Experimental[5]

2-(*p*-Dimethylaminobenzal)-1-indanone (V).—To an ice-cooled solution of 7.94 g. (0.0600 mole) of 1-indanone dissolved in 20 ml. of ethanol was added slowly an ice-cooled solution of 0.34 g. of potassium hydroxide (0.0060 mole) and 8.95 g. (0.0600 mole) of *p*-dimethylaminobenzaldehyde in 50 ml. of ethanol. The mixture was allowed to stand overnight in a refrigerator. Filtration and washing with ethanol gave 15.0 g. (99% yield) of yellow crystals, m.p. 161–162°. After recrystallization from dioxane, it had m.p. 164–165°; λ_{max} 271, 431 mμ (ϵ 17,400, 36,600); $\nu_{C=O}$ 1698 vs (1690 vs in acetonitrile), $\nu_{C=C}$ 1629 m, ν_{Ar} 1605 cm.$^{-1}$ vs.

The proton magnetic resonance spectrum in deuteriochloroform shows six methyl protons at 7.05 τ, two methylene protons (split by 2 c.p.s.) at 6.13 τ, two equivalent aromatic protons (*ortho* to the dimethylamino group and split by two equivalent protons *meta* to this grouping; J = 8 c.p.s.) at 3.37 τ, peaks corresponding to five aromatic and one vinyl proton in the range 2.3–2.9 τ, and the aromatic proton beta to the carbon group (split by the γ proton; J = 7 c.p.s.) at 2.15 τ.

Anal. Calcd. for $C_{18}H_{17}ON$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.32; H, 6.50; N, 5.26.

2-(*p*-Nitrobenzal)-1-indanone.—The same procedure as for V was followed, but using 9.07 g. (0.0600 mole) of *p*-nitrobenzaldehyde. Obtained was 12.8 g. (80% yield) of pale yellow crystals, m.p. 228–230°. Recrystallization from glacial acetic acid gave long pale yellow needles which were washed with petroleum ether and ether, m.p. 251–252°; λ_{max} 321 mμ; $\nu_{C=O}$ 1692 cm.$^{-1}$ (KBr pellet and LiF optics).

Anal. Calcd. for $C_{16}H_{11}O_3N$: C, 72.44; H, 4.18; N, 5.28. Found: C, 72.22; H, 4.14; N, 5.41.

2-(*p*-Dimethylaminobenzyl)-1-indanone (VI).—To a solution of 9.0 g. of 2-(*p*-dimethylaminobenzal) 1 indanone (V) in 900 ml. of dioxane was added 0.9 g. of 10% palladium on charcoal. The mixture was heated to 45–50° and quantitative hydrogenation carried out at atmospheric pressure. The solution was filtered and evaporated to dryness to give gray-brown crystals. Recrystallization from ethanol gave 6.4 g. (70% yield) of almost colorless crystals, m.p. 77–79°. Several additional recrystallizations raised the m.p. to 79–80°; λ_{max} 249, 293 mμ (ϵ 32,000, 6,700); $\nu_{C=O}$ 1715 vs (1710 cm.$^{-1}$ vs in acetonitrile), ν_{Ar} 1619 cm.$^{-1}$ s.

The p.m.r. spectrum in deuteriochloroform shows a sharp peak corresponding to six methyl protons at 7.12 τ, several peaks corresponding to five protons in the range 6.5–7.8 τ, two protons *ortho* and two protons *meta* to the dimethylamino group (constituting two superimposed AB systems; J_{AB} = 8 c.p.s.) at 3.35 and 2.90 τ, respectively, peaks corresponding to three aromatic protons in the range 2.4–2.9 τ, and the aromatic proton beta to the carbonyl group at 2.27 τ (J = 7 c.p.s.).

Anal. Calcd. for $C_{18}H_{19}ON$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.53; H, 7.28; N, 5.34.

