yield. Recrystallization from ethanol gave white plates, m.p. 309–311°.

Anal. Calcd. for $C_{33}H_{25}N_3O_3$: C, 77.48; H, 4.93; N, 8.21. Found: C, 77.46; H, 5.01; N, 8.13.

The melting point of a mixture of this material with that prepared in *A* by the benzoylation of the aniline adduct was not depressed.

Peroxytrifluoroacetic acid oxidation of 2-chloro-4-nitroaniline. Into a 200-ml. three-neck round bottom flask equipped with stirrer, reflux condenser, and dropping funnel was placed 65 ml. of trifluoroacetic acid. The liquid was heated to boiling (71°), and 5 g. of 2-chloro-4-nitroaniline was dissolved in the hot acid. To the refluxing solution was added 17.3 ml. of 30% hydrogen peroxide dropwise during a 30 min. period. The color of the solution bleached at first and then became deep red. The solution was heated under reflux for 1 hr. after the addition was complete, cooled to room temperature, and poured into ice water. The orange solid removed by filtration weighed 4.0 g. One gram of this material when extracted with petroleum ether (b.p. 80–100°) gave 0.17 g. of deep red insoluble material. The ether sol ble material melted at 57–59° and was undoubtedly the desired 2-chloro-1,4-dinitrobenzene. The red insoluble material was recrystallized from benzene, m.p. 280–281°.

Anal. Calcd. for $C_{18}H_9ClN_6O_{10}$: C, 42.83; H, 1.80; N, 16.65. Found: C, 42.88; H, 1.82; N, 16.26.

Acknowledgment. The authors are indebted to Mr. J. Nemeth, Mrs. M. Stingl, and Miss C. Higham for the microanalyses and to Mr. J. Brader for the infrared spectral determinations.

URBANA, ILL.

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Infrared Absorption and Structure of Certain Derivatives of Cyclopropane*

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The infrared absorptions of twenty derivatives of cyclopropane, mostly with carbonyl or other functional groups adjacent to the ring, have been obtained. Neither the 2.3μ nor the 9.8μ region, previously suggested for characterizing the C_3 ring, affords a clear indication of either the presence or absence of this group.

The infrared spectrum of unsubstituted cyclopropane has been studied in detail and most of the fundamental modes of vibration have been identified.[1–3] In studying the spectra of cyclopropane derivatives which were mostly hydrocarbons, a number of workers[4–6] have reported that a characteristic absorption near 9.8μ (1000–1020 cm.$^{-1}$) is invariably present. Another strong absorption near 11.6μ (866 cm.$^{-1}$) found in some derivatives does not occur consistently.[5] These absorption bands are also found in cyclopropane itself and have been assigned to a ring deformation and to a CH_2 wagging vibration.[3]

In more recent work,[7–9] questions have been raised as to the reliability and usefulness of these bands at longer wave lengths. While Wiberley and Bunce[7] confirmed the 9.8μ band in nine nonhydrocarbon cyclopropyl derivatives, they concluded that absorptions in this region were too common to provide a clear identification of the ring structure and suggested the use of C—H stretching bands at 3.23 and 3.32μ for CH_2 groups in the cyclopropyl system. Two additional ketones containing the cyclopropyl ring also showed[8] this pair of bands, whereas Cole[9] reported only a single band between 3.28 and 3.31μ (3024–3058 cm.$^{-1}$) in isocholestane and two other natural products. No such band was reported for 3-carene, where each of the carbons of the three-membered ring has at least one substituent. In work with dicyclopropyl ketone, -carbinol, and -methane,[10] the two C—H bands were again noted near 3.3μ (3030 cm.$^{-1}$) and 3.23μ (3100 cm.$^{-1}$), as well as several strong bands in the 9.6–10μ region.

In a recent summary of spectral-structure correlations for cyclopropane derivatives,[11] fourteen references are cited to support the use of a band between 9.8 and 10.0μ (1000–1020 cm.$^{-1}$) as indicating a cyclopropyl ring. The presence of a band in this position in the spectra of substances of unknown structure has also been interpreted as sup-

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[*] This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

(1) G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Co., Inc., New York, 1945, pp. 352–353.

