uct requires precautions, because it is a solid with an exceedingly high vapor tension.

Fluorination of Cyclo-$C_5F_6Cl_4$.—Fluorination with SbF_3Cl_2, as well as with a mixture of HgO + HF, was fruitless, and the starting material was recovered intact.

Summary

Octachlorocyclopentene was fluorinated as far as the hexafluoride cyclo-$C_5F_6Cl_2$ in one operation. The formula of the latter was demonstrated to be $\overline{CCl{=}CClCF_2CF_2CF_2}$ by opening the ring to yield perfluoroglutaric acid. Halogenation of the double bond of cyclo-$C_5F_6Cl_2$ was found exceedingly difficult, but chlorination was performed quantitatively in ultraviolet light, at 70°. The resulting cyclo-$C_5Cl_4F_6$ resisted all attempts at further fluorination.

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[8] This manuscript was originally received on July 10, 1944, and after examination by the editorial board was accepted for publication in THIS JOURNAL. It was, however, referred to the National Defense Research Committee and at their request was withheld from publication, in a confidential file, until clearance was granted on May 5, 1945.

[CONTRIBUTION OF THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Preparation of Cyclopentenes and Cyclopentanes. I[1]

BY GRANT CRANE,[2] CECIL E. BOORD AND ALBERT L. HENNE

In the course of a search for methods for the large scale preparation of monoalkylcyclopentanes, three procedures have been investigated: (1) condensation of an allylic chlorocyclopentene with a Grignard reagent to give an alkylcyclopentene which can be hydrogenated; (2) condensation of cyclopentanone with a Grignard reagent to yield an alkylcyclopentanol which can be dehydrated, then hydrogenated; (3) condensation of cyclopentadiene and a ketone to a fulvene derivative, and hydrogenation of the latter

Intermediate compounds, when not previously described in the literature, have been characterized, and additional data have been given for compounds already known.

First Method.—3-Chlorocyclopentene, prepared by 1,4-addition of hydrogen chloride to cyclopentadiene,[3,4] reacts with aryl-[5] or alkylmagnesium halides[6,7] to give 3-substituted cyclopentenes. The yields, based on the original cyclopentadiene, Table Ia, were 23–48% with primary alkylmagnesium halides, 20–27% with secondary, and only 2% with tertiary butylmagnesium chloride. Yields were slightly better with chlorides than with bromides. Reactions performed in copper vessels gave yields slightly better than in glass and distinctly better than in steel. Reversing the order of the addition, *i. e.*, adding the Grignard reagent to the 3-chlorocyclopentene, lowered the yields from 34–41% to 9–16%, in the case of propylmagnesium bromide.

TABLE Ia

3-ALKYLCYCLOPENTENES

R–Mg–X	Moles R–Mg–X	Moles C_5H_7Cl	Reaction vessel	Yield, %
Me-Mg-Cl	12	8.7	Copper	23.7
Et-Mg-Cl	12	8.5	Copper	48.3
Et-Mg-Br	3.7	3.0	Glass	42.7
n-Pr-Mg-Cl	20	14.1	Copper	47.5
n-Pr-Mg-Br	18	14.6	Iron	17.8
n-Pr-Mg-Br	8	7.34	Glass	37.9
n-Pr-Mg-Br	12	9.32	Copper	41.1
n-Pr-Mg-Br	11	8.95	Copper	15.6[a]
i-Pr-Mg-Cl	12	9.2	Copper	27.6
i-Pr-Mg-Br	3.7	3.7	Glass	20.0
n-Bu-Mg-Br	5	3.1	Glass	46.3
i-Bu-Mg-Br	5	3.1	Glass	39.0
s-Bu-Mg-Br	18	13.7	Copper	23.7
t-Bu-Mg-Br	18	14.2	Copper	2.0

[a] Order of addition reversed.

Ozonolysis of the alkylcyclopentenes yielded α-alkyl glutaric acids, showing that the side chains are in the 3-position. Table Ib lists the physical properties of the 3-alkylcyclopentenes produced. All were hydrogenated to the corresponding alkylcyclopentanes, the properties of which are summarized in Table II.

