magnetic resonance spectrometer using 100 kc. modulation. In a typical experiment an ESR sample tube containing *ca.* 5 mg. of solid I was placed in a variable temperature cavity which had been preheated to *ca.* 125°. The sample tube was flushed with nitrogen throughout the entire experiment. The spectrum which was obtained showed a resonance absorption with a *g* value near the free spin value and a line width of approximately 9 gauss. Similar experiments using evacuated sample tubes gave the same resonance absorption.

Reaction of I *with oxygen.* A flask containing 100 ml. of benzene was fitted with an oxygen inlet attached to a fritted disk. Oxygen was bubbled vigorously through the benzene for 0.5 hr. The flask was then irradiated with a Westinghouse Co. 275 watt sun lamp while maintaining a vigorous stream of oxygen through the benzene. A solution of 0.34 g. (1.1 mmoles) of I in 30 ml. of benzene was added dropwise to the irradiated benzene and the purple color of I was slowly discharged. When addition was complete and no purple color remained, the solvent was removed by evaporation leaving a yellow oil which solidified upon standing. The infrared spectrum of this material was essentially identical to that of 1,4-dibenzoylbenzene. The solid weighed 310 mg. (99%). Despite the clean infrared spectrum, this material was difficult to recrystallize, probably because of the presence of polymeric material from the decomposition of I. The solid was recrystallized twice from ethanol and once from cyclohexane to give white plates of 1,4-dibenzoylbenzene, m.p. 161–163°, mixed m.p. 157–162°.

Reaction of I *with acetic acid.* Solid bisdiazo compound, (I), prepared as described above from 1.57 g. (0.005 mole) of 1,4-dibenzoylbenzene dihydrazone, was dissolved in a minimum amount of ether and added dropwise to a solution of 3 ml. of acetic acid in 25 ml. of ether. The purple color of I slowly disappeared. When addition was complete the reaction mixture was stirred (*ca.* 10 hr.) until the purple color was completely gone. The ether solution was then extracted with aqueous sodium bicarbonate, dried (magnesium sulfate), and evaporated to give a yellow oil. The infrared spectrum of this oil indicated that it was mostly acetate (carbonyl band at 5.73 μ) with a small amount of diketone present. The oil was triturated with ethanol and cooled in Dry Ice. Upon warming to room temperature the oil solidified. This solid (0.17 g., m.p. 136–142°) was recrystallized twice from ethanol to give white crystals of 1,4-bis[α-acetoxybenzyl]benzene (II), m.p. 145–146.5°, lit.[10] m.p. 143–144°. The mother liquors from all crystallizations were combined and concentrated to give an oil which slowly solidified on standing. Total solid obtained was 0.285 g. (15.2%), based on dihydrazone).

Thermal decomposition of I *in toluene.* The bisdiazo compound, I (3.04 g., 98.2%), prepared from 3.14 g. (10 mmoles) of 1,4-dibenzoylbenzene dihydrazone, was dissolved in a minimum amount of toluene and this solution was added dropwise to *ca.* 30 ml. of refluxing toluene. The reaction was carried out in a nitrogen atmosphere and the toluene had been refluxing under nitrogen for 0.5 hr. before addition was started. The purple color of I was discharged slowly. The toluene was distilled off through a fractionating column at atmospheric pressure. The residue was a thick, viscous, yellow oil which was fluorescent in ultraviolet light. A portion (500 mg.) of this oil was chromatographed on a column of *ca.* 65 g. of Woelm, activity grade I, neutral alumina. Elution of the column with carbon tetrachloride gave 70 mg. of a white solid which was sublimed to white plates, m.p. 50.5–52.5° (mixed m.p. 50.5–51.5°). The infrared spectrum of this material was identical to that of authentic dibenzyl. Elution of the column with benzene–carbon tetrachloride (40:60) gave a colorless oil (180 mg.) which had a bluish fluorescence in ultraviolet light. Finally elution of the column with chloroform-benzene (30:70) gave a yellow oil (230 mg.). Attempts to crystallize the colorless and yellow oils failed. These oils appear to be polymeric in nature.