2-(*m*-Bromo-*p*-dimethylaminobenzyl)-1-indanone (VII).—To a solution of 21.2 g. (0.0800 mole) of 2-(*p*-dimethylaminobenzyl)-1-indanone (VI) in 75 ml. of chloroform was added over a period of 1 hr. with stirring and in the presence of sunlight, a solution of 12.8 g. (0.0800 mole) of bromine in 25 ml. of chloroform. After standing for an additional 30 min. the solution was evaporated and the product recrystallized from ethanol to give 25.8 g. (76% yield) of the hydrobromide of VII. This product, m.p. 123°, was hygroscopic and gave an instantaneous precipitate with alcoholic silver nitrate; λ_{max} 246, 287 mμ (ϵ 19,800, 4800); $\nu_{C=O}$ 1712 cm.$^{-1}$ vs (in acetonitrile).

Extraction of 10 g. of the hydrobromide by 150 ml. of 5% aqueous sodium carbonate and 100 ml. of ether, washing the ether layer, drying over anhydrous magnesium sulfate, and evaporation gave 7.5 g. (81% yield) of crude VII. Recrystallization from ether–petroleum ether gave pure VII, m.p. 71–72°; λ_{max} 247, 289 mμ (ϵ 30,500, 8100); $\nu_{C=O}$ 1719 vs, ν_{Ar} 1614 cm.$^{-1}$ m.

The p.m.r. spectrum in deuteriochloroform shows a sharp peak corresponding to six methyl protons at 7.22 τ, several peaks corresponding to five protons in the range 6.5–7.8 τ, a complex series of peaks corresponding to six aromatic protons in the range 2.4–3.1 τ, and the signal from the aromatic proton beta to the carbonyl at 2.23 τ (J = 7 c.p.s.).

Anal. Calcd. for $C_{18}H_{18}ONBr$: C, 62.80; H, 5.27; N, 4.07. Br, 23.22. Found: C, 62.99; H, 5.35; N, 4.17; Br, 23.01.

An acetonitrile solution 0.01 *M* in VII and 0.03 *M* in piperidine, maintained in sealed bulbs at 91.9°, underwent no reaction as measured either by reduction in base concentration or by increase in bromide ion concentration[6] during a period of 30 hr.

2-(*m*-Bromo-*p*-dimethylaminobenzyl)-1-indanone Methiodide (VIII).—A mixture of 20 ml. of ethanol, 15 ml. of methyl iodide, and 7.0 g. of 2-(*m*-bromo-*p*-dimethylaminobenzyl)-1-indanone (VII) was maintained in a sealed tube at 60° for 15 hr. and then allowed to stand at room temperature for 2 days. Ether extraction left 2.8 g. (28% yield) of crude VIII. Recrystallization from ethanol gave pure VIII, m.p. 152–153°; λ_{max} 242, 295 mμ (ϵ 25,700, 4700).

Anal. Calcd. for $C_{19}H_{21}ONBrI$: C, 46.92; H, 4.35; N, 2.88; Br + I, 42.54. Found: C, 47.01; H, 4.45; N, 2.92; Br + I, 42.70.

Neither an acetonitrile solution 0.0082 *M* in VIII nor an acetonitrile solution 0.0041 *M* in VIII and 0.0239 *M* in tetraethylammonium bromide developed any acidity[6] during 3 days in sealed bulbs at 91.9°.

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[5] Melting points were read with a calibrated thermometer. Infrared spectra were measured with a Perkin-Elmer Model 21 double beam recording instrument employing, unless otherwise stated, sodium chloride optics and matched sodium chloride cells with carbon tetrachloride solutions. The ultraviolet spectra were determined with a Cary Model 11-MS recording spectrophotometer using reagent grade methanol solutions. The proton magnetic resonance spectra were obtained with a Varian A-60 instrument *using a trace of tetramethylsilane (τ 10.00) as internal reference.*

[6] Acid–base titrations in acetone using Lacmoid, *i.e.*, resorcinol blue, as indicator. Bromide titrations by potentiometric titration in acidified acetone against aqueous silver nitrate.

