture of 1-*ethynylquinitol* (VIII), m. p. 100—105°, in 50% yield. The same compound could also be obtained (72% yield) by saponifying 4-benzoyloxy-1-ethynyl*cyclo*hexanol (IV) by means of sodium in methanol. When the glycol was refluxed with 85% formic acid, the normal rearrangement occurred, and 4-*hydroxy*-1-*acetyl*cyclo*hexene* (IX) was obtained in *ca.* 60% yield. Some dehydration also occurred, and 2 : 3-dihydroacetophenone (VI) could be isolated. The structure of (IX) was confirmed by its light-absorption properties and by benzoylation to (V). The best overall yield of (IX) is obtained by carrying out the acetylene condensation on the keto-benzoate, saponifying (IV), and then carrying out the formic acid rearrangement on the ethynyl-glycol. On acetylation it gave the required 4-*acetoxy*-1-*acetyl*cyclo*hexene*.

Attempts have also been made to obtain substituted acetyl*cyclo*hexenes of type (XII), containing both a methyl group and an ester group in the desired positions. A Michael condensation with cyclic ketones, followed by reduction and dehydration, should then give compounds closely analogous to provitamin D.



When (III) was condensed with methylmagnesium iodide, the 4-benzoyloxy-1-methyl*cyclo*hexanol (X; R = Bz) so formed was always contaminated with starting ketone, even when a 40% excess of Grignard reagent was used. Some phenyldimethylcarbinol was also obtained, indicating that reaction with the ester grouping had taken place to some extent. Treatment of the mixture of (III) and (X; R = Bz) with potassium hydrogen sulphate gave pure 4-*benzoyloxy*-1-*methyl*cyclo*hexene* (XI; R = Bz) in 42% yield [based on (III)]. Hydrolysis produced 1-*methyl*cyclo*hex*-1-*en*-4-*ol* (XI; R = H), and this yielded the *acetate* (XI; R = Ac). When either the acetate or the benzoate was treated with acetyl chloride and stannic chloride in carbon disulphide (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1151) a complex mixture was obtained, from which pure compounds could only be separated with much difficulty in rather poor yields. Some success resulted from the employment of the Girard reagent, and the *semicarbazone* of the desired ketone (XII; R = Bz) could be isolated; the experiments, however, have not been completed for the reason indicated below.

At the same time as the above work was being carried out it appeared desirable, in view of the unpromising results we have obtained in certain Michael condensations, to investigate the condensation between 1-acetyl-2-methyl*cyclo*hexene and α-tetralone (cf. Huber, *Ber.*, 1938, **71**, 725); α-tetralone was preferred to *cyclo*hexanone because of the superior results obtained in its condensation with acetyl*cyclo*hexene (Robinson *et al.*, *J.*, 1935, 1285; 1936, 759). When crude 1-acetyl-2-methyl*cyclo*hexene was condensed with α-tetralone in the presence of potassium *iso*propoxide in pyridine (Huber, *loc. cit.*), a 27% yield of high-boiling material was obtained which on chromatographic purification yielded only a very small amount of crystalline product. When the condensation was carried out with pure 1-acetyl-2-methyl*cyclo*hexene (forthcoming publication) the high-boiling liquid yielded a negligible quantity of crystalline material.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions unless otherwise stated.)

Quinitol Monobenzoate (II).—Quinitol (810 g.; *cis–trans*-mixture) was dissolved in chloroform (2·5 l.; freed from alcohol by shaking with sulphuric acid) and dry pyridine (1·9 l.). A solution of benzoyl chloride (960 g.) in chloroform (2·0 l.) was added, with stirring, during 5 hours, the temperature being kept at 0—5° by external cooling. After standing overnight at room temperature, the chloroform solution was freed from pyridine by thorough extraction with water and then with dilute sulphuric acid. Drying (Na_2SO_4) and removal of solvent, followed by fractionation of the residue, gave the *cis–trans*-mixture of quinitol monobenzoate (901 g.; 59%) as a colourless very viscous oil, b. p. 175—178°/0·2 mm.; the residue (*ca.* 250 g.) had m. p. 138—143° and consisted mainly of the isomeric dibenzoates.