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[CONTRIBUTION FROM THE ORGANIC BASIC RESEARCH LABORATORY, DOW CHEMICAL CO.]

The Cracking and Rearrangement of Diallyl Ketals to α-Allyl Ketones

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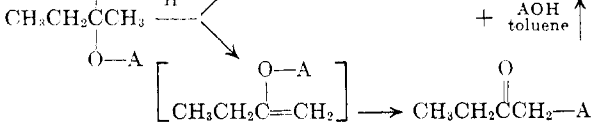
Several diallyl ketals were cracked in the presence of acid and rearranged to *alpha* allyl-substituted ketones in high yields. The use of 2,2-dimethoxypropane made possible the preparation of *alpha* allyl-substituted ketones from ketones and allyl alcohol without isolation of the intermediate diallyl ketals.

The cracking of acetone diallyl ketal to allyl isopropenyl ether and the subsequent quantitative Claisen rearrangement of the ether to 5-hexen-2-one (allylacetone) was reported by Hurd and Pollack[1] in 1938. No reference was found on the use of this procedure for the preparation of other ketones substituted with allyl groups at the *alpha* carbon atoms.

By a modification of the procedure of Hurd and Pollack we have obtained excellent yields of several *alpha* allyl-substituted ketones by the cracking and rearrangement of the corresponding diallyl ketals. The diallyl ketals are easily prepared[2] by alcohol and ketone interchange reactions with 2,2-dimethoxypropane which is commercially available.[3]

The reaction may be illustrated (Equation 1) by the preparation of 3-methyl-5-hexen-2-one and 6-hepten-3-one from 2-butanone diallyl ketal. The



A = $CH_2{=}CH{-}CH_2{-}$ (1)

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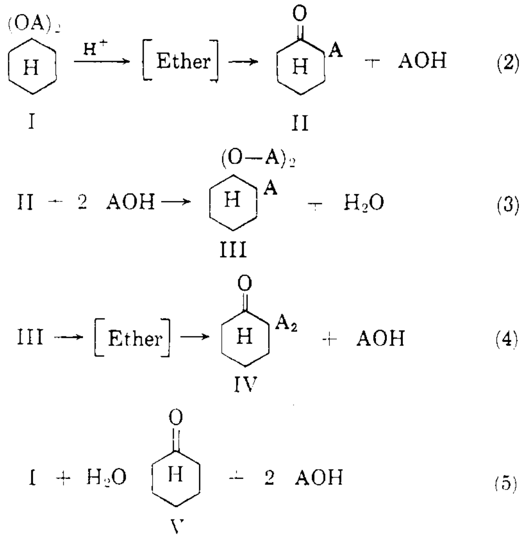
[1] C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1909 (1938).

[2] N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960).

[3] The Dow Chemical Co.

ketals were heated in acidified toluene solution and the allyl alcohol produced was removed continuously as its azeotrope with toluene by distillation at atmospheric pressure. The use of a solvent also minimized the acid catalyzed polymerization of the intermediate unsaturated ether. Yields of allyl-substituted ketones were above 90% with all of the ketals examined, except acetone diallyl ketal. With ketals of unsymmetrical ketones about ten times as much allylation occurred at the more substituted of the two *alpha* carbon atoms.

If the allyl alcohol is not removed from the reaction mixture as it is formed, other reactions occur which complicate the system, illustrated in Equations 2–5 with cyclohexanone diallyl ketal. The main products were II, IV, and V.



A = CH_2=CH—CH_2—

The allyl-substituted ketones are also conveniently prepared from ketones and allyl alcohol in a single reaction mixture. Conditions are chosen to prepare the diallyl ketal from the ketone to be allylated, allyl alcohol, and 2,2-dimethoxypropane according to the procedure of our previous paper.[2] After the acetone and methanol have been distilled, the distillation is continued until allyl alcohol no longer passes over. Further distillation then gives the α-allyl ketone. Some 5-hexen-2-one is usually obtained from acetone diallyl ketal which is formed by exchange of allyl for methyl groups in the 2,2-dimethoxypropane.