A Convenient Method for Utilizing the Allyl Grignard Reagent

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It is the purpose of this paper to point out and emphasize a convenient synthetic technique which has been known for a number of years but has been overlooked and even discouraged. The method of utilizing the allyl Grignard reagent reported here has been referred to as the Barbier–Grignard procedure.[1] In this procedure the organomagnesium compound is not formed as an intermediate in the presence of an excess of carbonyl compound as Barbier[2a,3,4] did, nor is the functional addend withheld until the preparation of the Grignard reagent is complete. Rather a solution of the alkyl halide and the functional addend is added to the magnesium metal to which a small amount of allyl halide has been added to start the reaction; there is no large excess of carbonyl compound present at any time. The application of the Barbier–Grignard procedure to allylic halides has been employed periodic-

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[1] H. R. Henze, B. B. Allen, and W. B. Leslie, *J. Org. Chem.*, **7**, 326 (1942).

[2] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, (a) p. 3; (b) p. 27; (c) p. 143.

[3] G. H. Richter, "Textbook of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 170.

[4] P. Barbier, *Compt. rend.*, **128**, 110 (1899).

ally,[5−10] but the method has never been emphasized nor has the apparent generality of the reaction been appreciated. The Barbier–Grignard procedure appears to have been used routinely whenever the allyl Grignard reagent was desired before Gilman[11] discovered the technique required to make successfully allylmagnesium bromide. Since this discovery, it has been more common to make the allyl Grignard reagent in a separate step, especially in the light of studies such as Henze's.[1]

Recently the author has had occasion to use the Barbier–Grignard method successfully in a number of cases; some of them are verifications of reported cases and several are new examples. In the preparation[11] of the very useful allyl Grignard reagent, its coupling with allyl halide is avoided by slowly adding the allyl halide in very dilute solution to a large excess of magnesium. Some of these disadvantages are overcome by forming the ether-insoluble allylmagnesium chloride.[2b] In the present method the allyl Grignard is formed only as a transient intermediate, thus obviating the need for dilute solution and a large excess of magnesium and allowing the fast addition of the reagents to the magnesium. In most cases, addition can be as rapid as the vigor of the reaction will allow. The yields are generally high and in many cases are higher than those reported in the two step procedure. It is emphasized, however, that it was *found critical to the success of this method to start the reaction with a small amount of allyl halide in ether before beginning the addition of allyl halide and functional addend.* An unawareness of this technique probably accounts for the preference for the two-step procedure by workers such as Henze[1] and Bacon and Farmer.[12] The success of this reaction seems to depend on the fact that the allylic Grignard reacts with the carbonyl compound at a much higher rate than it reacts with the allylic halide.

In a recent volume of *Organic Syntheses* there is a report[15] of the synthesis of 1,5-hexadien-3-ol by the standard two-step procedure, preparation of allylmagnesium bromide followed by reaction with acrolein. Table I compares this report with the same preparation carried out by the simultaneous addition of allyl bromide and acrolein and points out the advantages in time and materials of the latter method.

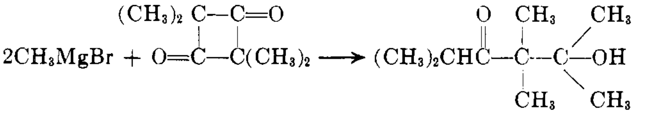
In addition, the reaction has been carried out using allyl bromide or chloride with a number of different functional addends. These results are summarized in Table II.