TABLE Ib

3-ALKYLCYLCOPENTENES

Alkyl group	B. p., °C. 760 mm.	d^{20}_4	$n^{20}D$	M. R. L. and L.	M. R. Calcd.
Methyl-	64.9	0.7622	1.4207	27.29	27.24
Ethyl-	98.1	.7830	1.4321	31.85	31.86
n-Propyl-	125.9	.7910	1.4359	36.38	36.48
i-Propyl-	121.2	.7941	1.4380	36.40	36.48
n-Butyl-	151.6	.7990	1.4407	41.03	41.10
s-Butyl-	149.7	.8092	1.4464	40.97	41.10
i-Butyl-	143.6	.7936	1.4393	41.19	41.10
t-Butyl-	139.1	.8066	1.4430	40.83	41.10

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(1) This paper represents a part of the dissertation submitted by Grant Crane to the Graduate School of Ohio State University in partial fulfillment of the requirements for the Ph.D. degree. Presented in part before the Organic Division of the American Chemical Society at the Detroit meeting, September 11, 1940.

(2) Research Assistant of the staff of the American Petroleum Institute Hydrocarbon Research Project at Ohio State University. Grateful acknowledgment is made for the support received, from the above project, for this work. Presently, Lieutenant Colonel, U. S. Marines, Pacific Theatre.

(3) Kraemer and Spilker, *Ber.*, **29**, 552 (1896).

(4) Noeldechen, *ibid.*, **33**, 3348 (1900).

(5) v. Braun and Kuhn, *ibid.*, **60B**, 2551 (1927).

(6) v. Braun, Kamp and Kopp, *ibid.*, **70B**, 1753 (1937).

(7) Plate, *Compt. rend. acad. sci. U. R. S. S.*, **24**, 257 (1939) (in English).

TABLE II

ALKYL CYCLOPENTANES

Alkyl group	F. p., °C.	B. p., °C. 760 mm.	d^{20}_4	n^{20}_D	M. R. L. and L.	M. R. Calcd.
Methyl-	.....	71.6	0.7480	1.4098	27.86	27.71
Ethyl-	.....	103.7	.7660	1.4200	32.44	32.33
n-Propyl-	−118.7	130.8	.7761	1.4266	37.06	36.94
i-Propyl-[a]	−116.1	126.4	.7774	1.4269	37.02	36.94
i-Propyl-[b]	−111.7	126.4	.7763	1.4260	37.01	36.94
n-Butyl-	.....	156.7	.7840	1.4318	41.74	41.56
s-Butyl-	Glass	154.5	.7934	1.4357	41.57	41.56
i-Butyl-	Glass	148.3	.7807	1.4300	41.77	41.56
t-Butyl-	−96	144.9	.7894	1.4338	41.63	41.56

[a] From 3-isopropylcyclopentene. [b] From dimethylfulvene.

Second Method.—1-Alkylcyclopentanols were prepared by adding cyclopentanone to a Grignard reagent. 1-Propylcyclopentanol, obtained in 60% yield, was dehydrated and hydrogenated by procedures described in the literature.[8,9] 1-Isopropylcyclopentanol was obtained in only 3.6% yield, confirming previous reports,[9,10] and when the order of addition of the reactants was reversed, no 1-isopropylcyclopentanol was obtained. In the preparation of 1-allyl and 1-methallylcyclopentanol it was necessary to add a mixture of cyclopentanone and the allylic chloride to magnesium in ether to prevent the formation of diallyl and dimethallyl, respectively. Along with the alkylcyclopentanols, three by-products were formed: cyclopentanol by reduction of cyclopentanone, and cyclopentylidine- and dicyclopentylidene-cyclopentanone by condensation of cyclopentanone with itself.

The cyclopentanols were dehydrated and hydrogenated by standard procedures.

Third Method.—Dimethylfulvene has been prepared by the condensation of acetone and cyclopentadiene in the presence of an equimolecular quantity of sodium ethoxide[9,11,12] or a concentrated solution of potassium hydroxide in methanol.[13]

In this work, conditions for the reaction were varied widely. As little as 5 g. of sodium in 100 ml. of ethanol, or 100 ml. of a 10% solution of potassium hydroxide for a 5-mole run gave yields of the same order (30–60%) as those obtained with much larger quantities of condensing agent. The smaller quantities also lowered the tendency to form large amounts of high boiling residue. Sodium hydroxide, in spite of its much lower solubility in methanol or ethanol, proved a satisfactory condensing agent. The best results were obtained using 100 ml. of 20% potassium hydroxide in ethanol for a 5-mole run.

Because the formation of dimethylfulvene involves the reaction of an active methylene with a keto group, it was thought that ammonia might be employed as a catalyst as in the Knoevenagel reaction. Yields of 25–38% of dimethylfulvene were obtained by stirring equivalent quantities of cyclopentadiene and acetone with an equal volume of concentrated (28%) aqueous ammonia. Using alcoholic ammonia to make the reaction mixture homogeneous increased the yields to 50–72%. Dimethylfulvene prepared with alcoholic ammonia was not hydrogenated readily, probably because of amine impurities, but no difficulty was experienced with that prepared with aqueous ammonia.