Mono- and diallylated ketones may be further allylated in this manner by repeating the process. However, increased substitution of the ketone in the *alpha* positions results in reduced reactivity in formation of diallyl ketals. Although yields based on unrecovered starting material were generally high in this further allylation, conversions of mono- and disubstituted ketones decreased with the amount of substitution, and the simultaneous reaction of the acetone diallyl ketal also present resulted in greater production of 5-hexen-2-one.

Hurd and Pollack obtained only a small amount of allylacetone from acetone diallyl ketal,[1] but, if the reaction is conducted in a mixture of benzene and decalin, allylacetone is obtained in over-all yields of about 90%. The benzene removes the by-product allyl alcohol as an azeotrope boiling well below allyl isopropenyl ether, while the decalin serves to provide a higher reaction temperature in the distillation flask for the rearrangement of the ether.

Certain ketones are known to react with alcohols to establish an equilibrium in which considerable amounts of ketal are present.[4] We have found that cyclohexanone and allyl alcohol belong to this group. By slowly distilling an acidified mixture of cyclohexanone, benzene, and large excess of allyl alcohol, we obtained 2-allylcyclohexanone and 2,2-diallylcyclohexanone in small yield. The remainder of the product consisted of a mixture of substances of higher boiling points which was not further examined. Brannock has successfully allylated aldehydes by a similar process.[5] With ketones this procedure is probably limited to those which will yield considerable amounts of the corresponding diallyl ketal in equilibrium with the ketone and allyl alcohol. For example, it failed when an acidified solution of acetone and allyl alcohol was refluxed for ninety-one hours; neither acetone diallyl ketal nor 5-hexen-2-one could be detected by gas chromatography. Under different conditions, however, 5-hexen-2-one can be obtained directly from acetone and allyl alcohol. Other ketones react similarly. These reactions will be presented in a forthcoming paper.

In one experiment the intermediate allyl enyl ether was isolated and characterized, providing evidence in addition to that of Hurd and Pollack[1] that the conversion of diallyl ketals to allyl-substituted ketones by this method proceeds through the ether. The ether will rearrange with or without acid. The carbonium ion resulting from protonation of the double bond of the enyl ether may also be an intermediate in a simultaneously occurring process, but no evidence has been obtained to establish this point.

EXPERIMENTAL

Ketals. The preparation and properties of the diallyl ketals used in this work are described in a previous paper,[2] with the exception of 5-hexen-2-one diallyl ketal which was prepared from 5-hexen-2-one, allyl alcohol, and 2,2-dimethoxypropane in a similar manner and had the following physical properties: b.p. 89° (10 mm.), n_D^{24} 1.4452, d_{24} 0.882 g./ml.

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(4) In view of the work of D. G. Kubler and L. E. Sweeney, *J. Org. Chem.*, **25**, 1437 (1960), and unpublished work of our own which fully corroborate their results, the work of O. H .Wheeler, *J. Am. Chem. Soc.*, **79**, 4191 (1957), may be interpreted as demonstrating the presence of ketals instead of hemiketals.

TABLE I

α-ALLYL KETONES FROM KETONE DIALLYL KETALS

Ketone	α-Allyl Ketone	Yield, %	B.P.	Mm.	n_D^{25}	d^{25} G./Ml.
Butanone	3-Methyl-5-hexen-2-one[a]	79 (6)[b]	79 136	100 760	1.4217	0.835
Butanone	5-Hepten-3-one[c]	4 (5)	86	100	1.4230	0.838
3-Pentanone	4-Methyl-6-hepten-3-one[d]	91	95	104	1.4246	0.832
5-Hexen-2-one	3-Allyl-5-hexen-2-one[e]	86	71	17	1.4447	0.858
5-Hexen-2-one	1,8-Nonadien-5-one[f]	6.4	81	17	1.4462	0.860
Cyclopentanone	2-Allylcyclopentanone[g]	93	62	10	1.4579	0.926
Cyclohexanone	2-Allylcyclohexanone[h]	98	91	18	1.4666	