4-*Benzoyloxy*cyclo*hexanone* (III).—Chromium trioxide (130 g.), dissolved in water (75 c.c.) and "AnalaR" acetic acid (300 c.c.), was added to a stirred and cooled solution of quinitol benzoate (295 g.)

in acetic acid (500 c.c.), the temperature being kept below 35°. The reaction was completed by leaving the solution overnight at room temperature; ether (2 l.) was added, and most of the acetic acid was removed by repeated washings with water. After the solution had been washed with sodium hydroxide solution and water, and then dried, the ether was removed; the residue completely solidified. One crystallisation from ether–light petroleum (b. p. 40—60°) gave the keto-ester (244 g.; 83%) as plates, m. p. 63° (Dimroth, Schmeil, and Daake, *loc. cit.*, give m. p. 63—64°; Owen and Robins, *loc. cit.*, give m. p. 62°).

4-*Benzoyloxy*-1-*ethynyl*cyclo*hexanol* (IV).—To a solution of sodium acetylide in liquid ammonia (1200 c.c.), prepared from sodium (35 g.), the ferric nitrate catalyst of Vaughn, Vogt, and Nieuwland (*J. Amer. Chem. Soc.*, 1934, **56**, 2120) being used to catalyse the formation of sodamide, 4-benzoyloxy*cyclo*hexanone (70 g.) in dry ether (400 c.c.) was added during 1 hour with stirring and cooling (alcohol–carbon dioxide). Nitrogen was introduced during the addition and during the subsequent 7 hours' stirring, after which ammonium chloride (100 g.) was slowly added, and the mixture was left overnight without cooling to expel ammonia. Ether and water were added, and a small amount of black tar was filtered off. After being washed with dilute acid and water, the ethereal layer was dried, the solvent removed, and the residue fractionated. This gave the *cis–trans*-mixture of 4-*benzoyloxy*-1-*ethynyl*cyclo*hexanol* (68·2 g.; 87%) as a light yellow very viscous liquid, b. p. 170—172°/0·05 mm. (Found: C, 73·45; H, 6·6. $C_{15}H_{16}O_3$ requires C, 73·75; H, 6·6%).

4-*Benzoyloxy*-1-*acetyl*cyclo*hexene* (V).—The above ethynylcarbinol (5·5 g.) was refluxed with formic acid (55 c.c.; *d* 1·2) for 3 hours. The bulk of the acid was removed through a short column under reduced pressure, the residue was taken up in ether, and the remaining acid was removed by shaking with sodium hydrogen carbonate solution. Removal of solvent and fractionation of the residue gave two fractions: (*a*) 2 : 3-*Dihydroacetophenone* (0·7 g.; 25%), b. p. 92—93°/23 mm., $n_D^{22^\circ}$ 1·5285, $n_D^{33^\circ}$ 1·5221, a faintly yellow mobile pungent-smelling liquid, which on exposure to air quickly became darker (Found: C, 78·7; H, 8·3. $C_8H_{10}O$ requires C, 78·65; H, 8·25%). Light absorption: Maximum, 3020 A.; $\varepsilon = 7000$. (A specimen of 2-methyl-2 : 3-dihydrobenzaldehyde had light absorption: Maximum, 3030 A.; $\varepsilon = 8000$.) The 2 : 4-*dinitrophenylhydrazone* separated from acetic acid in very dark red needles, m. p. 194° (Found: N, 18·4. $C_{14}H_{14}O_4N_4$ requires N, 18·55%). Light absorption (in chloroform): Maximum, 3970 A.; $\varepsilon = 25{,}500$. (*b*) 3·2 G., b. p. 138—145°/10^{-3} mm., obtained solid by the following method. The *semicarbazone* (obtained in 73% yield from the fraction having this boiling point, from a previous experiment) separated from much ethanol in small needles, m. p. 202—203° (decomp.) (Found: N, 14·4. $C_{15}H_{19}O_3N_3$ requires N, 13·95%). The ketone was regenerated by stirring the semicarbazone with dilute sulphuric acid and light petroleum (b. p. 60—80°) for 6 hours under reflux. Isolation left a residue, which gradually solidified, and, on seeding the fraction above (*i.e.*, 3·2 g.) with this material, it also slowly solidified. Crystallisation from ether–light petroleum (b. p. 40—60°) gave 4-*benzoyloxy*-1-*acetyl*cyclo*hexene* (2·0 g.; 36%) as plates, m. p. 65°, which on further crystallisation was raised to 69° (Found: C, 73·8; H, 6·7. $C_{15}H_{16}O_3$ requires C, 73·75; H, 6·6%). Light absorption: Maximum, 2290 A.; $\varepsilon = 14{,}500$. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in red prisms, m. p. 211° (Found: C, 59·25; H, 4·6; N, 12·85. $C_{21}H_{20}O_6N_4$ requires C, 59·4; H, 4·75; N, 13·2%).

