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.

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.

[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.

(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).

Experimental

The following five compounds were prepared, and their absorption spectra determined: 2-benzal-3-methylcyclohexanone, inactive (I) and optically active (II), 2,6-dibenzal-3-methylcyclohexanone (III), 2,5-dibenzalcyclopentanone (IV), and 3-methyl-2-hydroxy-Δ^2-cyclohexenone (V).

Optically active methylcyclohexanone-3 was first prepared from active pulegone by the method of Rupe and Glenz.[7] Using the resulting active ketone for II, and inactive 3-methylcyclohexanone for I and III, the method of Wallach[8] was followed in the preparation of all three compounds. I melts at 60°[9] while the corresponding optically active II melts at 43°.[10] This large difference in melting point led us to prepare both in order to compare their absorption spectra, which proved to be identical, as was to be expected. The method of Wallach[8] was used also in the preparation of IV from cyclopentanone. More difficulty
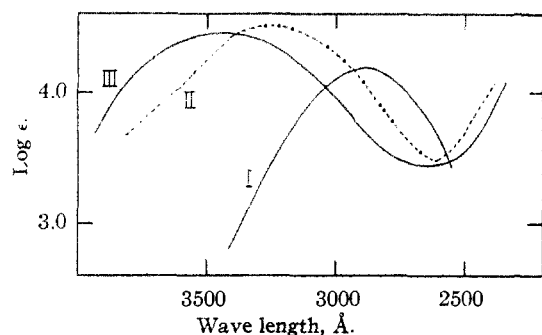

Fig. 1.—Absorption spectra of 2-benzal-3-methyl-cyclohexanone (I); 2,6-dibenzal-3-methyl-cyclohexanone (II); 2,5-dibenzal-cyclopentanone (III).
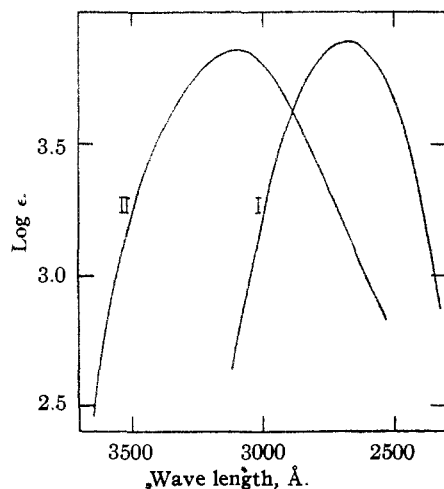

Fig. 2.—Absorption spectrum of 3-methyl-2-hydroxy-Δ^2-cyclohexanone (I) in ethyl alcohol; (II) in 0.1 N sodium hydroxide.

(7) Rupe and Glenz, *Ann.*, **436**, 203 (1924).

(8) Wallach, *Ber.*, **29**, 1596 (1896).

(9) Tetry, *Bull. soc. chim.*, [3] **27**, 304 (1902).

(10) Cornubert and Humeau. *ibid.*, **49**, 1485 (1931).

was experienced in the preparation of V. Wallach's[11] method was modified by using half as much bromine, the quantity indicated by his earlier method.[12] It should be mentioned, as a warning to future workers, that the fumes from the intermediate dibromomethylcyclohexanone cause painful burns on the backs of the hands, even when rubber gloves are worn for protection.

All five compounds were carefully purified by repeated recrystallizations from the appropriate solvents, until their melting points were sharply as recorded in the literature.

The absorption spectra were determined in absolute alcohol solutions, by the methods previously reported from this Laboratory.[13]

For further study of V, its absorption spectrum was determined also in water and in tenth normal sodium hydroxide.

The results are recorded in Figs. 1 and 2.

Discussion

Table I assembles the data for the absorption maxima of the compounds shown in the curves.

TABLE I

Compound	Solvent	λ_{max}, Å.	log ϵ
2-Benzal-3-methyl-cyclohexanone (inactive)	Alcohol	2880	4.20
2-Benzal-3-methyl-cyclohexanone (active)	Alcohol	2890	4.20
2,6-Dibenzal-3-methyl-cyclohexanone	Alcohol	3280	4.54
2,5-Dibenzal-cyclopentanone	Alcohol	3440	4.44
3-Methyl-2-hydroxy-Δ^2-cyclohexenone	Alcohol	2685	3.88
3-Methyl-2-hydroxy-Δ^2-cyclohexenone	Water	2690	3.88
3-Methyl-2-hydroxy-Δ^2-cyclohexenone	NaOH (0.1 N)	3120	3.86

It should first be noted that the optically active and optically inactive forms of 2-benzal-3-methyl-cyclohexanone show identical absorption within the limits of experimental error. (The curve for the inactive compound is not shown in Fig. 1, since it follows almost exactly that for the active compound, but the position of its maximum is included in Table I.) This identity in absorption indicates that the electronic configurations must be energetically the same in the racemic compound as in the optically active compound.

