

4-Amino-2,5-dimethylphenylarsonic Acid (2,5-Dimethyl-4-aminophenylarsonic Acid).—4.1 g. of the crude nitro acid was reduced in the usual way with 30 g. of ferrous sulfate in 90 cc. of water. The filtrate from the ferrous hydroxide was acidified with hydrochloric acid until congo red just began to change color and on rubbing the acid separated quickly as glistening scales. After filtering off and washing with ice water the yield was 3.0 g. A portion was recrystallized from water, forming thin, nacreous, serrated, almost colorless platelets containing one molecule of water of crystallization as described by Benda and Kahn,¹ who prepared the acid by the direct arsenation of *p*-xylydine. The amino acid is readily diazotizable and is sparingly soluble in cold water or alcohol, quite easily on boiling. When rapidly heated to 210°, then slowly, the anhydrous substance melts at 213–4° with decomposition.

Anhydrous subst. (Kjeldahl), 0.1526 g; 6.35 cc. 0.1 *N* HCl.

Calcd. for C₈H₁₂O₃NAs: N, 5.72. Found: 5.83.

3-Amino-4-hydroxyphenylarsonic Acid.—This substance, previously obtained by the reduction of 3-nitro-4-hydroxyphenylarsonic acid by the use of sodium hydrosulfite or sodium amalgam,² is also most conveniently prepared by the use of ferrous sulfate.

58.4 g. of 3-nitro-4-hydroxyphenylarsonic acid was reduced in the usual manner with 440 g. of ferrous sulfate. On acidifying the dark-colored filtrate with acetic acid and rubbing, the aminohydroxyphenylarsonic acid separated in characteristic form. The yield was 42 g., or 80% of the theory. The recrystallized acid darkens and softens at about 220° and finally decomposes at about 290°.

Subst., 0.1525; Kjeldahl, 6.9 cc. 0.1 *N* HCl.

Calc. for C₈H₉O₄NAs: N, 6.01. Found: 6.34.

NEW YORK CITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE.]

THE ABSORPTION SPECTRA OF SOME DERIVATIVES OF CYCLOPROPANE.

BY EMMA P. CARR AND C. PAULINE BURT.

Received July 15, 1918.

A comparison of the ultraviolet absorption spectra of certain derivatives of cyclopropane and their isomeric ethylenic derivatives with the spectra of the corresponding saturated derivatives of propane has shown distinct differences in the absorptive power of the 3 types of compounds and has given results of interest with regard to the effect of ring formation on absorption spectra.

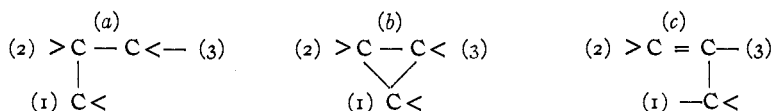
The substances used in this investigation were made available through

¹ Benda and Kahn, *Ber.*, 41, 1676 (1908).

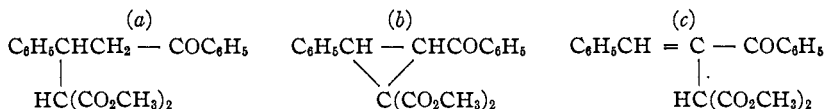
² D. R. P. 224,953; Ehrlich and Bertheim, *Ber.*, 45, 757 (1911).

the courtesy of Dr. E. P. Kohler and his co-workers of Harvard University and Dr. Dorothy Hahn of this laboratory. The cyclic compounds were ketonic derivatives of cyclopropane and of cyclopropane dicarboxylic acid in which a carbonyl and carboxyl groups are in direct union with the ring. Although these compounds are somewhat complex for the study of the effect of ring-formation on absorption, the corresponding cyclic, ethylenic, and open-chain saturated derivatives had been prepared in a high degree of purity and their constitutions established,¹ and in the limited number of substances examined spectrographically certain definite relationships are evident.

