[Contribution from the College of Pharmacy and the Spectrographic Laboratory of the University of California, San Francisco]

The Ultraviolet Absorption Spectra of α-Phenylcarbonyl Compounds. II[1]

By Edward L. Alpen,[2] W. D. Kumler and L. A. Strait

In Part I of this series[3] we have considered the ultraviolet absorption spectra of some α-phenylcarbonyl compounds, pointing out that a band at 295 mμ with a molecular extinction of more than tenfold that of a simple aliphatic carbonyl compound is characteristic of the α-phenylcarbonyl grouping. We have further extended these studies and are reporting them here.

Results

The spectra of 1,1-diphenylbutanone-2 and 1,3-diphenylpropanone-2 (Fig. 1) are very similar in the longer wave length region, both having the 295 mμ band with a molecular extinction of 200–250. There is a difference in the intensity of the phenyl band as might be expected considering the nature of the phenyl placement in the two compounds. It is noteworthy that the intensity of the 295 mμ band in these two compounds is about half that found in 3,3-diphenylbutanone-2.[3] The fine structure of these three α-diphenyl ketones has all the major inflections at almost identical wave lengths, and in addition the detail is qualitatively similar to that found in the 295 mμ band of the monophenyl ketones. The spectra of 1,3-diphenylpropanone-2 has been previously reported[4,5] but the curves have insufficient resolution and accuracy at the shorter wave lengths.

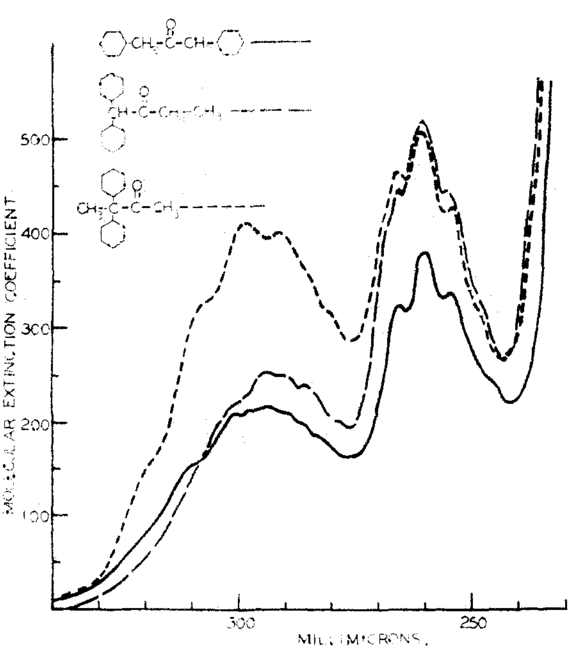

Fig. 1.

1-Mesitylpropanone-2 has been previously prepared by several workers[6] but its ultraviolet absorption spectrum has never been reported. The sample prepared by us shows the same phenylcarbonyl interaction that is found in the unsubstituted phenyl series. A band (Fig. 2) is present, $\lambda_{max.}$ 295 mμ, $\epsilon_{max.}$ 120, which may be considered to be analogous to the same band found in the compounds previously discussed. The 295 mμ band is distorted and lifted at shorter wave lengths by the presence of the band $\lambda_{max.}$ 270 mμ. This shorter wave length band is attributable to the mesityl grouping, and it is in all respects normal when compared to other compounds containing the mesitylene nucleus.