4-*Hydroxy*cyclo*hexanone* (VII).—4-Benzoyloxy*cyclo*hexanone (40 g.) was refluxed with dry methanol (160 c.c.) containing sodium (0·4 g.) for 15 hours. After the addition of a little water, the cooled solution was saturated with carbon dioxide, and the methanol was taken off under reduced pressure. As the complete separation of methyl benzoate and the keto-alcohol by fractional distillation is difficult, water was added to the residue, and the ester was removed by ether extraction. The aqueous layer, after removal of water and distillation of the residue, gave 4-hydroxy*cyclo*hexanone (14·6 g.; 70%), b. p. 97—98°/0·5 mm., $n_D^{18^\circ}$ 1·4834 (Dimroth, *Ber.*, 1939, **72**, 2043, gives b. p. 128—131°/12·5 mm.; Aldersley, Burkhardt, Gillam, and Hindley, *J.*, 1940, 10, give b. p. 83—85°/0·6 mm.). The keto-alcohol is much more soluble in water than in ether, and continuous ether extraction of the aqueous solution for 24 hours removed only *ca.* 20%. The 2 : 4-dinitrophenylhydrazone crystallised from aqueous methanol in orange needles, m. p. 150° (Dimroth, *loc. cit.*, gives m. p. 151°).

1-*Ethynylquinitol* (1-*Ethynyl*cyclo*hexane*-1 : 4-*diol*) (VIII).—(*a*) 4-Hydroxy*cyclo*hexanone (13 g.) in dry ether (80 c.c.) was added to a solution of sodium acetylide, prepared from sodium (20 g.) in liquid ammonia (700 c.c.) during 15 minutes. The cooled mixture was stirred in nitrogen for 22 hours; ammonium chloride (100 g.) was then gradually added, and stirring was continued for a further hour. The semi-solid residue remaining after the ammonia had been expelled was thoroughly extracted with ether, and the inorganic salts were filtered off. The solvent was removed from the dried filtrate, and distillation of the residue gave the *cis–trans*-mixture of 1-*ethynylquinitol* (7·8 g.; 49%) as a very viscous liquid, b. p. 107—108°/10^{-2} mm. After several days at room temperature it completely solidified, and crystallisation of a small portion from ether gave small needles, m. p. 100—105° (Found: C, 68·1; H, 8·75. $C_8H_{12}O_2$ requires C, 68·55; H, 8·65%).

(*b*) 4-Benzoyloxy-1-ethynyl*cyclo*hexanol (5·2 g.) was refluxed with dry methanol (25 c.c.) containing sodium (0·06 g.) for 7 hours. A little water was added to the cooled solution, which was then saturated with carbon dioxide. Removal of solvent under reduced pressure, followed by fractionation of the residue, gave 1-ethynylquinitol (2·15 g.; 72%), b. p. 152—154°/22 mm., which when seeded went completely solid, and after crystallisation from ether had m. p. 95—100°. In one experiment, in which the time of refluxing was increased to 22 hours, some decomposition occurred, and a low yield of a solid, m. p. 146°, was obtained. This did not depress the m. p. of the product above and may be a pure isomer.

4-*Hydroxy*-1-*acetyl*cyclo*hexene* (IX).—1-Ethynylquinitol (7·9 g.) was refluxed with formic acid (79 c.c.; *d* 1·2) for 2½ hours. The acid was distilled off through a short column at reduced pressure, and the residue was refluxed with water (80 c.c.) for 30 minutes to hydrolyse any formate present. The water was distilled off at reduced pressure, and fractionation of the residue gave 4-*hydroxy*-1-*acetyl*cyclo*hexene* (4·9 g.; 62%) as a somewhat viscous pleasant-smelling liquid, b. p. 134—136°/2 mm., 106—107°/0·02 mm., $n_D^{31^\circ}$ 1·5088 (Found: C, 68·05; H, 8·75. $C_8H_{12}O_2$ requires C, 68·55; H, 8·65%). Light absorption: Maximum, 2290 A.; $\varepsilon = 8500$. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark red plates, m. p. 226—227° (Found: N, 17·2. $C_{14}H_{16}O_5N_4$ requires N, 17·5%).