TABLE I

TWO-STEP *vs.* ONE-STEP PREPARATION OF 1,5-HEXADIEN-3-OL

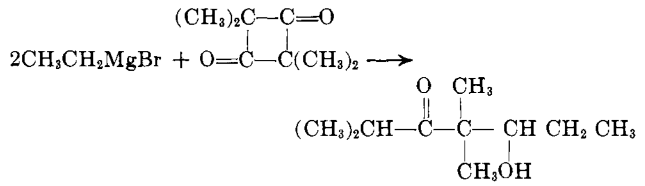
	Two-step[15]	One-step
G.-atoms of Mg	6.28	2.9
Moles of allyl bromide	2.90	2.5
Moles of acrolein	1.86	2.0
Total volume of ether	2960 ml.	900 ml.
Total time of addition of reagents	6 hr.	3 hr.
Boiling point	62–65° (50 mm.)	38–39° (11 mm.)
$n^{25}D$	1.4440	1.4450
Yield	57–59%	66%

The reaction with tetramethyl-1,3-cyclobutanedione appears worthy of comment. Erickson and Kitchens[16] reported that methyl Grignard reacted with tetramethyl-1,3-cyclobutanedione to form an open chain diadduct **1**.

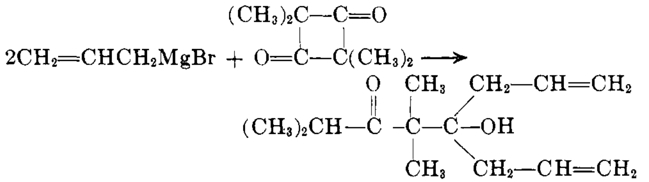


1

The ethyl Grignard formed only a reduced open chain monoadduct.

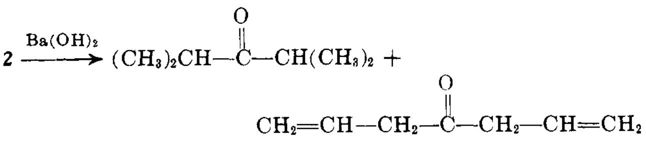


Allyl Grignard reacted with tetramethyl-1,3-cyclobutanedione under the conditions reported in this paper to form an open chain diadduct.



2

The fact that a diallyl rather than monoallyl adduct was formed was suggested by a boiling point more consistent with a C_{14} keto alcohol than with a C_{11} keto alcohol. The proton magnetic resonance (p.m.r.) spectrum of the product showed two allyl groups per four methyl groups and, therefore, confirmed that two moles of allyl Grignard had added to one mole of tetramethyl-1,3-cyclobutanedione. The p.m.r. spectrum also showed one hydroxyl per two allyl groups and an isopropyl group; thus the structure **2** analogous to structure **1** was indicated. The structure **2** was proven by carrying out the cleavage reaction reported by Erickson and Kitchens[16] for this type of compound.



$$2 \xrightarrow{Ba(OH)_2} (CH_3)_2CH-\overset{O}{\overset{\|}{C}}-CH(CH_3)_2 + CH_2{=}CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH{=}CH_2$$

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(5) W. Jaworsky, *Ber.*, **42**, 435 (1909).

(6) F. G. Fischer, *ibid.*, **76**, 735 (1943).

(7) I. N. Nazrov and I. I. Zaretskaya, *J. Gen. Chem. USSR*, **27**, 693 (1957).

(8) N. A. Milas and A. McAlevy, *J. Am. Chem. Soc.*, **57**, 580 (1935); R. T. Arnold and E. C. Coyner, *ibid.*, **66**, 1542 (1944); N. G. Gaylord and E. I. Becker, *J. Org. Chem.*, **15**, 305 (1950).

(9) I. Matzurevich, *J. Russ. Phys. Chem. Soc.*, **43**, 973 (1911); *Chem. Abstr.*, **6**, 480 (1912).

(10) R. Ya. Levina and D. M. Trakhtenburg, *J. Gen. Chem. USSR*, **6**, 764 (1936); *Chem. Abstr.*, **30**, 6338 (1936).

(11) H. Gilman and J. H. McGlumphy, *Bull. soc. chim. France*, **43**, 1322 (1928).

