Dehalogenation of the product of the addition of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to allyl acetate. Zinc, 28.8 g. (0.44 g.-atom) and 150 cc. of dioxane were placed in a 500-cc. flask equipped with a stirrer, reflux condenser, and pressure-compensated addition funnel. A few drops of concd. hydrochloric acid were added, and the flask was stirred and heated to reflux. The addition product, 78 g. (0.2 mole) was placed in the addition funnel and slowly added. The condenser was allowed to warm to 40° and any material that passed through was collected in a cooled trap. About 10 ml. of product was obtained which on redistillation had a boiling point 37–38°, n_D^{20} 1.3424; reported[5] b.p. 38°, n_D^{27} 1.3435.

The peroxide initiated addition of dibromodifluoromethane to allyl acetate. The halomethane, 1110 g. (5.2 moles), allyl acetate, 130 g. (1.3 moles) and benzoyl peroxide, 8 g. (0.03 mole) were placed in a cooled 1.4-l. steel autoclave and sealed. After heating and rocking at 90° for 12 hr., the autoclave was cooled and the contents were distilled. Excess dibromodifluoromethane, 800 g., boiling at 22.5–24.5° was recovered, and then a product boiling at 95–109°/5 mm. This material was redistilled at 71–73°/2 mm. A yield of 163 g. (41%) was obtained. No reaction occurred under similar conditions with vinyl acetate.

The gamma radiation-induced reactions of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane and dibromodifluoromethane with allyl acetate. In a 60-ml. glass tube (22 mm. in diameter) were sealed 77 g. (0.28 mole) of the haloethane and 7.0 g. (0.07 mole) of allyl acetate. The tube was wrapped with friction tape and the sample was then exposed to a cobalt^{60} source with a flux rate of 4.5×10^5 roentgens per hr. After exposure for an hour the tube was cooled and opened. Upon distillation 12 g. of pure product, b.p. 85–86°/3.5 mm., n_D^{25} 1.4654, d_4^{25} 1.8196, $MR_{D(obsd.)}$ 56.55, $MR_{D(calcd.)}$ 57.3, was obtained.

Anal. Calcd. for $C_7H_8BrClF_3O_2$: C, 22.3; H, 2.10; F, 15.1. Found: C, 21.4; H, 2.0; F, 15.3.

In the same manner, 100 g. (0.48 mole) of dibromodifluoromethane and 6 g. (0.06 mole) of allyl acetate were treated to give 8 g. of pure product boiling at 72°/2.4 mm. n_D^{20} 1 4631, d_4^{20} 1.8153, $MR_{D(obsd.)}$ 47.13, $MR_{D(calcd.)}$ 46.6.

Anal. Calcd. for $C_6H_8Br_2F_2O_2$: C, 23.2; H, 2.58; Br, 51.6; F, 12.52. Found: C, 23.7; H, 2.49; Br, 52.3; F, 12.0.

The gamma radiation-induced reactions of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane and dibromodifluoromethane to vinyl acetate. These reactions were carried out in an identical manner with those in the previous section. The dibromodifluoromethane addition gave no higher boiling materials while the other addition product decomposed during distillation.

The peroxide initiated addition of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to vinyl acetate and allyl acetate. In a 500-cc. three-neck flask equipped with stirrer, reflux condenser, and pressure-compensated addition funnel were placed 10 g. (0.04 mole) of benzoyl peroxide and 400 g. (1.45 moles) of the perhalo compound, which had been prepared by the addition of bromine to chlorotrifluoroethylene, according to the method of Park, Lycan, and Lacher.[7] The flask was heated to 90° and 31 g. (0.36 mole) of redistilled vinyl acetate added at such a rate as to maintain mild reflux. The flask was heated an additional 4 hr. at 90° and then distilled at 150 mm. to recover the excess 1,2-dibromo-2-chloro-1,1,2-trifluoroethane, 200 g. boiling at 43.47° being obtained. The pressure was lowered to 2 mm. and 198 g. of material boiling from 72–85° (largely 78°) was distilled. Upon redistillation through a more efficient column the product obtained distilled at 73°/2 mm. and had the following physical properties: n_D^{25} 1.4531, d_D^{25} 1.9905, $MR_{D(calcd.)}$ 51.4.

Anal. Calcd. for $C_6H_6Br_2ClF_3O_2$: C, 19.9; H, 1.66; Br, 43.8; F, 15.8. Found: C, 20.4; H, 1.58; Br, 44.5; F, 15.6.

A similar reaction using allyl acetate was also performed. Allyl acetate, 45 g. (0.45 mole) was slowly added to 500 g. (1.81 moles) of the haloethane and 10 g. (0.04 mole) of benzoyl peroxide. The product boiling at 84–88°/1.4 mm. was obtained, 128 g. (76%), n_D^{20} 1.4670. A solid had sublimed over the product. Upon drying this material melted at 110–112°.