(2) A. W. Baker and R. C. Lord, *J. Chem. Phys.*, **23**, 1636 (1955).

(3) Hs. H. Günthard, R. C. Lord, and T. K. McCubbin, Jr., *J. Chem. Phys.*, **25**, 768 (1956).

(4) J. D. Bartleson, R. E. Burk, and H. P. Lankelma, *J. Am. Chem. Soc.*, **68**, 2513 (1946).

(5) J. M. Derfer, E. E. Pickett, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 2482 (1949).

(6) V. A. Slabey, *J. Am. Chem. Soc.*, **74**, 4928 (1952).

(7) S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

(8) F. J. Piehl and W. G. Brown, *J. Am. Chem. Soc.*, **75**, 5023 (1953).

(9) A. R. H. Cole, *J. Chem. Soc.*, 3807 (1954).

(10) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.*, **78**, 112 (1956).

(11) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen and Co., Ltd., London, 1954, pp. 27–28.

porting the presence of a cyclopropane ring in several instances.[12–14]

The availability of twenty cyclopropane derivatives, many of them heavily substituted, has made it possible to contribute additional evidence bearing on the reliability of infrared evidence for the C_3 ring. While those expert in the field may already be aware of the limitations, it is felt that some attempted applications indicate a need for additional information on this point. The substances examined are listed in Table I. For those samples not specifically described in previous papers, the source and criteria of purity used are noted in the Experimental Section.

Infrared absorptions near 10 microns. Infrared spectra were obtained in the 2–16μ region, using pressings in potassium bromide or mineral oil mulls for the solids. No differences have been noted which might be due to interaction with potassium bromide. These spectra have been made available to the National Research Council Committee on Spectral Absorption Data[15] for future publication in the NRC-NBS series of reference spectra.

To illustrate the spectral region of particular concern in this paper, the absorptions between 9 and 11μ are reproduced in Fig. 1. In general, the strongest bands in each complete spectrum show less than 5% transmission. Of the 20 spectra, 3 show no significant absorption maxima between 9.8 and 10.0μ (compounds II, III, and IV), and three others (compounds VIII, XIV, and XIX), show only bands which appear on the sides of stronger absorptions which lie outside the region in question. In order to include an absorption from all of the compounds, it would be necessary to widen the region from a lower limit of 9.66μ to an upper limit of 10.05μ.

To obtain an indication of the extent of interference from noncyclopropane structures which absorb in the 9.7–10.05μ region, 200 spectra were selected by the use of a table of random sample numbers[16] from the first 9,400 spectra in the Sadtler file.[17] Examination showed that although none were of cyclopropanes, 50% contained one or more moderate or strong absorptions between 9.7 and 10.05μ. In the more limited range between 9.75 and 9.90μ, similar interference was noted in 31% of the cases. In a separate survey of unpublished spectra of 200 compounds selected at ran-

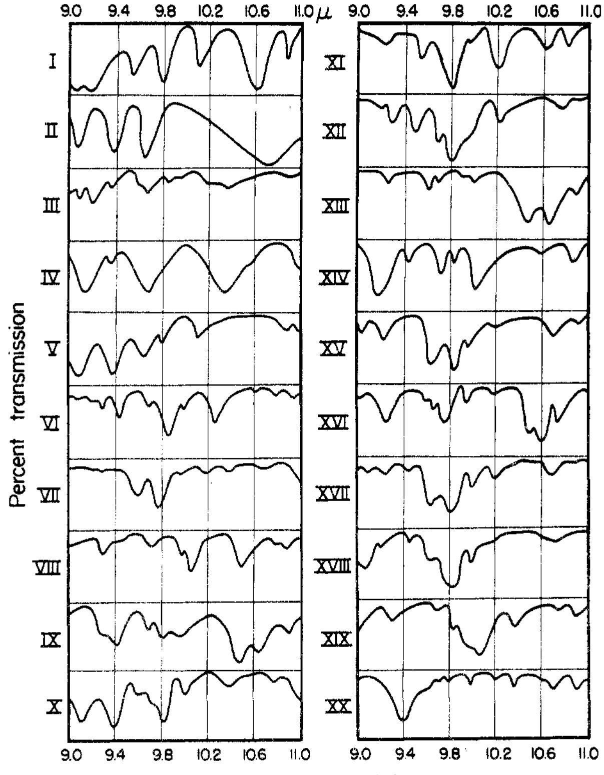

FIG. 1. INFRARED ABSORPTIONS IN THE 9–11μ REGION FOR COMPOUNDS IDENTIFIED IN TABLE I.