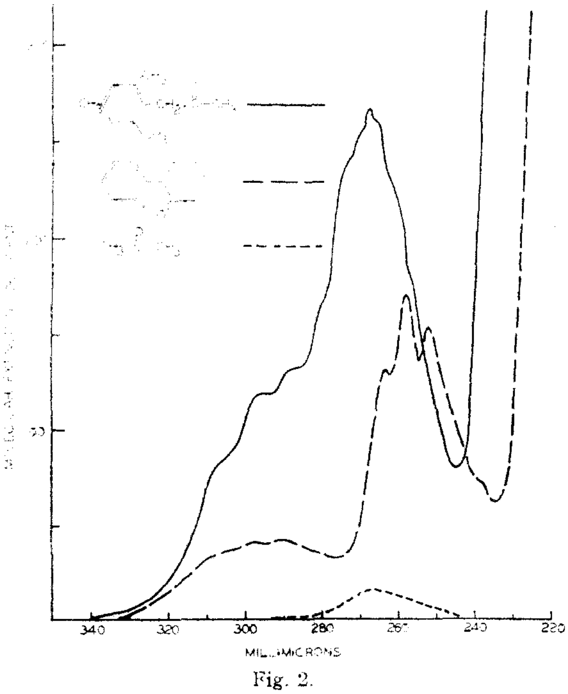

Fig. 2.

Although the details of the α-phenylcarbonyl band are somewhat obscured by the presence of the overlapping mesityl absorption band, the basic pattern of fine structure found in the phenyl ketones still persists.

Some earlier workers have reported the spec-

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[1] An abstract in part of a dissertation submitted by E. L. A. in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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[3] Kumler, *et al.*, This Journal, **72**, 1463 (1950).

[4] Ramart-Lucas and Salmon-Legagneur, *Bull. soc. chim., France*, (4) **51**, 1069 (1932).

[5] Ley and Dirking, *Ber.*, **67**, 1331 (1934).

[6] Fuson, Rabjohn, Shenk and Wallace, *J. Org. Chem.*, **9**, 187 (1944).

trum of desoxybenzoin, the aromatic analog of the α-phenyl ketones,[4,5,7] but the limitations of their methods make remeasurement worthwhile.

By comparison of the curve for desoxybenzoin (Fig. 3) with that of propiophenone, it is evident that there has been an increase in the intensity of the longer wave length band, and, as in other α-phenyl compounds, there arises a series of minor peaks within this longer wave length band. Because we are dealing here with an aromatic rather than a purely aliphatic ketone, we cannot make a direct comparison of the position of these minor peaks, but qualitatively there is a marked similarity in the relationship of these bands to each other on comparing the aliphatic and this aromatic–aliphatic compound.

The difference between the curves of desoxybenzoin and propiophenone at shorter wave lengths are too small to be significant.

The cyclic analog of the α-phenyl ketone was next prepared and studied. The ultraviolet absorption spectrum of 2-phenylcyclohexanone has not been previously reported. In Fig. 2 are presented the data on the absorption of this compound in hexane solution from 220–340 mμ.

Examination of this curve reveals that, although the phenyl bands are present, the 295 mμ band that we found to be characteristic of all other α-phenylcarbonyl compounds we have studied, is of low intensity. It has a $\lambda_{max.}$ 290 mu but its intensity, $\epsilon_{max.}$ 40, is far less than would be predicted if the phenyl interaction were normal.

Discussion

In paper I of this series we discussed the possibility that coumaran type structures formed by interaction of the ortho position of the phenyl group with the ketone oxygen might give rise to the absorption band under consideration. This possibility was excluded on the basis of dipole moment data, but we wished to present more chemical evidence against this structure. For this reason, we prepared the mesityl derivative of acetone and found it to have a normal α-phenylcarbonyl absorption. On this basis we can exclude all forms of the coumaran type.

The 295 mμ band has been explained in the previous paper[3] from the quantum mechanical standpoint as arising from perturbations between the carbonyl and phenyl groups, and in terms of the organic chemist's language as arising from no-bond resonance or hyperconjugation. However, we are not using hyperconjugation in the usual sense, for we are postulating that whole groups can be involved in the no-bond resonance and not just hydrogen atoms. That hyperconjugation in the ordinary sense does not account for the high extinction of the 295 mμ band is indicated by the curves in Fig. 1 where 3,3-diphenylbutanone-2 with no hydrogen available for hyperconjugation has a 295 mμ band with an extinction coefficient about twice that of 1,1-diphenylbutanone-2 with one hydrogen available, and 1,3-diphenylpropanone-2 with four hydrogens available has an even smaller extinction coefficient. The hydrogens on the opposite side of the carbonyl to the phenyl groups are not considered since hyperconjugation forms involving them would not be expected to raise the extinction.