Four different series of compounds were examined, of which the first two were represented by all 3 types of compounds and the last two by cyclic and open-chain saturated derivatives. In a given series the substituents in the molecule remain constant and the compounds differ only in the type of combination of the 3 central carbon atoms as represented by (a), (b) and (c).²



The different series vary in the nature of the substituents of the 3 central carbon atoms. For example, Series II differs from Series I in the substitution of the anisoyl group for the benzoyl group, bound to carbon atom (3); Series III from Series I, in the substitution of the methyl group for hydrogen bound to carbon atom (3); Series IV in the substituents of carbon atom (1). In each series the substituents of carbon atom (2) are hydrogen and the phenyl group. The three types of compounds in Series I are shown by the following formulas:



A study of the absorption spectra curves which were obtained shows a similar variation in general absorption of the compounds of the Types a, b, and c in each of the series examined, thus showing that the relative influence of the substituents is slight as compared with the effect of varying the form of linkage between the central carbon atoms. In general, it may be said that distinct differences in the absorptive power

¹ E. P. Kohler and J. B. Conant, *THIS JOURNAL*, **39**, 1404 (1917); Dorothy A. Hahn, *Ibid.*, **38**, 1517 (1916).

² It will be noted that the compounds of Type a and Type c are not strictly analogous since they differ in the point of attachment of carbon atom (1). The compounds which correspond completely in the series we have studied have never been prepared but the effect of so slight a structural difference on the absorption spectra is practically negligible.

of each of the 3 types of compounds are shown and these differences are characteristic of the particular form of linkage of the central carbon atoms.

In each series the saturated open-chain compounds (Type *a*) show the least general absorption, the cyclic derivative (Type *b*) slightly greater general absorption and in Series I and II, where the ethylenic derivatives have been prepared, the unsaturated compounds (Type *c*) show the greatest general absorption.

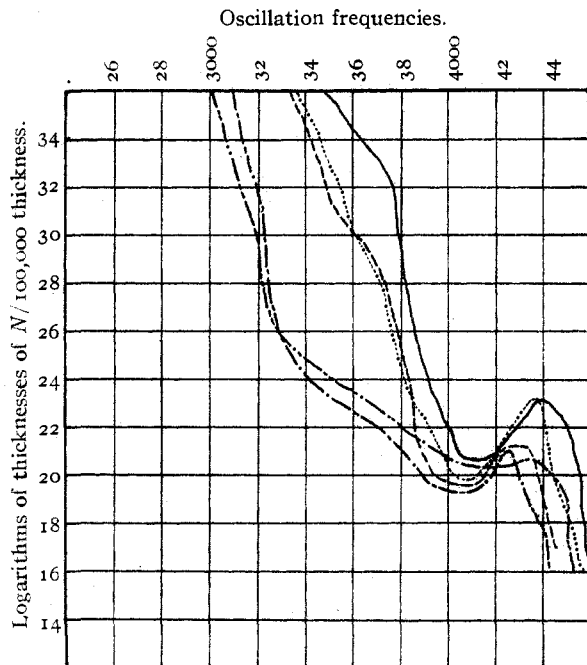


Fig. 1.

- Methylphenyl-benzoyl-ethylmalonate.
- Methyl-2-phenyl-3-benzoyl-cyclopropanedicarboxylate, m. p. 92°.
- - - - Methyl-2-phenyl-3-benzoyl-cyclopropanedicarboxylate, m. p. 72°.
- . . . Methyl- β -benzoyl- γ -phenylvinylmalonate, m. p. 147°.
- . . . Methyl- β -benzoyl- γ -phenylvinylmalonate, m. p. 119°.

The greater general absorption of an unsaturated substance as compared with the corresponding open-chain saturated compound is well known and an examination of the graphs in Figs. 1 and 2 shows such a relationship both from the standpoint of the wave length absorbed by a given thickness of solution or by the dilution to which absorption persists.

It is pointed out by Rosanov¹ that ring-formation in the case of cyclopentane and cyclohexane affects the absorption very little, the degree

¹ N. A. Rosanov, *J. Russ. Phys. Chem. Soc.*, 48, 1221 (1916).

of absorption of pentane and cyclopentane being one and the same. The data obtained in this investigation show, however, that closure of the ring in the cyclopropane derivatives shifts the absorption toward the red but to a less extent than is the case with the ethylenic isomer.