MATERIALS CENTRAL
WRIGHT AIR DEVELOPMENT DIVISION
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Synthesis of 2,4-Dimethyl-3-hydroxy-6-oxoheptanal

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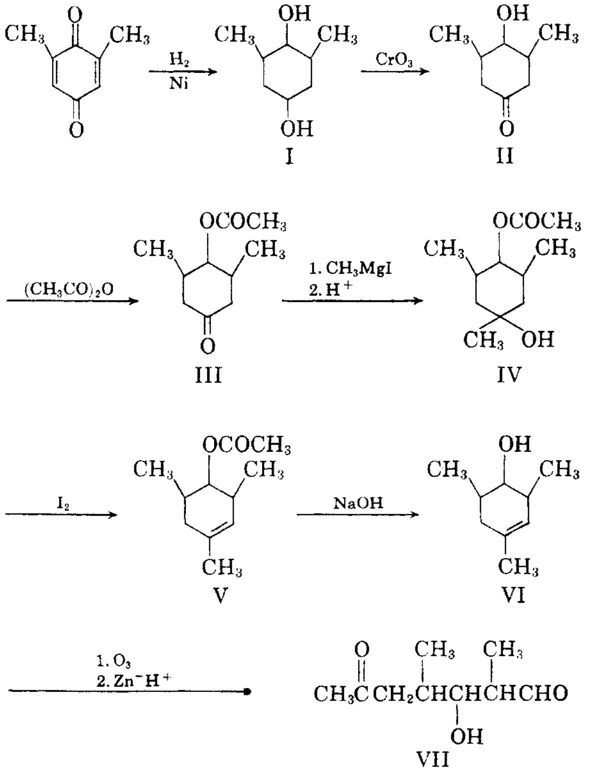
In connection with another problem 2,4-dimethyl-3-hydroxy-6-oxoheptanal was synthesized. The synthetic route used is outlined in the accompanying flow sheet. The reduction of *m*-xyloquinone was never very satisfactory. The crude product was a complex mixture, and purification resulted in low yields of I. It was assumed that use of a limited amount of chromic oxide would result in oxidation of I at the less hindered hydroxyl to give II rather than the isomeric hydroxyketone although this point was never unequivocally shown.



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(7) J. D. Park, W. R. Lycan, and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 711 (1951).

EXPERIMENTAL[1]

2,6-Dimethyl-1,4-cyclohexanediol (I). Ten grams of *m*-xyloquinone was reduced in ethanol over Raney nickel at 500 lbs. p.s.i. at 180°. The yield of product boiling at 85–90° at 0.3 mm. was 1.42 g. (13.5%). A redistilled sample was analyzed.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.70; H, 11.28.

3,5-Dimethyl-4-hydroxycyclohexanone (II). A solution of 0.9 g. (0.009 mole) of chromic oxide in 11 ml. of water was added dropwise to 2 g. (0.014 mole) of 2,6-dimethyl-1,4-cyclohexanediol in 95 ml. of glacial acetic acid. After the solution had stood for 2 hr. at room temperature and had been warmed for 15 min. on the steam bath, solvents were removed *in vacuo*. The residue was dissolved in water and extracted with chloroform. The chloroform extracts were washed with water and concentrated *in vacuo*. The residue was distilled at a bath temperature of 86° at 0.5 mm., n_D^{25} 1.4690. The ultraviolet spectrum showed absorption at 285 mμ, ϵ 25, the infrared spectrum at 2.80, 2.94, and 5.88 μ. The *2,4-dinitrophenylhydrazone* melted at 143–145° (from ethanol).

Anal. Calcd. for $C_{14}H_{18}N_4O_5$: C, 52.17; H, 5.63; N, 17.39. Found: C, 51.95; H, 5.69; N, 17.25.

The *p-toluenesulfonate* melted at 125–127° (from methanol).

Anal. Calcd. for $C_{15}H_{20}O_4S$: C, 60.78; H, 6.80; S, 10.82; mol. wt., 296.4. Found: C, 60.86; H, 7.04; S, 10.65; mol. wt. (ebull.), 266.8.

4-Acetoxy-3,5-dimethylcyclohexanone (III). A solution of 5.0 g. (0.035 mole) of 3,5-dimethyl-4-hydroxycyclohexanone and 35.8 g. (0.35 mole) of acetic anhydride in 120 ml. of dry pyridine was heated on the steam bath for 2 hr. The cooled solution was added to water which was then saturated with sodium bicarbonate. After evaporation of the solvent *in vacuo*, the residue was dissolved in water and extracted with ether. The ether extracts were dried and evaporated in *vacuo*. Distillation gave 3.33 g. (51%), b.p. 120° at 12 mm. The ultraviolet spectrum showed only end absorption; the infrared spectrum had bands at 5.78 and 5.83 μ.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.76; $CH_3CO(1)$, 23.37. Found: C, 65.01; H, 8.80; CH_3CO, 15.57.