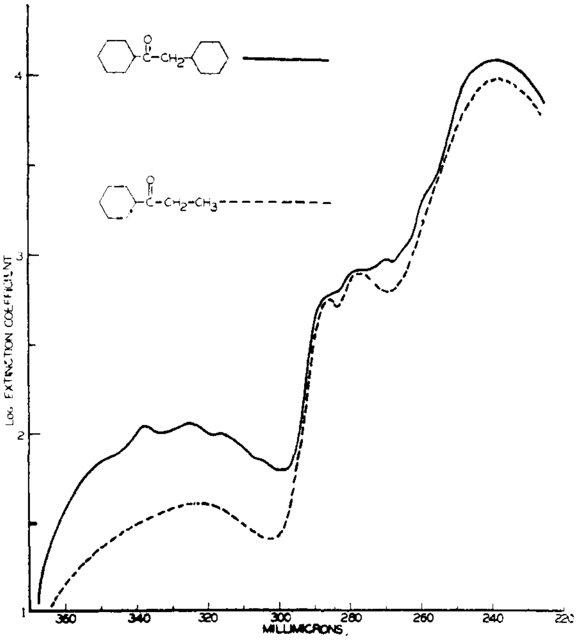

Fig. 3.

The facts can be reconciled if we assume that whole groups can take part in the no-bond resonance and a steric effect operates such that increased hindrance brings about an increased releasing tendency for the no-bond group. Because of the small size of the hydrogen atom its participation in no-bond resonance would not be greatly affected by steric factors. Thus mesitylpropanone with two methyl groups which might interfere sterically has a 295 mμ band with an extinction coefficient comparable to the extinction coefficient of this band in other unsubstituted mono-α-phenylcarbonyl compounds.

The high extinction coefficient of 3,3-diphenylbutanone-2 over that of 1,1-diphenylbutanone-2 and 1,3-diphenylpropanone-2 is attributed to the greater steric hindrance increasing the contribution of no-bond resonance structures in the first compound as compared with the other two compounds.

Insofar as these no-bond resonance forms contribute they would tend to cause the carbonyl group, the α-carbon, and one of the benzene rings to be coplanar. The Fisher–Hirschfelder–Taylor models indicate that the attainment of such a configuration would involve considerable strain but the strain would be less in a compound like 3,3-diphenylbutanone-2 than it would be in the

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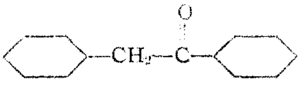
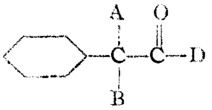
[7] Ramart-Lucas and Guerlain, *Bull. soc. chim. France*, [4] **49**, 1860 (1931).

case of 2-phenylcyclohexanone. In this connection it is interesting that the 295 mμ band in 2-phenylcyclohexanone has a low extinction coefficient of 40 as would be expected if the no-bond resonance structures made almost no contributions in this molecule.

The spectrum of desoxybenzoin



enables one to evaluate roughly the interaction energy between the carbonyl group and the α-phenyl group. In paper I it was pointed out that if we place a group D in the compound



such that D itself is capable of resonance with the carbonyl, then the α-phenylcarbonyl band may disappear because this resonance would be in competition with the no-bond resonance we have assumed is responsible for the high extinction of the 295 mμ band. Phenylacetic acid accordingly does not show a 295 mμ band. Here the resonance between the carbonyl and hydroxyl (carboxyl resonance) is of the order of 28 kcal. and apparently this is large enough to completely exclude the no-bond resonance. In Fig. 3 it is seen that desoxybenzoin has a long wave length band of about 10 times the extinction of the long wave length band in phenyl ethyl ketone. We interpret this as indicating an interaction between the carbonyl and the α-phenyl group and therefore that the no-bond resonance is not excluded by the direct resonance between the carbonyl and the adjacent phenyl group. The energy of the no-bond resonance may therefore be of the order of 3–5 kcal.