It is of interest to note the close similarity in the character of the absorption of the cyclic compounds and their open-chain analogs, since they differ only in the greater general absorption of the cyclic substances, already noted, and in the slightly greater tendency toward selective

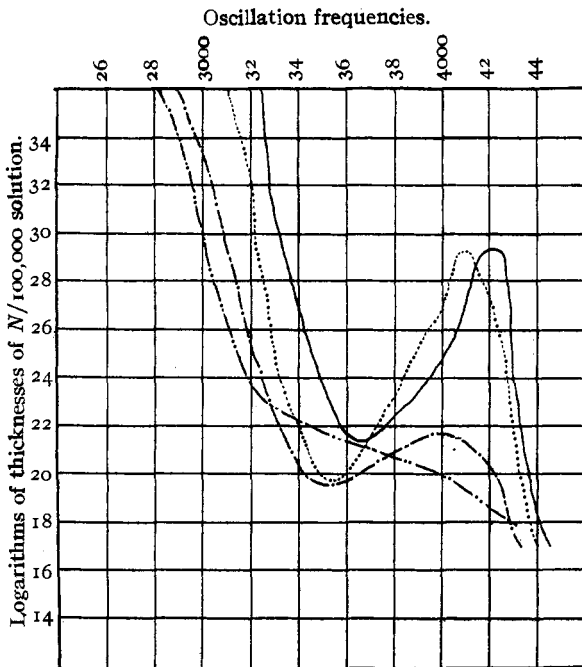


Fig. 2.

- Methylphenyl-anisoyl-ethylmalonate, m. p. 104°.
- Methyl-2-phenyl-3-anisoyl-cyclopropanedicarboxylate, m. p. 86°.
- - - - Methyl- β -anisoyl- γ -phenyl-vinylmalonate, m. p. 112°.
- - - - Methyl- β -anisoyl- γ -phenyl-vinylmalonate, m. p. 82°.

absorption. In the two series in which the ethylenic derivatives have been prepared, the curves for these substances differ markedly from those of the isomeric cyclopropane derivatives. These results show the cyclopropanes as closely related to the open-chain saturated compounds and intermediate in character between the isomeric olefinic and analogous open-chain saturated derivative; a conclusion which is in accord with evidence from a study of the chemical properties and certain other physical properties of these three types of compounds.¹

¹ A brief review of the results of investigations of the effect of ring-formation on different physical properties is given by Thole (*J. Chem. Soc.*, 105, 2004 (1914)).

The effect of conjugated double linkages in increasing the general absorption of substances has been established¹ and from this the more general conclusion stated by Macbeth and Stewart² that "the introduction of a center of residual affinity into a saturated molecule increases that molecule's power of absorbing light." In the cyclopropane ring all of the carbon atoms are nominally saturated; yet in the compounds examined, where the ring is adjacent to a carbonyl group, the effect of the ring-formation on the absorption spectra is similar to that of the introduction of an unsaturated center, the general absorption of the cyclic compound being greater than the open-chain derivative but less than the unsaturated. These facts lead to the conclusion that the cyclopropane ring is a center of residual affinity and as such can form a "conjugated system" with the carbonyl group differing from the unsaturated compound only in quantity of free affinity. This corroborates Kohler's conclusion³ from a study of the chemical reactions, that a "cyclopropane ring and a carbonyl group can form a 'conjugated system' which is identical in properties with that found in many ethylenic compounds."

From the work of Bruhl,⁴ Tschugaeff,⁵ and Zelinsky and Zelikow⁶ on the refractivity of cyclopropane derivatives and their isomeric unsaturated compounds, it is shown that the refractivity of unsaturated compounds is higher by about 1.8 than the values calculated from the sum of the elements, while for cyclopropane derivatives, which show a similar but smaller anomaly, the average difference is about 0.82. Thus the optical character of the cyclopropane ring is similar to that of the ethylene bond but marks an intermediate stage between the saturated and the unsaturated, a conclusion which is in direct accord with our results in absorption spectra.