(12) R. G. R. Bacon and E. H. Farmer, *J. Chem. Soc.*, 1065 (1937). These authors were unable to prepare 2-methyl-4-penten-2-ol using the Barbier–Grignard procedure as reported by Jaworsky[5] and instead used the two-step method. Fischer[6] successfully repeated Jaworsky's preparation. DuPont[13] at at first repeated Bacon and Farmer's preparation but subsequently[14] found Fischer's method superior.

(13) G. DuPont and M. Darmon, *Bull. soc. chim. France*, 240 (1954).

(14) G. DuPont, R. Dulou, and G. Christen, *ibid.*, 820 (1954).

(15) J. C. H. Hwa and H. Sims, *Org. Syn.*, **41**, 49 (1961).

(16) J. L. E. Erickson and G. C. Kitchens, *J. Am. Chem. Soc.*, **68**, 492 (1946).

TABLE II

ALLYLIC CARBINOLS PREPARED BY THE BARBIER–GRIGNARD PROCEDURE

Allyl halide[a] (moles)	Magnesium, g.-atoms	Functional addend (moles)	Ether, ml.	Addition time, hr.	Product	Yield, %	Properties		
							B.p., °C.	Mm.	n^{25}D
B (2.5)	2.9	Acrolein (2.0)	900	3	1,5-Hexadien-3-ol	66	38–39[b]	11	1.4450[b]
B (2.23)	2.26	Acetone (2.0)	800	2	2-Methyl-4-penten-2-ol[c1]	74[d]	117.0–117.3[e]	Atm.	1.4246[e]
C (2.25)	2.26	Methyl isopropyl ketone (2.0)	800	3.5	2,3-Dimethyl-5-hexen-3-ol	70	56–58[f]	16	1.4411
B (1.12)	1.07	Cyclohexanone (1.02)	600	1.3[g]	1-Allylcyclohexanol[c2]	48	70–72[h]	8	1.4761[h]
B (1 65)	1.7	Ethyl carbonate (0.5)	600	0.8	Triallylcarbinol	70	68–70[i]	8	1.4685[i]
C (1.37)	2.14	Ethylene oxide (1.3)	650	4[j]	4-Pentenol	72	134–136[k]	Atm.	1.4288[k]
B (0.21)	0.214	Ethylene oxide (0.2)	60	0.5[l]	4-Pentenol	41	132–136[k]	Atm.	1.4320[k]
B (1.24)	1.44	1,2,5,6-Tetrahydrobenzaldehyde (1.0)	400	1.7	α-Allyl-3-cyclohexene-1-methanol[c3]	72	109–111[m]	16	1.4922[m]
C (0.55)	0.56	Ethyl formate[n] (0.25)	265	1.2	Diallylcarbinol[o]	52	51–52[p]	13	1.4479
B (1.25)	1.44	Tetramethyl-1,3-cyclobutanedione (0.5)	500	2	5-Allyl-5-hydroxy-2,4,4-trimethyl-7-octen-3-one (**2**)[q]	61	81–84	0.35	1.4723