An interpretation that is certainly not excluded by the evidence is that the interaction between the carbonyl and the phenyl groups takes place directly through space. This could just as well account for such salient features as the benzenoid character of the fine structure in the 295 mμ band system, the fact that the band in 3,3-diphenylbutanone-2- has a much higher extinction than in 1,1-diphenylbutanone-2, and the absence of the 295 mμ band in the acid amide and ester compounds.

Experimental

The absorption spectra were measured in solution in hexane with a Beckman Quartz Spectrophotometer, Model DU. Solutions were made up in volumetric flasks from weighed quantities of the compounds.

Materials

Hexane.—Eastman Kodak Co. practical grade hexane (from petroleum) b. p. 62–67° was used. Batches were selected that gave transmission values against air of 95% or better.

1,1-Diphenylbutanone-2.—This ketone was prepared by the method of Walton, Ofner and Thorp,[8] using Winthrop-Stearns commercial grade diphenyl acetonitrile; yield 57 g. (65%) of ketone, b. p. 155–157° at 4 mm., from 75 g. of nitrile; $n^{25}\mathrm{D}$ 1.5693. This crude ketone was refluxed for 0.5 hour with 50% sulfuric acid to hydrolyze any unreacted nitrile. Extracted and redistilled, the pure ketone boiled at 157–164° at 4 mm., $n^{25}\mathrm{D}$ 1.5701. Final purification was carried out *via* the semicarbazones as previously described[3]; m. p. of the pure semicarbazone 190–191°; b. p. of pure ketone 158–164° at 4 mm. After recrystallization from petroleum ether it melted at 35–36°.

1,3-Diphenylpropanone-2.—This ketone was prepared by the method outlined by Vogel[9]; 22 g. of ketone was obtained from 75 g. of phenylacetic acid; b. p. 165–167° at 5 mm.; yield 23%. This ketone was purified through the semicarbazone as above (m. p. 119–121°). The purified ketone boiled at 131–132° at 1 mm., m. p. 36–37°. It was possible to recrystallize the crude ketone from a mixture of chloroform and ligroin giving a final m. p. of 36–37°. This product was spectroscopically pure as compared with a sample purified through the semicarbazone; 2,4-dinitrophenylhydrazone m. p. 106–107°.

Desoxybenzoin (α-Phenylacetophenone).—Prepared by the method of "Organic Syntheses," Coll. Vol. II, p. 156, 1943, from 1 mole (136 g.) of phenylacetic acid; yield 130 g., b. p. 145–160° at 5 mm., m. p. 45–46°. This crude product was crystallized once from methanol giving m. p. 52–55°. Because of the difficulty with oiling out, the compound was crystallized once from ligroin. This was followed by two more crystallizations from methanol giving a final product melting 55.5–56°; yield of pure ketone, 24 g.

1-Mesitylpropanone.—Mesitylacetonitrile was prepared by the method of "Organic Syntheses," Vol. 25, 65 (1945). The mesitylacetonitrile was submitted to the Grignard reaction as follows (*cf.* Fuson, *et al.*[6]). The Grignard reagent was formed as usual from 147 g. of methyl iodide and 25.2 g. of magnesium turnings in ether. To the methylmagnesium iodide was added 28 g. of mesitylacetonitrile in 250 ml. of dry xylene. As much ether as possible was distilled off and the mixture refluxed an additional hour. After standing overnight the reaction mixture was poured on 500 g. of ice and 500 ml. of concentrated hydrochloric acid. The water layer was separated and refluxed to hydrolyze the ketimine hydrochloride. The ketone was extracted from the cooled hydrolyzing mixture; 13.8 g., b. p. 130° at 10 mm. was recovered; yield 49.5% of theoretical. The ketone was purified by several crystallizations from ligroin. The melting point of the final product was 59–60° (lit. 60–61°). The semicarbazone gave white needles from alcohol, m. p. 196–197°. The ketone had a characteristic caramel-like odor.