Along with the expected isopropylcyclopentane, the hydrogenation of dimethylfulvene produced a large amount of high boiling material. Hydrogenation over platinum oxide in ethanol at room temperature introduced approximately enough hydrogen to saturate two of the three double bonds, yielding incompletely saturated isopropylcyclopentane in about 50% yield. Similar results have been reported by others.[12,14] A higher boiling fraction (b. p. 64–44° at 17 mm.), apparently a saturated polymer, melted at 69.5–70.5° after recrystallization from methanol. Hydrogenation in an inert hydrocarbon solvent at higher temperatures and pressures over nickel[7] gave the best results. Yields of 38–55% of isopropylcyclopentane were obtained, the remainder being high boiling material. Different temperatures and pressures had little effect on yields.

Experimental

3-Alkylcyclopentenes.—Cyclopentadiene was diluted with an equal volume of dry ether and hydrogen chloride was passed in at Dry Ice temperature until a slight excess over the theoretical was added. The 3-chlorocyclopentene solution was further diluted with ether to bring the total to 300–400 ml. of ether per mole and was used immediately or stored in the cold for not more than a few days. The solution was added slowly to a 25% excess of Grignard reagent in a steel, copper or glass vessel, provided with a powerful stirrer, a water jacket, and a metal reflux condenser of large capacity. Free hydrogen chloride in the 3-chlorocyclopentene reacted very vigorously to destroy some alkylmagnesium halide, but this was compensated by the use of an excess of Grignard reagent. After hydrolysis with dilute acid and removal of the ether the crude 3-alkylcyclopentene was steam distilled to separate it from a gummy residue which otherwise interfered with the fractional distillation by evolving hydrogen chloride and solidifying in the flask. During the fractionation, which was done in a glass helix-packed column, the presence of a small amount of dicyclopentadiene caused a depression in the distillation temperature when it reached its decomposition temperature, forming monomeric cyclopentadiene, boiling at 40°. The 3-alkylcyclopentenes were refractionated at least once and the center of the constant-boiling cut was taken for physical constants. Beilstein tests for halogen were negative.

Standard procedures were used in hydrogenating the 3-alkylcyclopentenes to the alkylcyclopentanes. The 3-methyl-, 3-isopropyl-, and 3-*t*-butylcyclopentenes were hydrogenated over platinum oxide catalyst at room temperature and under low pressure; the others were hydrogenated over nickel on kieselguhr at higher temperatures and pressures. Before physical constants were taken the alkylcyclopentanes were washed with concen-

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(8) Chavanne and Becker, *Bull. soc. chim. Belg.*, **36**, 591 (1927).

(9) Pines and Ipatieff, THIS JOURNAL, **61**, 1076 (1939).

(10) Meerwein, *Ann.*, **405**, 156 (1914).

(11) Thiele, *Ber.*, **33**, 671 (1900).

(12) Kazanskiĭ, Plate and Gnatenko, *ibid.*, **69B**, 954 (1936).

(13) Thiele and Balhorn, *Ann.*, **348**, 6 (1906).

(14) Kazanskiĭ and Tatevosyan, *J. Gen. Chem.* (U. S. S. R.), **9**, 2248 (1939).

trated sulfuric acid and fractionally distilled from metallic sodium.

Cyclopentanols.—1-Propylcyclopentanol, m. p. −17.0°, b. p. 72° at 12 mm., d^{20}_{4} 0.9046, n^{20}_{D} 1.4538, and 1-isopropylcyclopentanol, m. p. 21–22°, b. p. 70° at 15 mm., d^{25}_{4} 0.9135, n^{25}_{D} 1.4560, were prepared, dehydrated over iodine and hydrogenated by standard procedures.

A solution of 63 g. of 1-propylcyclopentanol in 70 g. of absolute ethanol was hydrogenated directly to propylcyclopentane over nickel catalyst at 250° under 250 atm. of hydrogen, yielding a two-phase mixture of water, alcohol and propylcyclopentane.

1-Allylcyclopentanol was prepared by adding 536 g. (7 moles) of allyl chloride and 504 g. (6 moles) of cyclopentanone in 3000 ml. of dry ether to 146 g. (6 atoms) of magnesium turnings and 1500 ml. of dry ether in a copper reaction vessel. The reaction was started with a little undiluted allyl chloride. Stirring was continued overnight before hydrolyzing the mixture with dilute hydrochloric acid. A 54% yield of 1-allylcyclopentanol, b. p. 63° at 10 mm., d^{20}_{4} 0.9247, n^{20}_{D} 1.4683, was obtained. A similar run, in a glass vessel, with 2 moles of methallyl chloride gave a 25% yield of 1-methallylcyclopentanol, b. p. 98.5° at 40 mm., d^{20}_{4} 0.9244, n^{20}_{D} 1.4720.