[a] B = allyl bromide; C = allyl chloride. [b] Ref. 15 reports b.p. 62–65° (50 mm.), n^{25}D 1.4440. [c] Previously made using the Barbier–Grignard procedure. Yields: (1) 39% (ref. 5), 70–75% (ref. 6), 70% (ref. 14); (2) 81% (ref. 9), 31% (ref. 10); (3) 85% (ref. 7). [d] Crude yield 82%, b.p. 103–115°, n^{25}D 1.4242. [e] Ref. 1 reports b.p. 118.0–118.2°, n^{20}D 1.4263. [f] S. B. Schryver, *J. Chem. Soc.*, **63**, 1327 (1893), reports b.p. 151–153°. [g] Refluxed for 5 hr. after addition of reactants. [h] Ref. 10 reports b.p. 69–71° (5 mm.), n^{22}D 1.476. [i] B. N. Dashkevich, I. V. Smolanska, and Yu. Yu. Tsmur, *Nauch. Zap., Uzhgorodsk. Gos. Univ.*, **22**, 81 (1957); *Chem. Abstr.*, **54**, 14100*f* (1960), report b.p. 72–73° (16 mm.), n^{20}D 1.4650. [j] The reaction was terminated before the addition of reagents was complete because a nonstirrable gel formed. Dilution with ether did not help. The amounts of reactants shown are those actually added. [k] L. A. Brooks and H. R. Snyder, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 698, report b.p. 134–137°; L. E. Schniepp and H. H. Geller, *J. Am. Chem. Soc.*, **67**, 54 (1945), report b.p. 139–140°, n^{25}D 1.4270. [l] A stirrable reaction mixture was observed throughout. [m] Ref. 7 reports b.p. 96–97° (7 mm.), n^{20}D 1.4940. [n] Purified by the method of G. H. Coleman and D. Craig, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 179. [o] 3,5-Dinitrobenzoate, m.p. 61–62°; J. L. Everett and G. A. R. Kon, *J. Chem. Soc.*, 3131 (1950), report m.p. 62–63°. As in an analogous reaction, Coleman and Craig, footnote *n*, the diallylcarbinol was contaminated with a carbonyl containing impurity. Ten grams were purified by the method of Coleman and Craig to give 7.2 g. of carbonyl free diallyl carbinol, b.p. 50.5–51° (12 mm.), n^{25}D 1.4490. [p] Everett and Kon, footnote *o*, report b.p. 49–51° (16 mm.). [q] *Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 74.95; H, 10.78. Found: C, 74.83, 75.06; H, 10.71, 10.89. In addition, 23 g. of lower boiling material was obtained. This was shown (p.m.r.) to consist of diisopropyl ketone and diallyl ketone in approximately equivalent amounts.

Diisopropyl ketone and diallyl ketone (contaminated with some allyl propenyl ketone) were isolated in 83% yield each. It is interesting to note that the rather simple ketone, diallyl ketone, has not previously been reported. Its structure follows from its reduction to the known diallyl carbinol and from its completely consistent p.m.r. spectrum. The p.m.r. and ultraviolet spectra of the yellow diallyl ketone suggested that about 10% of the diallyl ketone had rearranged to allyl propenyl ketone during the course of its preparation and isolation. This was not unexpected, since it is reported[7] that ethyl allyl ketone isomerizes to ethyl propenyl ketone merely upon fractionation (130°). However, it was observed that **2** could also be cleaved thermally *without* base catalysis. The cleavage was slower, but the yields were substantially the same and the diallyl ketone so obtained was colorless and found to contain at most traces of the rearranged ketone. Thus, not surprisingly, the rearrangement of diallyl ketone to allyl propenyl ketone appears to be base-catalyzed.

The Barbier–Grignard method has been shown to be a convenient method for utilizing the allyl Grignard reagent, but it is probably also applicable to Grignard reactions not involving allyl halides. In fact, as long ago as 1911, Davies and Kipping[17] reported the successful application of the Barbier–Grignard method to benzyl and ethyl halides. They also pointed out the need for first starting the reaction with a small amount of the halide. Benzyl halide can be thought of as being rather analogous to allyl halide, but the success with ethyl halide suggests the technique may have general application in the Grignard reaction. Indeed it would seem that the work of Davies and Kipping has never received the attention it merits.

Experimental[18]

Allylic Carbinols by the Barbier–Grignard Procedure, General Method.—A solution of a few grams of allyl bromide or chloride and a few crystals of iodine in about 30% of the ether to be used was added to the magnesium turnings in a flask which had been flamed and purged with nitrogen. When the allyl halide was reacting smoothly with the magnesium, addition of a solution to the rest of the allyl halide and the functional addend in ether was started. Addition was carred out at a rate to maintain gentle reflux of the ether while cooling with ice–water. The reaction mixture was refluxed for 1–2 hr. after the addition was complete. The product was isolated by the method commonly used[2c] for Grignard reactions and after removal of the ether the crude product was distilled through a 6-in. vacuum jacketed Vigreux column fitted with a variable take-off head. The quantities employed, the yields, and the properties of the allylic carbinols prepared are summarized in Table II.