4-Acetoxy-1,3,5-trimethylcyclohexanol (IV). A solution of methylmagnesium iodide (from 0.82 g. of magnesium and 3 ml. of methyl iodide in 10 ml. of dry ether) and 3.2 g. (0.017 mole) of 4-acetoxy-3,5-dimethylcyclohexanone was refluxed, acidified with hydrochloric acid, and extracted with ether. The extracts were dried and concentrated *in vacuo*. Distillation gave 1.3 g. (38%) of diol monoacetate, b.p. 80° at 0.3 mm., n_D^{25} 1.4608. The infrared spectrum showed absorption at 2.82, 2.90, and 5.84 μ.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.96; H, 10.02; $CH_3C(4)$, 30.02; $CH_3CO(1)$, 21.49; mol. wt., 200.3. Found: C, 66.16; H, 10.59; CH_3C, 21.65; CH_3CO, 10.48; mol. wt. (ebull.), 184.3.

2,4,6-Trimethyl-3-cyclohexenyl acetate (V). A solution of 8.3 g. (0.041 mole) of 4-acetoxy-1,3,5-trimethylcyclohexanol and 0.55 g. of iodine in 70 ml. of dry toluene was refluxed for 4 hr. removing water continuously as formed. The toluene solution was washed with 5% sodium hydrosulfite solution and water and evaporated *in vacuo*. Distillation gave 3.48 g. (46%) of product, b.p. 82–93° at 11 mm., n_D^{25} 1.4638. This material gave the usual olefin tests, and the infrared spectrum no longer showed hydroxyl absorption but did show carbonyl absorption. A fractionated sample was analyzed.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.47; H, 9.96; $CH_3CO(1)$, 23.61; $CH_3C(4)$, 33.00; mol. wt., 182. Found: C, 72.12; H, 10.24; CH_3CO, 18.68; CH_3C, 25.19; mol. wt. (ebull.), 184.2.

2,4,6-Trimethyl-3-cyclohexenol (VI). A solution of 2,4,6-trimethylcyclohexenylacetate (prepared from 4.0 g. of IV and not distilled) and 10 g. of sodium hydroxide in 40 ml. of 50% alcohol was refluxed for 3 hr. The reaction mixture was diluted with water and extracted with ether. The ether extracts were dried, evaporated *in vacuo* and the residue was distilled. The yield of product boiling at 85–97° at 12 mm. was 0.8 g. The infrared spectrum showed absorption at 2.80 2.94, and 6.05 μ.

Anal. Calcd. for $C_9H_{16}O$: C, 77.10; H, 11.50; mol. wt., 140.2. Found: C, 77.96; H, 11.53; mol. wt. (ebull.), 131.

2,4-Dimethyl-3-hydroxy-6-oxoheptanal (VII). The 2,4,6-trimethyl-3-cyclohexenol from 2.0 g. of V was dissolved in 100 ml. of purified ethyl acetate. Ozone was bubbled through the cooled solution for 1.5 hr. After removal of the ethyl acetate *in vacuo* the residue was stirred for 18 hr. in 10 ml. of dry ether and 1.1 g. of glacial acetic acid with 0.8 g. of zinc dust. The zinc was removed and washed with ether which was added to the filtrate. This solution was washed with 5% sodium carbonate solution. The ether solution was dried and concentrated *in vacuo*. Attempted purification of the product was unsuccessful as distillation caused decomposition. The infrared spectrum had a band at 2.90 μ indicative of hydroxyl and carbonyl absorption bands at 5.82 and 5.88 μ.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.77; H, 9.37; $CH_3C(3)$; 26.19. Found: C, 62.98; H, 9.31; CH_3C, 18.50.

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[1] Melting points are uncorrected.

An Adduct of Hexachlorocyclopentadiene with Acenaphthylene

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Hexachlorocyclopentadiene has been shown to be an extremely versatile reactant in the diene synthesis.[1] During the course of a study involving Diels-Alder reactions of hexachlorocyclopentadiene, its addition to acenaphthene was tried. In view of the fact that naphthalene acts as a dienophile in this reaction,[2] it was expected that acenaphthene also might function in this manner, either through the five-membered ring or the naphthalene part of the molecule.

The reaction was effected by prolonged heating of the reactants and gave a monoadduct together with considerable tar. The properties and analysis of the product were best explained by assuming it was an addition product of acenaphthylene, the latter having been formed by the dehydrogenating action of hexachlorocyclopentadiene (chlorination followed by dehydrochlorination).

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[1] H. E. Ungnade and E. T. McBee, *Chem. Revs.*, **58**, 249 (1958).

[2] A. A. Danish, M. Silverman, and Y. A. Tajima, *J. Am. Chem. Soc.*, **76**, 6144 (1954).