[a] Lit.[6] b.p. 135° (760). [b] Figures in parentheses represent additional amounts not isolated but shown by gas chromatography to be present in intermediate fractions or distillation residues. [c] *Anal.* Calcd. for $C_7H_{12}O$: C, 74.94; H, 10.79. Found: C, 75.17; H, 10.73. [d] Lit.[7] b.p. 153–156° (atm.). [e] Lit.[8] n_D^{25} 1.4448. [f] *Anal.* Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.81; H, 10.15. [g] *Anal.* Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.31; H, 9.89. [h] Lit.[9] n_D^{25} 1.4672.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.46; H, 10.28. Found: C, 73.41; H, 10.10.

Pyrolysis and rearrangement of diallyl ketals in toluene. The diallyl ketal of the selected ketone is dissolved in toluene, and *p*-toluenesulfonic or phosphoric acid is added so that the acid concentration is 0.2–0.5 g./l. The volume of toluene taken is about twice that of the allyl alcohol calculated to result from the reaction, based on 1 mole per mole of ketal. This amount provides sufficient toluene to form the azeotrope, which is about 50% allyl alcohol by volume, while leaving an excess which minimizes discoloration of the reaction mixture and formation of by-products. The mixture is then distilled through a fractionating column at atmospheric pressure and the azeotrope of toluene and allyl alcohol is collected at about 92°. When the temperature rises above that of the azeotrope, the acid in the reaction mixture may be neutralized although this is not always necessary. Distillation is continued at reduced pressure to remove excess toluene after which the products are collected. The results are given in Table I.

With ketals of unsymmetrical ketones, the two *alpha* carbon atoms are not equivalent and two products are obtained. The structures of these products were assigned on the basis of the infrared spectra of pure samples (gas chromatography). The criterion for identification was the presence or absence of absorption at 7.4 mμ because of the methylcarbonyl group.

Acid-catalyzed pyrolysis of cyclohexanone diallyl ketal without solvent. One mole of cyclohexanone diallyl ketal (196 g.) was acidified with 0.1 g. of *p*-toluenesulfonic acid. The reaction solution was heated under reduced pressure (60 mm.), and volatile material was distilled through a fractionating column. In about 1 hr. 57 g. (0.98 mole) of allyl alcohol was obtained at 40°. After cooling the reaction solution and neutralizing the acid with potassium carbonate, the distillation was resumed, giving 49 g. of allyl 1-cyclohexen-1-yl ether, b.p. 75–78° (16 mm.), n_D^{24} 1.4727, d_{24} 0.920 g./ml. On continued distillation, 58 g. of 2-allylcyclohexanone (n_D^{24} 1.4669) was collected at 89° (16 mm.), and the 29 g. of residue (n_D^{24} 1.4688) was slightly impure 2-allylcyclohexanone (vapor phase chromatography and infrared).

The allyl cyclohexenyl ether was characterized as follows. Its infrared spectrum was consistent with the structure assigned and showed that it was 95% pure with about 3% of 2-allylcyclohexanone. Gas chromatography corroborated this analysis. Taking 138 for the molecular weight and using measured density and refractive index, the molar refraction found is 42.1, calcd. from bond refractions 42.5. Addition of the stoichiometric amount of allyl alcohol and a trace of acid gave a quantitative yield of cyclohexanone diallyl ketal. Hydrolysis gave allyl alcohol and cyclohexanone.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.11; H, 10.29.

Two samples of the allyl cyclohexenyl ether, one with a trace of *p*-toluenesulfonic acid, were heated overnight in the steam bath in sealed tubes. Both samples were converted quantitatively to 2-allylcyclohexanone. The pyrolysis of the ketal and subsequent rearrangement of the ether thus result in a 98% yield of 2-allylcyclohexanone.