In considering the formulas of the compounds examined, it is evident that two geometrical isomers are theoretically possible with each of the olefinic and cyclic derivatives and two stereoisomers in the case of the saturated open-chain compounds since these contain an asymmetric carbon atom. Such geometrical isomers in Series I have been prepared and studied; in Series II, only the two unsaturated isomers have been isolated; in Series III, two isomeric cyclic compounds. The results of the spectrographic study of these isomers will be considered in detail in the discussion of the different series, but, in general, it may be said that the absorptive powers of geometrical isomerides are not identical, and in

¹ Crymble, Stewart, Wright and Glendinning, *J. Chem. Soc.*, **99**, 451 (1911); Crymble, Stewart, Wright and Miss Rea, *Ibid.*, **99**, 1262 (1911).

² Macbeth and Stewart, *Ibid.*, **111**, 829 (1917).

³ *Loc. cit.*, 1409.

⁴ *Ber.*, **25**, 1954 (1892); **32**, 1228 (1899); *Z. physik. Chem.*, **7**, 179 (1891).

⁵ *Ber.*, **33**, 3122 (1900).

⁶ *Ibid.*, **34**, 2859, 2867 (1901).

each pair that was examined the lower melting isomer shows slightly greater general absorption. Previous investigations of ethylenic isomerides¹ have shown that the symmetrical or trans-form gives the greater general absorption; this would suggest that the low melting isomers are therefore the symmetrical forms but the differences in general absorption of the pairs of isomers, examined by us, are so slight that it is difficult to draw any conclusions in this matter.

The limited number and the complexity of the compounds that have been studied spectrographically make it inadvisable to draw definite conclusions other than those pointed out previously concerning the influence of ring-formation on general absorption; consideration of the data obtained suggests, however, that ring-formation is an influencing factor in selective absorption. In general, the cyclic compounds show a similar though slightly greater tendency toward selective absorption than the corresponding saturated compounds and in the two series where ethylenic compounds are studied the cyclic compound showed a decidedly greater selective absorption.

Experimental.

The absorption spectra of the alcoholic solution of varying thickness were photographed and the limits of absorption plotted according to the usual Hartley method. A Fery spectrograph manufactured by Adam Hilger, London, was used in connection with a sparking outfit which consisted of a transformer, a condenser and a suitable holder for the electrodes. The source of light was the carbon-uranium-molybdenum arc (the so-called "Jones electrodes").² Wratten and Wainwright photographic plates were used for the larger part of the investigation, although a part of the work was done on Seeds negative films, manufactured by the Eastman Kodak Company.

The procedure was as follows: a 0.001 *N* solution in absolute alcohol was prepared and placed in a Baly absorption tube, and a series of photographs through thicknesses varying from 1 to 40 mm. was taken; the solution was then diluted to 0.0001 *N* and a similar series of spectrograms taken. Uniform time of 30 seconds was given to each exposure and every precaution was taken to insure uniformity of conditions as far as possible. The limits of absorption were measured by means of a transparent millimeter scale. A standard plate upon which was photographed in successive exposures the spectra of the cadmium, zinc, iron, copper, and the carbon-uranium-molybdenum arcs had been prepared previously and the lines of known frequency identified. From these data a curve had been plotted using the reading of the millimeter scale as abscissas and the vibration

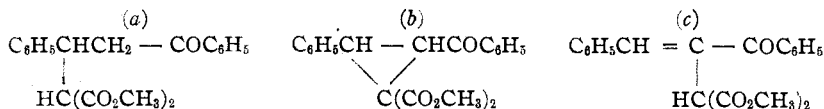
¹ Magini, *J. chim. phys.*, **2**, 403 (1904); Stewart, *J. Chem. Soc.*, **91**, 199, 1537 (1907); Bielecki and Henri, *Ber.*, **46**, 2607 (1913).

² *Carnegie Inst. Publications*, **110**, 9 (1909).

frequencies as ordinates. By reference to this curve the readings on the millimeter scale could be expressed in frequencies. The graphs were then plotted, using the oscillation frequencies of the limits of absorption as abscissas and the logarithms of the thickness of an 0.00001 *N* solution as ordinates.