The aqueous distillate was extracted with ether; the extract was dried, and the solvent evaporated, to give 2 : 3-dihydroacetophenone (1·2 g.), b. p. 94°/25 mm., $n_D^{32^\circ}$ 1·5223. The 2 : 4-dinitrophenylhydrazone had m. p. 192°, undepressed on admixture with the sample obtained above.

Benzoylation of 4-*Hydroxy*-1-*acetyl*cyclo*hexene*.—The hydroxy-ketone (1·2 g.) and benzoyl chloride (1·8 g.) were dissolved in pyridine (7·5 g.), and the solution was kept at room temperature overnight. Working up yielded an oil which partly solidified on being seeded. Crystallisation from ether–light petroleum (b. p. 40—60°) gave 4-benzoyloxy-1-acetyl*cyclo*hexene (0·84 g.; 40% yield), m. p. 66—67°, undepressed on admixture with the specimen prepared above. The mother liquors were treated with alcoholic 2 : 4-dinitrophenylhydrazine sulphate solution to give the 2 : 4-dinitrophenylhydrazone of the ketone (1·31 g.; 36%), m. p. 210—211°, undepressed on admixture with the authentic specimen.

4-*Acetoxy*-1-*acetyl*cyclo*hexene*.—4-Hydroxy-1-acetyl*cyclo*hexene (4·4 g.) was dissolved in pyridine (20 c.c.), and a solution of acetyl chloride (3·5 g.) in pyridine (40 c.c.) was slowly added with ice-cooling. The mixture was heated on the steam-bath for some minutes and was then kept at room temperature overnight. Working up, followed by distillation of the residue, gave 4-*acetoxy*-1-*acetyl*cyclo*hexene* (4·8 g.), b. p. 135—136°/3 mm., $n_D^{28^\circ}$ 1·4792 (Found : C, 66·15; H, 7·7. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·75%). Light absorption : Maximum, 2280 A.; ε = 10,000. The compound is a mobile liquid with a pungent odour, and is appreciably soluble in water. The 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol in red plates, m. p. 161—162° (Found : N, 15·6. $C_{16}H_{18}O_6N_4$ requires N, 15·45%).

4-*Benzoyloxy*-1-*methyl*cyclo*hexene* (XI; R = Bz).—A solution of methylmagnesium iodide (from magnesium, 9·45 g.; 40% excess) in ether (600 c.c.) was cooled in ice, and a solution of 4-benzoyloxy*cyclo*hexanone (60 g.) in ether (600 c.c.) was gradually added during 1 hour. The fine white suspension was stirred in nitrogen for another 16 hours, after which it was decomposed with dilute sulphuric acid. Isolation by means of ether, followed by distillation, gave a small fore-run (7 g.) of crude phenyldimethylcarbinol, and then crude 4-benzoyloxy-1-methyl*cyclo*hexanol (47·1 g.) as a viscous liquid, b. p. 158—161°/10^{-2} mm., $n_D^{19^\circ}$ 1·5297. By means of 2 : 4-dinitrophenylhydrazine reagent it was found to be contaminated with considerable amounts of starting ketone, but no attempt at purification was made at this stage. The hydroxy-ester (43 g.), well mixed with finely ground potassium hydrogen sulphate (20 g.), was heated at 130°/0·1 mm. for 15 minutes; dehydration was then complete. The temperature was then raised, and the product which distilled (b. p. 130—170°/0·1 mm.) was dissolved in ether and freed from the small amount of benzoic acid which it contained by shaking with sodium hydrogen carbonate solution. After being dried and evaporated, the product was fractionated to give 4-*benzoyloxy*-1-*methyl*cyclo*hexene* (22·4 g.) as a mobile liquid, b. p. 108—109°/0·02 mm., 141—143°/4 mm., $n_D^{29^\circ}$ 1·5258, $n_D^{20^\circ}$ 1·5300, quite free from ketone (Found: C, 77·35; H, 7·5. $C_{14}H_{16}O_2$ requires C, 77·75; H, 7·45%). The higher-boiling fractions partly solidified, and unchanged 4-benzoyloxy*cyclo*hexanone could be recovered.