Acid-catalyzed pyrolysis of cyclohexanone diallyl ketal without removal of the allyl alcohol. Fifty milliliters of cyclohexanone diallyl ketal acidified with 50 mg. of *p*-toluenesulfonic acid was heated under reflux for 5 hr. The temperature of the refluxing liquid fell from 131° to a constant value of 115°. The solution was then cooled and analyzed by gas chromatography. Allyl alcohol, 2-allylcyclohexanone, 2,2-diallylcyclohexanone, and cyclohexanone accounted for more than 95% of the sample. The three ketones were present in approximate mole ratio of 2:1:1, respectively. No cyclohexanone diallyl ketal remained.

Cracking and rearrangement of acetone diallyl ketal in benzene and decalin. A solution composed of 1.0 gram-mole of acetone diallyl ketal, 0.2 g. of *p*-toluenesulfonic acid, 350 ml. of benzene, and 325 ml. of *cis*-decalin was fractionally distilled at atmospheric pressure. After 10 hr. the calculated amount of allyl alcohol had been removed as its azeotrope with benzene and the temperature in the distillation flask had reached 155°. By vapor chromatography the residue was shown to contain 0.91 mole of 5-hexen-2-one. Further distillation under reduced pressure gave 0.87 mole of 5-hexen-2-one, b.p. 55° (50 mm.), n_D^{24} 1.4182, d_{24} 0.838 g./ml. (lit.[10] n_D^{20} 1.4200).

Allylation of ketones with allyl alcohol in the presence of 2,2-dimethoxypropane. A solution composed of 2.0 gram-moles of cyclohexanone, 4.4 moles of allyl alcohol, 2.2 moles of 2,2-dimethoxypropane, 0.2 g. of *p*-toluenesulfonic acid, and 1 l. of benzene was distilled through a 3-ft., vacuum-jacketed column packed with glass helices and operated at a reflux ratio of 10. After 475 ml. of distillate (benzene, methanol, acetone) had been collected at 55–60°, the distillation was continued with a reflux ratio of 3 until the distillation flask temperature reached 190°, at which time the overhead temperature was 95°. Distillation of the clear, yellow residue was then continued at reduced pressure and gave 2-allylcyclohexanone in 85% yield (1.70 moles) and 2,2-diallyl-

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(5) K. C. Brannock, *J. Am. Chem. Soc.*, **81**, 3379 (1959).

(6) J. Colonge and G. Clerc, *Bull. soc. chim. France*, 836 (1955).

(7) A. C. Cope, K. E. Hoyle, and D. Heyl, *J. Am. Chem. Soc.*, **63**, 1850 (1941).

(8) R. B. Davis and P. Hurd, *J. Am. Chem. Soc.*, **77**, 3284 (1955).

(9) P. Anziani, A. Aubry, G. Barrand, M. M. Claudon, and R. Cornubert, *Bull. soc. chim. France*, 408 (1955).

(10) L. Stein and G. Murphy, *J. Am. Chem. Soc.*, **74**, 1041 (1952).

cyclohexanone[11] in 7.8% yield (0.156 mole), b.p. 119° (14 mm.), n_D^{25} 1.4840, d_{25} 0.937 g./ml., (lit.[12] b.p. 116–118° (14 mm.), n_D^{14} 1.4887).

This procedure was repeated with several other ketones using the same molar amounts of reactants, solvent, and acid in the same apparatus, and as nearly as possible under the same conditions. Final temperatures in the distillation flask were 175° to 195°. The products were then distilled at reduced pressure. Some 5-hexen-2-one was formed in each experiment except with cyclohexanone. The results are given in Table II. Physical properties of some of the compounds in Table II are given in Table III.