Dimethylfulvene.—Approximately 5 moles of cyclopentadiene and an equivalent amount of acetone were placed in a Florence flask cooled with ice, and 100 ml. of a 20% solution of potassium hydroxide in ethanol was added through a reflux condenser. When the vigorous reaction was complete, the flask was stoppered and kept cool over night. The water layer was separated, the low-boiling materials were removed under vacuum, and the dimethylfulvene was distilled rapidly from a Claisen flask. The 60–70° cut was stored in the absence of air and in the cold until it was hydrogenated. Using alcoholic ammonia, the condensation was carried out by allowing 5 moles each of cyclopentadiene and acetone with 250 ml. of a saturated solution of ammonia in ethanol to stand for two days in a flask with an escape vent.

Hydrogenation of Dimethylfulvene.—Dimethylfulvene was hydrogenated in 2 to 3 times its volume of hexane or petroleum ether boiling up to 85°. The amount of nickel on kieselguhr used as catalyst was about 10% of the weight of the fulvene. Under pressures of about 30 atmospheres, hydrogen absorption began at about 120° with fresh catalyst, or at 60–80° with catalyst activated in a previous hydrogenation. The heat of hydrogenation raised the temperature to 180–200°. The hydrogenated product was distilled, and the 123–126° fraction was rehydrogenated (undiluted) over fresh catalyst at 200° under pressures up to 150 atmospheres. Rehydrogenation of the 126–35° fraction also gave pure isopropylcyclopentane.

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Summary

The condensation of Grignard reagents with cyclopentanone has given: 1-propyl-, 1-isopropyl-, 1-allyl-, and 1-methallylcyclopentanol. The last two are new. Dehydration yielded the corresponding 1-alkylcyclopentenes.

The condensation of 3-chlorocyclopentenes with Grignard reagents has given the 3-alkylcyclopentenes: methyl-, ethyl-, *n*-propyl-, *i*-propyl-, *n*-butyl-, *s*-butyl-, isobutyl-, and *t*-butyl-. All excepting the first two are new. The first has been prepared for the first time by this method.

Dimethylfulvene has been prepared by the condensation of acetone with cyclopentadiene in the presence of various alkaline agents, including aqueous ammonia.

The alkylcyclopentenes and dimethylfulvene have been hydrogenated to the corresponding alkylcyclopentanes.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

Absorption Spectra of Certain α,β-Unsaturated Ketones, including Benzal Compounds

BY HELEN S. FRENCH AND MURIEL E. T. HOLDEN[1]

Some years ago absorption spectra were used as evidence for two different types of conjugation in camphorquinone and benzalcamphor.[2] The present investigation was undertaken with the hope of obtaining further optical evidence for these two types of conjugation in corresponding compounds in the cyclohexane and cyclopentane series. It was soon found from a study of the literature[3] that the absence of the bridge structure of camphor decreased the stability of α-diketones and increased the stability of the mono-enol configuration in the simpler alicyclic compounds. The problem thus resolved itself into two problems, first, the determination of the effect of α-benzal groups on the absorption spectra of cyclic mono. ketones, and the comparison of this effect with the earlier results on benzal camphor; second, the determination of the absorption spectrum of the enol of the cyclic α-diketone, 3-methyl-1,2-cyclohexanedione, its differences from that of camphorquinone, and the application of those differences to give evidence for its structure. All of these compounds are α,β-unsaturated ketones, a class of compounds whose absorption has recently been studied extensively by Woodward,[4] and by Gillam and his co-workers.[5,6]

Our results should offer further contributions to the study of similar compounds.

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(1) An abstract of a thesis submitted in partial fulfillment of the degree of Master of Arts.

(2) Lowry and French, *J. Chem. Soc.*, **125**, 1921–1927 (1924).

(3) Notably Wallach, *Ann.*, **437**, 150–152 (1924).

(4) Woodward, THIS JOURNAL, (a) **63**, 1123 (1941); (b) **64**, 76 (1942); (c) Woodward and Clifford, *ibid.*, **63**, 2727 (1941).

(5) Gillam, Lynas-Gray, Penfold and Simonsen, *J. Chem. Soc.*, 62 (1941).

(6) Gillam and West, *ibid.*, 483, 486, 671 (1942).