1-*Methyl*cyclo*hex*-1-*en*-4-*ol* (XI; R = H).—4-Benzoyloxy-1-methyl*cyclo*hexene (11 g.) was refluxed with dry methanol (50 c.c.) containing sodium (0·15 g.) for 7 hours. A methanolic solution of potassium hydroxide (75 c.c.; 15%) was added, and the solution was kept at room temperature for 40 hours. After addition of water, the product was isolated with ether to give 1-*methyl*cyclo*hex*-1-*en*-4-*ol* (4·6 g.) as a colourless, mobile liquid, b. p. 89°/26 mm., $n_D^{22^\circ}$ 1·4803 (Found : C, 74·65; H, 11·15. $C_7H_{12}O$ requires C, 74·95; H, 10·8%). The 3 : 5-*dinitrobenzoate* crystallised from light petroleum (b. p. 60—80°) in felted needles, m. p. 107° (Found : N, 9·55. $C_{14}H_{14}O_6N_2$ requires N, 9·15%).

4-*Acetoxy*-1-*methyl*cyclo*hexene* (XI; R = Ac).—The carbinol (4 g.), acetic anhydride (8 g.), and pyridine (30 c.c.) were kept at room temperature for 16 hours. Water was added, and the suspension was well shaken to decompose excess of acetic anhydride; the organic material was extracted with ether, from which pyridine was removed by shaking with dilute sulphuric acid. Drying, evaporation of solvent, and distillation of the residue gave 4-*acetoxy*-1-*methyl*cyclo*hexene* (4·85 g.) as a mobile sweet-smelling liquid, b. p. 90°/23 mm., $n_D^{24^\circ}$ 1·4548 (Found : C, 69·9; H, 8·85. $C_9H_{14}O_2$ requires C, 70·1; H, 9·15%).

Semicarbazone of 5-*Benzoyloxy*-1-*acetyl*-2-*methyl*cyclo*hexene* (XII; R = Bz).—Stannic chloride (12·0 g.) and carbon disulphide (29 g.) were cooled to −15°, and a mixture of 4-benzoyloxy-1-methyl*cyclo*hexene (10·25 g.) and acetyl chloride (3·8 g.) was added to the stirred and cooled solution. The mixture was stirred for another hour at room temperature, and was then left overnight. The dark red complex which had separated was decomposed with water, and the organic material was extracted with chloroform. The chloroform layer after being washed repeatedly with dilute hydrochloric acid, was dried and evaporated. The brown residue was distilled; the required product was contained in the fraction (6·7 g.), b. p. 160—200° (bath temp.)/10^{-4} mm. The lower-boiling fraction partly solidified; pressing on a porous tile, followed by crystallisation from methanol, gave 1-*chloro*-4-*benzoyloxy*-1-*methyl*cyclo*hexane* (0·55 g.) as needles, m. p. 85° (Found : C, 66·6; H, 6·4. $C_{14}H_{17}O_2Cl$ requires C, 66·55; H, 6·75%). No pure product could be obtained from the higher-boiling fraction by fractional distillation, nor could a solid derivative be prepared. This fraction was heated under reflux with glacial acetic acid (6·2 g.) and Girard reagent T (6·0 g.) in ethanol (70 c.c.) for 1 hour. The ketonic fraction, after isolation, was distilled to give a product (3·1 g.) which seemed homogeneous, as all the fractions had constant b. p. 174°/0·02 mm., $n_D^{26^\circ}$ 1·539. However, analysis clearly showed it to be a mixture of 2-chloro-5-benzoyloxy-1-acetyl-2-methyl*cyclo*hexane and 5-benzoyloxy-1-acetyl-2-methyl*cyclo*hexene (Found : C, 70·75; H, 6·8; Cl, 5·15. 42% of $C_{16}H_{19}O_3Cl$ + 58% of $C_{16}H_{18}O_3$ requires C, 70·55; H, 6·8; Cl, 5·05%). With semicarbazide acetate, the *semicarbazone* of the keto-ester was precipitated as an oil which slowly solidified. Crystallisation from methanol gave plates, m. p. 194—195° (Found : C, 64·2; H, 6·7; N, 13·5. $C_{17}H_{21}O_3N_3$ requires C, 64·7; H, 6·7; N, 13·35%).

The authors thank the Rockefeller Foundation for financial assistance, and one of them (F. S.) is indebted to the University of London for a Postgraduate Studentship. Light-absorption data were determined by Dr. E. A. Braude.

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[*Received, June 1st*, 1948.]