TABLE II

ALLYLATION OF KETONES USING 2,2-DIMETHOXYPROPANE

Starting Ketone	Conversion, %	Major Product	Yield, %[a]	5-Hexen-2-one, Moles
2-Allylcyclohexanone	59	2,2-Diallylcyclohexanone	97	0.86
2,2-Diallylcyclohexanone	23	2,2,6-Triallylcyclohexanone(I)	85	1.3
2-Propylcyclohexanone[b](II)	59	2-Allyl-2-propylcyclohexanone (III)	95	0.64
Cyclopentanone	67	2-Allylcyclopentanone	95	0.47
2-Allylcyclopentanone	35	2,2-Diallylcyclopentanone(IV)	93	1.0
2,2-Diallylcyclopentanone	12	2,2,5-Triallylcyclopentanone (V)	56	1.2
Acetophenone	41	1-Phenyl-4-penten-1-one(VI)	84	0.46

[a] Based on conversion. [b] Prepared by catalytic hydrogenation of 2-allylcyclohexanone.

Allylation of cyclohexanone by allyl alcohol without added ketal. Two moles (196 g.) of cyclohexanone, 2 moles (116 g.) of allyl alcohol, 1.5 g. of *p*-toluenesulfonic acid, and 200 ml. of benzene were combined and refluxed with a water trap in the condensate stream. After 7 days the rate of water production had become negligible, so the reaction solution was made basic by the addition of 1.0 g. of sodium hydroxide dissolved in 25 ml. of methanol. The solution was extracted with water, dried with potassium carbonate, and distilled under reduced pressure, giving 22 g. (8% yield) of 2-allylcyclohexanone, 14 g. of an intermediate fraction which was a mixture of 2-allylcyclohexanone and 2,2-diallylcyclohexanone, and 47 g. (13% yield) of 2,2-diallylcyclohexanone, b.p. 119° (14 mm.). The thick, high-boiling residue was not further examined, but was probably ketone condensation products.

In another experiment 1.0 gram-mole of cyclohexanone, 3.0 moles of allyl alcohol, 400 ml. of benzene, and 0.05 g. of *p*-toluenesulfonic acid were boiled together under a pressure of 120 mm. with a water trap in the reflux stream. After 16 hr. production of water had become very slow, so the reaction was stopped. Analysis of the reaction solution by infrared spectroscopy showed the presence of 0.44 mole of cyclohexanone diallyl ketal and 0.53 mole of cyclohexanone unchanged. Pyrolysis of the ketal by one of the foregoing methods would thus result in production of 2-allylcyclohexanone in over-all yield of 40 to 45%, or about 90% based on unrecovered cyclohexanone.

Acknowledgment. The authors are grateful to J. H. Brown, Jr., and L. F. Hatch for their advice and help, and to H. L. Spell for interpretation of the infrared spectrograms.

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TABLE III

PHYSICAL PROPERTIES OF SUBSTITUTED KETONES

Ketone[a]	B.P.,	P, Mm.	n_D^{25}	d_{25}, G./Ml.	C Calcd.	C Found	H Calcd.	H Found
I	98	1–2	1.4903	0.929	82.51	82.49	10.16	10.19
II[b]	78	10	1.4508	0.904				
III[11]	106	8	1.4716	0.917	79.94	80.15	11.18	11.20
IV[11]	104	18	1.4762	0.925	80.44	80.31	9.82	9.65
V	95	3	1.4817	0.919	82.30	82.23	9.87	9.81
VI[c]	126	16	1.5300	0.991				

[a] See Table II for names of ketones. [b] Lit.[13] b.p. 83–84° (13 mm.), n_D^{13} 1.4558, d_4^{13} 0.9145. [c] Lit.[14] b.p. 125–127° (16 mm.).

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(11) The 2,2-dialkyl derivatives of cyclohexanone and cyclopentanone were shown by vapor chromatography to contain 1 to 7% of the isomeric 2,6-dialkyl and 2,5-dialkyl derivatives, respectively.

(12) J. M. Conia, *Bull. soc. chim. France*, 537 (1950).

(13) G. Vavon and P. Anziani, *Bull. soc. chim.*, **41**, 1638 (1927).

(14) J. M. Conia, *Ann. chim. (Paris)*, **8**, 709 (1953).