2-Phenylcyclohexanone.—This ketone was prepared by two methods to ensure spectroscopic purity by comparison. The first method was that of Price and Karabinos[10] using Dow Chemical Co. technical (70%) 2-phenylcyclohexanol. This was redistilled through a 30″ Widmer column and the fraction boiling at 146–147° at 12 mm. was collected; yield of ketone on oxidation of the purified 2-phenylcyclohexanol, 29%. The boiling point of the product was 148–152° at 15 mm. Recrystallization three times from petroleum ether gave a final m. p. of 51.5–54°; semicarbazone m. p. 189–190° (lit. 189–190, 193°).

The alternate preparation was that of Newman and Farbman[11] by the Grignard reaction on 2-chlorocyclohexanone; 20 g. of ketone, b. p. 133–136° at 4 mm., m. p. 43–50°, was recovered from 58 g. of 2-chlorocyclohexanone. Two recrystallizations from petroleum ether gave a final product which was pure white, with a citron-like odor and m. p. 59°. The two products were of identical spectroscopic purity.

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[8] Walton, Ofner and Thorp, *J. Chem. Soc.*, 684 (1949).

[9] Vogel, "Practical Organic Chemistry," Longmans, Green & Co., London, 1948, p. 698.

[10] Price and Karabinos, THIS JOURNAL, **62**, 1159 (1940).

[11] Newman and Farbman, *ibid.*, **66**, 1550 (1944).

Summary

The previous study of the ultraviolet absorption spectra of α-phenylcarbonyl compounds has been extended to include 1,1-diphenylbutanone-2, 1,3-diphenylpropanone-2, 1-mesitylpropanone-2, desoxybenzoin and 2-phenylcyclohexanone.

The spectra of these compounds are reported and a long wave length band around 295 mμ of extinction 150–300 has been shown to be common to all except 2-phenylcyclohexanone. The observations are discussed in terms of no-bond resonance, direct action through space and steric hindrance.

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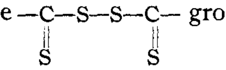
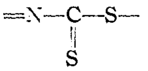
[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

Polarography of the Bis-(diethylthiocarbamyl) Disulfide–Diethyldithiocarbamate Ion Oxidation–Reduction System[1]

BY EARL C. GREGG AND WILLARD P. TYLER

Introduction

Bis-(diethylthiocarbamyl) disulfide is known to the medical profession as a treatment of alcoholism[2] and to the rubber industry as an accelerator of vulcanization. Polarographic reduction of compounds which contain the  $-\underset{\underset{S}{\Vert}}{C}-S-S-\underset{\underset{S}{\Vert}}{C}-$ group has been demonstrated by Proske[3,4,5] and by Kolthoff and Levitan.[6]

Proske made no systematic study of any one of the compounds he investigated, but confined his articles to reporting the feasibility of using the polarograph in the rubber laboratory for analysis for organic accelerators of vulcanization. Proske made one general statement which, prima facie, is not borne out by the evidence presented here, namely, that compounds containing the  $=N-\underset{\underset{S}{\Vert}}{C}-S-$ group are reducible at the d. m. e. at potentials in the vicinity of -0.4 volt *vs.* S.C.E. While this group is oxidizable in that potential region, actually, it does not reduce until the vicinity of -2.1 volts *vs.* S.C.E. is reached.