Discussion.

Series I.—Methylphenyl-benzoyl-ethylmalonate (*a*); methyl-2-phenyl-3-benzoyl-cyclopropanedicarboxylate (*b*), two isomers, melting points 72° and 92°; methyl-β-benzoyl-γ-phenylvinylmalonate (*c*), m. p. 119° and 147°. Fig. 1.



The preparation and properties of the compounds in this series have been discussed in full by Kohler and Conant.¹ This is the most complete of any of the series examined by us, since all 3 types of compounds are represented and the two pairs of geometrical isomers that are possible have been prepared and only the stereoisomer of the open-chain saturated substance is lacking.

Examination of the graph (Fig. 1) shows the difference in general absorption of the 3 types of compounds already pointed out. The ethylenic compounds ((*c*) m. p. 119° and 147°) exhibit the greatest absorptive power, since at logarithmic thickness of 36 the two ethylenic derivatives absorb to a frequency of 3000 and 3100, respectively; the cyclic isomers ((*b*), m. p. 72° and 92°) are next in order, absorbing to frequencies of 3270 and 3280 at the same thickness; and the saturated open-chain compound has the least absorptive power.

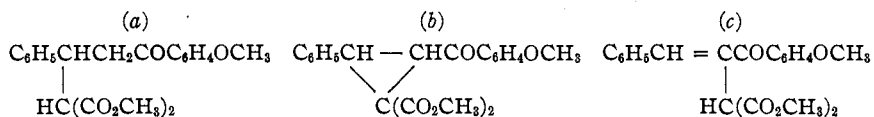
In their banded absorption, the cyclic and open-chain saturated analogs are very similar although the head of the band in the cyclic compounds is shifted toward the red. It will be seen from the graph that the band of the high-melting cyclic isomer (92°) shows somewhat greater persistence than that of the corresponding open-chain compound, while that of the low-melting isomer (72°) is less persistent and has only a shallow band. The two cyclic isomers are approximately similar in their general absorption although the low-melting (72°) shows slightly greater absorptive power to a logarithmic thickness of 30 and absorbs to a slightly greater dilution while the high-melting (92°) has the greater absorptive power from a logarithmic thickness of 30 to 23. These differences are, however, so slight that they are practically negligible.

The curves of the stereoisomeric unsaturated compounds show a broad shallow band in the high-melting isomer (147°) and only a tendency to

¹ *Loc. cit.*

band formation in the low-melting (119°). These curves differ markedly from those of the cyclic and saturated analogs, but show a close similarity between the two ethylenic isomers. Again, the two geometrical isomerides show slightly different general absorption, with the low-melting isomer having somewhat greater absorptive power, judged from the wave-length of light absorbed at a given dilution but the high-melting isomer absorbs at a greater dilution.

Series II.—Methylphenyl-anisoyl-ethylmalonate (*a*), m. p. 104° ; methyl-2-phenyl-3-anisoyl-cyclopropanedicarboxylate (*b*), m. p. 86° ; methyl- β -anisoyl- γ -phenylvinylmalonate, two isomers, m. p. 82° and 112° (*c*). Fig. 2.



The compounds of this series were prepared and studied by Dorothy A. Hahn,¹ of this laboratory. In this series, in which only one cyclic isomer has been prepared, the same order of absorptive power is evident; the open-chain saturated compound (104°) being the least and the unsaturated (112° and 82°) being the most absorbent, judged by the length of light waves absorbed. The low-melting unsaturated isomer (82°) does not, however, absorb at the greatest dilution. Both the cyclic and open-chain saturated compounds show a broad, well-defined band of considerable persistence and again the similarity between the curves of these two types is most evident. As in Series I the head of the band in the cyclic compound is shifted towards the red and the band shows greater persistence.

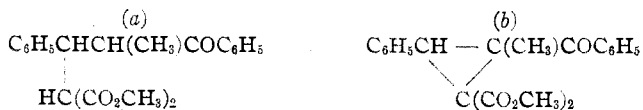
The character of the absorption shown by the unsaturated substances differs markedly from that of the other types in the series; in the high melting isomer (112°) there is a very shallow band while in the low-melting (82°), merely a "step-out."