TABLE I

CYCLOPROPANES

I	α-Hydroxyethyl-
II	Carboxy-
III	Ethyl chrysanthemumate
IV	Acetyl-
V	Dicyclopropyl ketone
VI	2-Benzoyl-1-nitro-1-phenyl- (isomer, m.p. 131°)[a]
VII	1,2-Dibenzoyl-1-phenyl- (isomer, m.p. 125°)[b]
VIII	1,2-Dibenzoyl-1-phenyl- (isomer, m.p. 129°)[b]
IX	Dioxime of above[b]
X	Monophenylhydrazone of same[b]
XI	1,2-Dibenzoyl-3-phenyl- (isomer, m.p. 119°)[c]
XII	1,2-Dibenzoyl-3-phenyl- (isomer, m.p. 151°)[c]
XIII	Dioxime of XI
XIV	2-(4-Chlorobenzoyl)-1-nitro-3-phenyl- (isomer, m.p. 121°)[d]
XV	2-Benzoyl-1-cyano-1,3-diphenyl- (isomer, m.p. 169.5°)[e]
XVI	2-Benzoyl-1-cyano-1,3-diphenyl- (isomer, m.p. 176.5°)[e]
XVII	2-Benzoyl-1-carboxamido-1,3-diphenyl-[f]
XVIII	2-Benzoyl-1-cyano-1-(4-nitrophenyl)-3-phenyl- (isomer, m.p. 150°)[g]
XIX	2-Benzoyl-1-cyano-1-(4-nitrophenyl)-3-phenyl- (isomer, m.p. 172°)[g]
XX	Methyl 3-phenylcyclopropane-1,1,2,2-tetracarboxylate

[a] C. F. H. Allen and M. P. Bridgess, *J. Am. Chem. Soc.*, **51**, 2151 (1929). [b] C. F. H. Allen and W. E. Barker, *J. Am. Chem. Soc.*, **54**, 736 (1932). [c] E. P. Kohler and W. N. Jones, *J. Am. Chem. Soc.*, **41**, 1249 (1919). [d] E. P. Kohler and L. I. Smith, *J. Am. Chem. Soc.*, **44**, 624 (1922). [e] E. P. Kohler and C. F. H. Allen, *J. Am. Chem. Soc.*, **46**, 1522 (1924). [f] C. F. H. Allen and R. Boyer, *Can. J. Res.*, **9**, 159 (1933). [g] C. F. H. Allen, *J. Am. Chem. Soc.*, **47**, 1733 (1925).

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(12) K. Hofmann, *Record Chem. Progr.*, **14**, 14 (1953).

(13) J. P. Verma, B. Nath, and J. S. Aggarwal, *Nature*, **175**, 85 (1955).

(14) K. K. Chakravarti and S. C. Bhattacharyya, *Perfumery Essent. Oil Record*, **46**, 256 (1955).

(15) E. C. Creitz, Sec'y., c/o National Bureau of Standards, Washington 25, D. C.

(16) L. H. C. Tippett, *Random Sampling Numbers*, Cambridge Univ. Press, Cambridge, 1927, Table VII.

(17) Samuel P. Sadtler and Son, Philadelphia, Pa., "Catalog of Infrared Spectrograms."

dom from the list of Eastman Organic Chemicals, 42% showed absorptions between 9.7 and 10.0μ which were at least as strong as the average shown by the compounds in Table I. We thus conclude that between one-third and one-half of all organic compounds might be expected to have one or more bands in this region which has been suggested as characterizing the cyclopropane ring.