Starting the Reaction.—A solution of a few crystals of iodine and 2 g. of allyl bromide in 50 ml. of ether was added to 14 g. of magnesium. Reaction set in with virtually no induction and a solution of 29 g. of acetone and 65 g. of allyl bromide in 150 ml. of ether was then added smoothly. In a parallel reaction a solution of a few crystals of iodine in 50 ml. of ether was added to 14 g. of magnesium. The iodine color dispersed almost immediately, but on addition of about 20 ml. of a solution of 29 g. of acetone and 67 g. of allyl bromide in 150 ml. of ether, no reaction could be induced even after refluxing for 1.5 hr. The reaction was started by adding small portions of an approximately 1 *M* ethereal solu-

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(17) H. Davies and F. S. Kipping, *J. Chem. Soc.*, **99**, 296 (1911).

(18) Melting points and boiling points are uncorrected. Starting materials were commercial reagent chemicals used without further purification unless otherwise indicated. Analyses are by Huffman Microanalytical Laboratories, Wheatridge, Colo.

tion of ethylmagnesium bromide. About 35 ml., or approximately enough to react with the acetone present, was added before a self-sustaining reaction set in. The remainder of the acetone–allyl bromide solution was then added without further difficulty.

Structure of 5-Allyl-5-hydroxy-2,4,4-trimethyl-7-octen-3-one (2).—A mixture of 22.7 g. of **2** and 0.2 g. of $Ba(OH)_2$ was heated in a 125–140° oil bath at a pressure of 20 mm. Distillate, b.p. 43–50° (20 mm.), was collected as it formed; 21.1 g. was collected in 90 min. Fractionation of 30.7 g. of such pyrolysate through a spinning-band column at 20 mm. gave (1) 13.6 g., 31–32°, $n^{25}D$ 1.3992; (2) 3.0 g., 36–51°, $n^{25}D$ 1.4410; and (3) 10.5 g., 51–53°, $n^{25}D$ 1.4421. Fractions 2 and 3 were yellow. Fraction 1 was identified as diisopropyl ketone by its characteristic p.m.r. spectrum, fraction 2 by p.m.r. analysis contained 8% diisopropyl ketone, 69% diallyl ketone, and 23% allyl propenyl ketone, and fraction 3 similarly contained 1% diisopropyl ketone, 91% diallyl ketone, and 8% allyl propenyl ketone. Fraction 3 showed a λ_{max} 225 mμ (isooctane); this is consistent with the presence of allyl propenyl ketone rather than dipropenyl ketone since the latter is reported[19] to have a λ_{max} 245, 251 mμ.

Fraction 3 did not give a sharp melting 2,4-dinitrophenylhydrazone or semicarbazone. However, treatment of 3 g. of fraction 3 with 0.5 g. of lithium aluminum hydride in 20 ml. of ether yielded 1.9 g. of diallyl carbinol, b.p. 53–54° (14 mm.), $n^{25}D$ 1.4490, 3,5-dinitrobenzoate m.p. 60.5–61.5°, m.m.p. 60–61.5° with an authentic sample. The infrared spectrum of this diallyl carbinol was identical with a spectrum of the material independently prepared (see Table II).