In examining the curves of the pair of ethylenic isomerides, a relationship quite parallel to that pointed out with the pair of isomers in Series I is evident. The high-melting isomer is the less absorptive and shows the greater tendency to banded absorption. In general, the results of our study of the compounds of Series II are in full accord with those obtained in Series I.

Series III.—Methylphenyl-benzoyl-propylmalonate (*a*), two isomers; methyl-2-phenyl-3-methyl-benzoyl-cyclopropanedicarboxylate (*b*), m. p., (101° and 133°). Fig. 3.²

¹ *Loc. cit.*

² We are indebted to Dr. Tenney L. Davis for the substances used in this series.



The constitutional formulas of the compounds of this series have not been fixed with the same degree of certainty with which the preceding two series have been established. The results of their spectrographic examination are included in this report, however, since from the relationships established in Series I and II, we have confirmatory evidence of the constitutions which have been reached from purely chemical evidence.

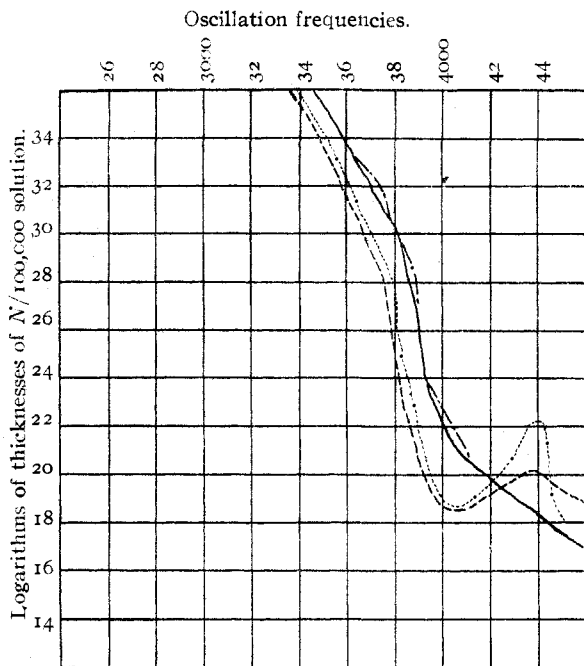


Fig. 3.

- Methylphenyl-benzoyl-propylmalonate, m. p. 90°-93°.
- - - - Methylphenyl-benzoyl-propylmalonate, m. p. 88°-90°.
- Methyl-2-phenyl-3-methyl-benzoyl-cyclopropanedicarbylate, m. p. 133°.
- - - - Methyl-2-phenyl-3-methyl-benzoyl-cyclopropanedicarbylate, m. p. 101°.

It is evident from the formula that no ethylenic derivatives are possible in this series. Examination of the graph shows the same relationship between the cyclic and open-chain saturated compounds that has been brought out in the previous series.

The cyclic compounds of this series differ from those of Series I by the substitution of the methyl group for the hydrogen of carbon atom (3) and it is interesting to note that the curves are practically identical, as would be anticipated. Again, in the pair of geometrical isomerides, the

high-melting isomer (133°) shows slightly less general absorption and an absorption band of greater persistence than the low-melting isomer (101°).

The open-chain saturated compound of this series has two asymmetric carbon atoms with the consequent possibility of stereoisomers. Of the two substances examined, one, melting point $90-93^{\circ}$, crystallizes from methyl alcohol in needles; the other, melting point $88-93^{\circ}$, crystallizes from methyl alcohol in rhombs. The two substances give identical curves which would be expected in the case of stereoisomers.

Series IV.—1,3-Dibenzoyl-2-phenylpropane (a); 1,3-dibenzoyl-2-phenylcyclopropane (b); 1,3-dibenzoyl-2-phenylcyclopropene (c). Fig. 4.