Our first problem, then, is concerned with the effect of the benzal group. All three benzal compounds are α,β-unsaturated ketones with exocyclic ethylene bonds and with the conjugated system extended by means of the resonance of the benzene ring. The work of Woodward[4b] and of Gillam[5,6] has shown that saturated substituents on the doubly-bound carbon atoms may shift the high-intensity absorption band of α,β-unsaturated ketones to 2520 Å. The effect of the ex-

(11) Wallach, *Ann.*, **437**, 172 (1924).

(12) Wallach, *ibid.*, **414**, 318 (1918).

(13) French and Gens. THIS JOURNAL, **59**, 2600 (1937).

tended conjugation in our mono-benzal compound is the shifting of this band still farther toward the red, to 2880 Å.

A similar effect in the much simpler benzalacetone has been shown by Lowry, Moreu and Mac-Coulsey[14] and more recently in benzalacetophenone by Cromwell and Johnson.[15]

The α,α'-dibenzal compound in the six-membered ring (2,6-dibenzal-3-methylcyclohexanone) has its absorption maximum shifted an additional 400 Å. toward the red, and the intensity slightly increased again to log ϵ = 4.54.

It is interesting in this connection to note that Ruzicka[16] and co-workers have shown the absorption maximum for a compound with one double bond on each side of the cyclic carbonyl group to be at the usual wave length for a simple α,β-unsaturated ketone, namely, $\Delta^{1,4}$-cholestadienone-3, absorbing at 2380 Å. with log ϵ = 4.55. When a longer conjugation is introduced, however, on one side of the carbonyl group as in $\Delta^{4,6}$-androstadiendione-3,17 the absorption maximum shifts to 2840 Å. with log ϵ = 4.7.

Since the absorption of no other dibenzal derivatives of cyclic ketones have been recorded in the literature, so far as we have been able to discover, we have studied for comparison the corresponding compound in the cyclopentane series.

The α,α-dibenzal compound in the five-membered ring (2,5-dibenzalcyclopentanone) has its absorption maximum shifted 160 Å. further toward the red, with approximately no change in intensity. More work is planned in this Laboratory on closely related derivatives of cyclopentanone and cyclohexanone before any conclusions are drawn concerning what seems to be a considerably greater strain in the five-atom-ring than in the six-atom-ring upon the introduction of two benzal groups.

As our second problem, the question of the structure of the potential α-diketone remains to be solved from the evidence of its absorption spectrum. The fact that all solutions are colorless, giving no selective absorption in the visible region, tends to eliminate the diketone structure and immediately to differentiate this compound from the less easily enolizable camphorquinone.[2] The two possible enols would be


I   II
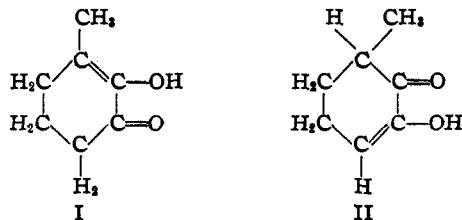
The intensity of the ultraviolet absorption band remains constant, within the limits of experimen-

tal error, in all three solvents, at log ϵ = 3.88. In water and alcohol the wave length of maximum absorption is essentially the same, 2685 Å. The case for the hydroxyl group as a substituent on the ethylene bond has never been fully presented. Gillam and co-workers[5,6] have done the most systematic work on it: when diosphenol is formed from piperitone, thereby changing a cyclic
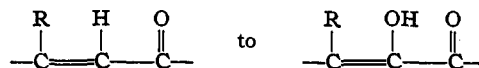
the absorption maximum is shifted from 2355 to 2740 Å. Several other similar cases are cited by Gillam.[17] In these, the absorption maxima of the hydroxyl substituted α,β-unsaturated diketones fall between 2640 and 2745 Å. Woodward[18] records the absorption maximum of a five-membered ring enolized β-diketone with the chromophore
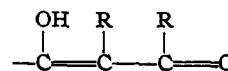
as at 2550 Å. Using Gillam and West's[6] generalization that a decrement of −110 Å. must be used when passing from a six-atom-ring compound to a corresponding five-atom-ring compound, this value becomes 2660 Å. for a corresponding six-atom-ring compound.

In general, then, it may be said that monoenols or hydroxyl-substituted α,β-unsaturated six-atom-ring ketones show an intense absorption maximum at 2700 ± 50 Å. Our compound in neutral solution is thus shown by spectrographic evidence to be represented correctly by either Formula I or Formula II.

In basic solution there is a further shift of 430 Å. toward the visible with no significant change in intensity. Stiller and Rosenheim[19] in studying the two enolic forms of cholestane-2,3-dione also observed that the wave length of maximum absorption was 480 Å. nearer the red in basic solution than in alcohol with very little change in intensity. Corresponding to this shift the number of resonance forms contributing to the actual structure must be increased. This may take place in one of two ways, either by the formation of the sodium salt of the mono-enol (ionized), or by the enolization of the second keto group in the molecule (ionized di-enol). The un-ionized monoenol (which we have proved exists in neutral solution) has three resonance forms, the ionized sodium enolate, five, and the ionized sodium dienolate, seven. To decide between these two possibilities, a comparison with camphorquinone was undertaken, since this compound has only one enolizable ketone group. Camphorquinone in neutral solution is obviously entirely in the diketo form, with a band at λ = 4650 Å., log ϵ =

(14) Lowry, Moreu and MacCoulsey, J. Chem. Soc., 3171 (1928).