It was found that **2** would cleave thermally without base-catalysis, but somewhat more slowly. Compound **2**, 11.2 g., was heated in a 130–160° oil bath at a pressure of 15 mm. and distillate, 10.0 g., was collected at 40–65° over a period of 5 hr. Fractionation through the spinning-band column at 15 mm. gave (4) 4.8 g., 24–25°, $n^{25}D$ 1.3982; (5) 0.8 g., 37–46°, $n^{25}D$ 1.4362; and (6) 3.5 g., 46–47°, $n^{25}D$ 1.4420. All fractions were colorless but fractions 5 and 6 yellowed on storage in soft glass containers. By p.m.r. analysis fraction 4 was substantially pure diisopropyl ketone; fractions 5 contained 13% diisopropyl ketone, 84% diallyl ketone, and 3% allyl propenyl ketone; and fraction 6 appeared to be better than 99% diallyl ketone and contained only traces of diisopropyl and allyl propenyl ketone. The λ_{max} at 225 mμ was absent in the ultraviolet spectrum of fraction 6.

Anal. of fraction 6. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.86, 76.04; H, 9.18, 9.24.

A 2,4-dinitrophenylhydrazone of fraction 6 was readily obtained, dark red platelets, m.p. 133–135°, from ethanol.

Anal. Calcd. for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 53.78, 53.91; H, 5.47, 5.31; N, 19.48, 19.18.

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Rates and Relative Rates of Chloro- and Iododesilylation. Evidence for a Four-Center Transition State

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Recently, the mechanisms of cleavage of carbon–metalloid bonds have received considerable attention.[1-3] The major uncertainty in the description of the activated complex for these reactions involves the significance to be ascribed to four-center interactions. As an approach to this problem we have evaluated the effectiveness of iodine monochloride and chlorine as reagents for desilylation of phenyltrimethylsilane.

The reaction between phenyltrimethylsilane and iodine monochloride in dry acetic acid at 25° yields iodobenzene and hexamethyldisiloxane as the only detectable products in greater than 90% yield.

Observations obtained in a typical kinetic experiment are presented in Table I.

The failure of second- or third-order rate laws to accommodate the data, Table I, and the observations of other kinetic studies[4] of iodination suggested the effective concentration of iodine monochloride was reduced by complex formation.

$$ICl + Cl^- \overset{K}{\rightleftharpoons} ICl_2^-$$

Rate law based on this equilibrium and a second-order rate-determining reaction between iodine monochloride and phenyltrimethylsilane is the following,

$$ICl + PhSiMe_3 \xrightarrow{k} \text{products}$$

$$\frac{-d[ICl]}{dt} = \frac{k[PhSiMe_3][ICl]}{1 + K[Cl^-]} \qquad (1)$$

where [ICl] is the titrimetric concentration. The calculated second-order rate constants, k, reported in Tables I and II are based on the known value, K = 250 l. mole^{-1}, for the equilibrium constant in acetic acid at 25°.[4] As illustrated in Table I, this rate law provides a good fit of the kinetic observations.[5]

Chlorodetrimethylsilylation by chlorine in 1.5% aqueous acetic acid at 25° was previously examined by Eaborn and Webster.[6] They report the reaction kinetics are satisfied by a second-order rate equation, but their typical data reveal the observed second-order rate constant decreases through the course of an experiment from an initial value of 5.3×10^{-2} to 2.8×10^{-2} l. mole^{-1} sec.$^{-1}$ at 85% reaction. In this study, dry acetic acid was adopted as the solvent for the reaction. It was found that the reaction obeyed second-order kinetics to 70–80% completion. The rate constant observed, 1.57×10^{-2} l. mole^{-1} sec.$^{-1}$, is somewhat less than reported by Eaborn and Webster. Presumably, the removal of water contributes to the reduction of the reaction velocity.[7]

Rate constants for iododesilylation and chlorodesilylation as determined in a series of independent experiments with different samples of phenyltrimethylsilane, iodine monochloride, and chlorine are summarized in Table II.

Comparison of the second-order rate constants indicates chlorodesilylation is eightfold less rapid than iododesilylation under identical conditions.[8] This finding contrasts sharply with the rate ratios observed

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