Infrared absorptions near 3.3 microns. Examination of the C—H stretching vibrations in the spectral region between 3.2 and 3.5μ requires, for optimum results, resolution greater than can be obtained with a spectrometer having a sodium chloride prism. Such spectra have been obtained on eighteen of the substances in Table I by using a lithium fluoride prism, with the results shown in Fig. 2. Since aromatic and ethylenic C–H's would also be expected to absorb in the 3.2–3.3μ portion of the range, it is not surprising that, for our highly substituted cyclopropanes, this region, likewise, shows ambiguities at least as serious as those noted for bands near 10μ.

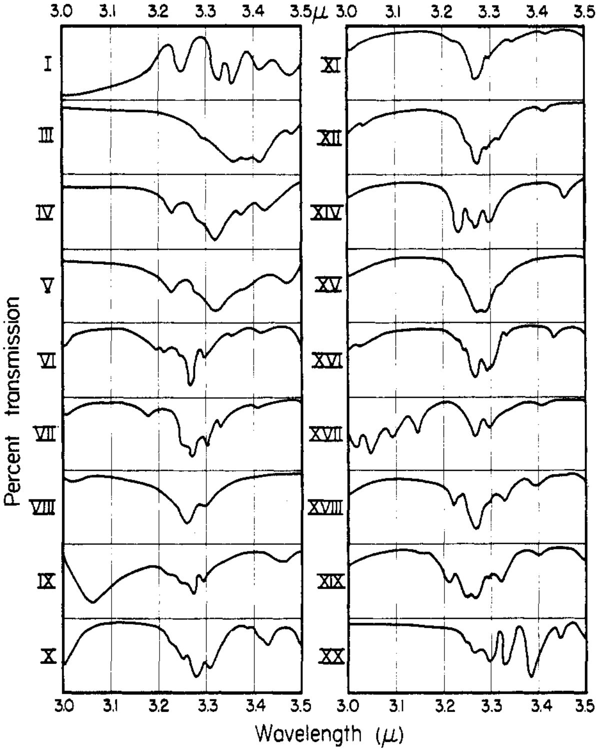

FIG. 2. INFRARED ABSORPTIONS IN THE 3.0–3.5μ REGION. Spectra obtained on potassium bromide pressings, except compounds I, III, IV, V as liquids and VII, VIII and XX as 5% solutions in CCl_4.

In the work of Wiberley and Bunce,[7] the two bands noted for cyclopropanes containing unsubstituted CH_2 groups at 3.23μ (3096 cm.$^{-1}$) and 3.32μ (3012 cm.$^{-1}$) are so close to the fundamental frequencies ν_6 (3090 cm.$^{-1}$) and ν_8 (3019 cm.$^{-1}$) for liquid cyclopropane[2] that it seems clear that the same parallel and perpendicular modes of vibration of ring CH_2 groups are involved. Since this is the case, it would be unrealistic to expect both bands in compounds containing only CHR or CR_2. In the eighteen compounds examined in this wave length range, ring CH_2's are found in I, IV, V, VII, VIII, and IX, but, in all but the simplest cases, they represent only a minor part of the molecule. In the experimentally determined spectra, only I, IV, and V show clearly the expected two bands. Most of the others show their strongest absorption between 3.26 and 3.28μ, with from one to three other bands in the 3.22–3.3μ region. In VII, VIII, and IX, there is no useful absorption at 3.23μ, even though a ring CH_2 is present in each, whereas in XIV, XVIII, and XIX, a band is observed at 3.22–3.23μ, although no such group is present.

Recent high-resolution work by Tallent and Siewers[18] on vinyl, aromatic, and heterocyclic =CH— absorptions show significant overlap into the region involving the cyclopropyl methylene groups. Tallent and Siewers and also Henbest, Meakins, Nicholls, and Taylor[19] show that there is close correspondence between C—H absorptions in a three-membered carbocylic ring and those in an epoxy system, which adds to the difficulty. One must, therefore, conclude that the general similarity between spectra of all of the phenyl and benzoyl cyclopropanes is attributable to the C–H's in the noncyclopropane parts of the molecule.