Experimental

A Sargent Model XX polarograph was used for recording all polarograms. The sensitivity dial settings were calibrated by means of a Shallcross Akra-ohm wire wound resistor of an accuracy $\pm 1/4\%$. Errors up to 6% were found in the current as determined by the sensitivity setting and the equation for converting sensitivity settings to current per millimeter.

A water jacketed cell which was connected to a large area S.C.E. as external anode by means of an agar salt bridge constituted the electrolysis cell system. All polarograms were measured on solutions maintained at 25.00 ± 0.02° by continuously circulating thermostated water through the water jacket by means of a Precision Scientific Company circulating bath. The solutions were deaerated with oil-pumped nitrogen passed through a solvent composition which was the same as that of the solution to be analyzed. All potential settings were measured to the nearest millivolt with a calibrated Beckman laboratory model G *p*H meter used as a potentiometer. All half wave potentials were corrected for *iR* drop. The *p*H measurements were obtained with the glass electrode and the Beckman model G *p*H meter. All *p*H measurements of buffered solutions were taken directly on solutions which were 60% ethanol by volume and were corrected for the water activity.[7]

All solutions were 60% ethanol by volume. The maximum suppressor used was 0.01% gelatin in all cases.

Oxalic acid–sodium oxalate, citric acid–sodium dihydrogen phosphate and ammonia–ammonium chloride buffer systems were used. Neutral solutions were 0.1 *M* lithium chloride.

The capillary tip must be cleaned before recording each polarogram: it was immersed in concd. nitric acid and rinsed with distilled water, immersed in ethanol and wiped dry, immersed in concd. nitric acid, rinsed and wiped dry.

In order to produce consistent polarograms of diethyldithiocarbamate ion, hydrolysis and air oxidation must be avoided. Hydrolysis in the 0.01 *M* stock solution was suppressed by adding two pellets of KOH per 100 ml. of stock solution. When the stock solution was diluted with neutral solvents, no additional base was necessary. Air oxidation of dilute solutions, 3×10^{-4} *M* and less, was averted by deaerating the diluents with nitrogen before adding the requisite aliquot of stock solution.

The rate of decomposition of bis-(diethylthiocarbamyl) disulfide by base was measured with the automatic recording polarograph. Across a neutral unbuffered solution of 10^{-3} *M* disulfide, the potential was set at -0.8 volt *vs.* S.C.E. which is well into the limiting current region of the reduction wave of the disulfide. The current sensitivity vernier was adjusted so that the limiting current was represented by the full chart width. Fifty ml. of solution in the cell was deaerated with nitrogen as usual. The chart was allowed to run while the constant applied potential was maintained. Without stopping the chart an aliquot of lithium hydroxide stock solution was added to the cell and a short burst of nitrogen bubbles was blown through the cell at the same time to insure complete and rapid mixing. The instant base was added was taken as zero time. The chart speed was accurately determined so that the chart length represented the time axis and the chart width represented the current or concentration axis.

Materials.—Sodium diethyldithiocarbamate: Eastman Kodak Co. white label sodium diethyldithiocarbamate was crystallized once from ethyl acetate and once from 2-propanol. The composition of the crystals was 75.5% sodium

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(1) Presented in part at the Pittsburgh conference on analytical chemistry and applied spectroscopy, February, 1950.

(2) *J. Am. Med. Assoc.*, **139**, 918–922 (1949).

(3) G. Proske, *Angew. Chem.*, **53**, 550 (1940); *Rubber Chem. and Technol.*, **XIV**, 914 (1941).

(4) G. Proske, *Kautschuk*, **16**, no. 1, 1–5 (1940); **16**, no. 2, 13–17 (1940); *Rubber Chem. and Technol.*, **XIV**, 470 (1941).

(5) G. Proske, *Die Chemie*, **56**, 24–28 (1943).

(6) Kolthoff and Levitan, Univ. of Minn., to Office of Rubber Reserve, unpublished report, June 18, 1943.

(7) Dole, THIS JOURNAL, **54**, 3095 (1932).