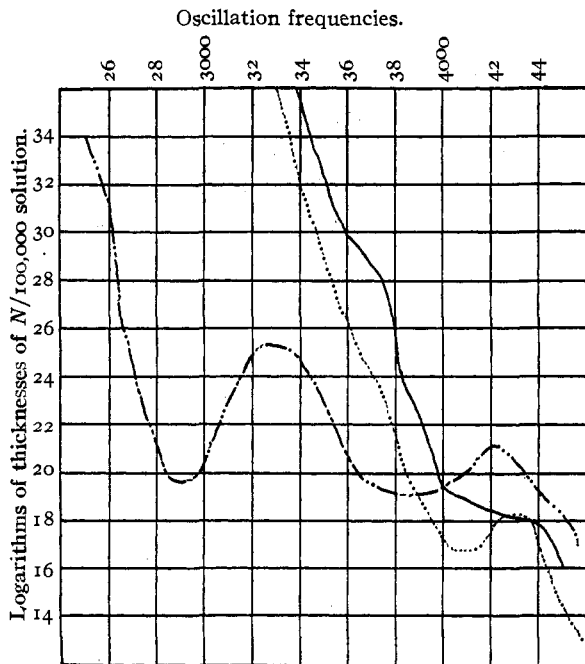
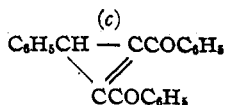
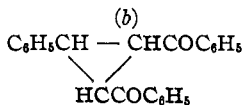
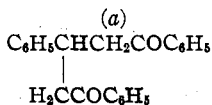


Fig. 4.

— 1,3-Dibenzoyl-2-phenylpropane, m. p. 84° .
 1,3-Dibenzoyl-2-phenylcyclopropane, m. p. 116° .
 - · - · - 1,3-Dibenzoyl-2-phenylcyclopropene.



The compounds of this series present a somewhat different relationship in structure from those of the preceding series. We are here comparing an open-chain propane derivative, a cyclopropane and a cyclopropene derivative. As will be noted from the formulas, the compounds of this series are not derivatives of cyclopropane dicarboxylic acid, as all the preceding compounds have been, but the conclusions with regard to the

effect of ring-formation on absorption, developed from a study of Series I and II, receive further support in an examination of the curves in Fig. 4. Closure of the ring in the cyclic compound (1116°) increases the general absorption of the molecule and increases the tendency to band-formation. There is only a "step-out" in the open-chain compound (82°) and a shallow band in the cyclic derivative.

The very great shifting of the absorption towards the red in the cyclopropane derivative and the appearance of a second absorption band is noteworthy in showing the fundamental influence of the unsaturated center on both the general and selective absorption of the molecule.

A comparison of the curves of all the cyclic substances examined in the different series, gives results of interest in showing the effects on selective absorption of the symmetrical arrangement of the groups about the cyclopropane ring. In the anisoyl derivative (Series II) we have the most unsymmetrical grouping about the ring and at the same time the most pronounced selective absorption, while in the dibenzoyl derivatives (Series IV), the most symmetrical arrangement of groups within the molecule, there is only the slightest tendency to banded absorption.

Summary.

Two series of cyclopropane derivatives, with their ethylenic isomers and their corresponding open-chain saturated compounds, have been examined spectrographically and their absorption curves plotted.

Two additional series of such compounds, consisting of cyclic and open-chain saturated analogs, have been examined in a similar manner.

The character of the absorption is closely related to the form of linkage of the 3 central carbon atoms and distinct differences in the absorption spectra of the corresponding cyclic, open-chain saturated and olefinic compounds are shown.

In each series the cyclic substance shows an absorption quite similar to that of its open-chain analog but in every case the general absorption is greater. Evidently closure of the ring increases the absorptive power of the molecule.

Ring-formation in the cyclopropanes causes a shifting of the absorption towards the visible but to a less extent than in the case of the isomeric ethylenic compounds. These facts justify the conclusion that the cyclopropane ring is a center of residual affinity similar in character but intermediate in quantity to that of the double linkage and as such can form a "conjugated system" with a carbonyl group in the proper position.

The absorption spectra of 4 pairs of geometrical isomerides have been determined. In each pair the isomer of lower melting point gave slightly greater general absorption and the isomer of higher melting point the greater tendency toward selective absorption.