(15) Cromwell and Johnson, THIS JOURNAL, 65, 316 (1943).

(16) Ruzicka, Cohen, Furter and van der Sluys-Veer, Helv. Chim. Acta, 21, 1735 (1938).

(17) Heywood and Kon, J. Chem. Soc., 713 (1940); Heilbron, Jones and Spring, ibid., 801 (1937).

(18) Woodward and Blout, THIS JOURNAL, 65, 562 (1943).

(19) Stiller and Rosenheim, J. Chem. Soc., 354 (1938).

1.57.[2] In alkaline solution[20] this band is still present, with intensity lowered to log ϵ = 1.17, while a new band appears at about λ = 3175 Å., log ϵ = 1.79. The band for our 3-methyl-2-hydroxy-Δ^2-cyclohexenone in alkaline solution is at 3120 Å., log ϵ = 3.88, and the ketone band is masked. Apparently the camphorquinone is only partially enolized. In fact, it is only about 1% enolized, as indicated by the ratio of intensities of the two bands. More accurately controlled conditions of solvent may permit a more accurate determination of the percentage of enolization, and we intend to pursue this investigation in this Laboratory. The similarity of position of the new band in the camphorquinone (which is incapable of forming a di-enol) with the band in a basic solution of our compound, we consider an indication of like chromophoric

groups in the two substances, and evidence that even in basic solution the mono-enol and not the di-enol is present.

Summary

New absorption spectra are presented for the α,β-unsaturated cyclic ketones, 2-benzal-3-methylcyclohexanone, inactive and optically active, 2,6-dibenzal-3-methylcyclohexanone, 2,5-dibenzalcyclopentanone, and 3-methyl-2-hydroxy-Δ^2-cyclohexenone.

Woodward's and Gillam's generalizations are noted, and a possible extension suggested to include the influence of hydroxyl substitution at the ethylene double bond.

Absorption spectra data are used as evidence for the structure of 3-methyl-2-hydroxy-Δ^2-cyclohexenone.

(20) French and Holden, unpublished data.

Adsorption–Desorption Isotherm Studies of Catalysts. I. Supported Catalysts in the Powder and Pellet Forms

BY HERMAN E. RIES, JR., ROBERT A. VAN NORDSTRAND, MARVIN F. L. JOHNSON AND HERMAN O. BAUERMEISTER

The pore structure characteristics of catalysts in the powder and pellet forms are of considerable importance in the study of catalytic processes. Hysteresis effects observed in adsorption–desorption isotherm experiments are related to the pore structure of the adsorbent.[1,2,3] Although there exists at present no well-established theory to account for hysteresis phenomena, sound experimental relationships may point the way to a better understanding of adsorption and desorption as related to surface forces and pore structure.

Interesting similarities have been observed in the adsorption–desorption hysteresis effects obtained with two catalysts both in the pellet and powder forms. The two catalysts, H-A and H-G, are supported catalysts similar in chemical composition. They have widely different surface areas, 120 and 225 sq. m. per g., respectively, as calculated by the Brunauer, Emmett and Teller method.[4] Both catalysts are studied in the form of 0.125-inch pellets (P) and in the form of ground pellet (GP) material (100-mesh). A sample of the unpelleted (UP) powder used in preparing H-G pellets is also studied. When time permits, this investigation will be extended to include the support, the unsupported catalyst and related materials of interest.

Experimental

The apparatus and methods employed are essentially the same as described by Emmett and Brunauer.[5,6] A brief description and a photograph of the adsorption apparatus in use in these laboratories have been previously presented.[7] Several modifications of the experimental procedure have subsequently been introduced. These apply to the studies reported in this paper with the exception of Experiments 56 and 103.

A vapor pressure thermometer using nitrogen replaces the oxygen vapor pressure thermometer formerly used. Errors in reading the saturation pressure, p_0, are thus reduced threefold. The nitrogen and helium used in these experiments are obtained from the Ohio Chemical Company. The nitrogen, of 99.8% purity, is further purified by means of copper gauze at 500°, a drying tube of phosphorus pentoxide, and a Dry Ice–acetone trap. The helium now used for the dead space measurements at liquid nitrogen temperatures is 99.9% pure and is obtained in special Pyrex flasks.

All isotherm experiments are performed at liquid nitrogen temperatures ($-195°$) with nitrogen as the adsorbate. Adsorption equilibrium is reached in time intervals varying from ten

(1) Emmett and De Witt, THIS JOURNAL, 65, 1253 (1943).

(2) Cohan, ibid., 60, 433 (1938); 66, 98 (1944).

(3) Brunauer, "The Adsorption of Gases and Vapors," Vol. I, Princeton University Press, Princeton, New Jersey, 1943.

(4) Brunauer, Emmett and Teller, THIS JOURNAL, 60, 309 (1938).

(5) Emmett, "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942.

(6) Emmett and Brunauer, THIS JOURNAL, 59, 310 (1937).

(7) Ries, Van Nordstrand and Teter, Ind. Eng. Chem., 37, 310 (1945).