The data of Roberts and Chambers[20] indicate that the inherent weakness of C—H stretching absorptions in the cyclopropyl structure (as compared with C—H bonds in larger rings) would also make difficult any identification based on the 3μ region of the infrared spectrum.

To illustrate the difficulties encountered in using the 3.3μ absorptions to distinguish between a cyclopropane derivative and a closely similar compound not containing the C_3 ring, methyl 3-phenylcyclopropane-1,1,2,2-tetracarboxylate (XX) was compared with methyl benzaldimalonate (XXI). The second of these contains two aliphatic hydrogen atoms, which are absent in the ring structure of the first. The spectra obtained from 5% solutions (0.5 mm. cell) in carbon tetrachloride are reproduced in Fig. 3, which is plotted in terms of relative absorption, the base line being that for a carbon tetrachloride blank. When examined as a mull or a potassium bromide pressing, the tetracarboxylate (XX) showed only a single band at 3.308μ, whereas, in solution, separate bands were observed at 3.298 and 3.328μ. No similar effect of crystallinity was noted in any of the other materials which were ex-

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(18) W. H. Tallent and I. J. Siewers, *Anal. Chem.*, **28,** 953 (1956).

(19) H. B. Henbest, G. D. Meakins, B. Nicholls and K. J. Taylor, *J. Chem. Soc.*, 1459 (1957).

(20) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73,** 5030 (1951).

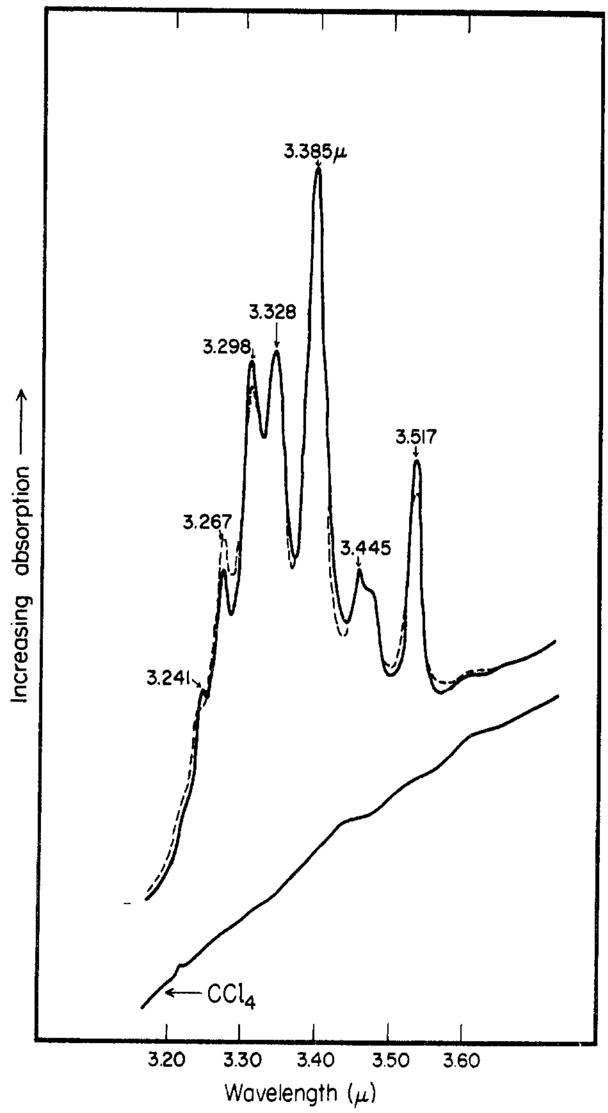


FIG. 3. COMPARISON OF METHYL 3-PHENYLCYCLOPROPANE-1,1,2,2-TETRACARBOXYLATE (- - - -) AND METHYL BENZALDIMALONATE (——) IN THE 3.2–3.6μ REGION.

amined both in solution and as solids. From the results in solution (Fig. 3), we conclude that only slight differences in the relative intensities of minor peaks can be detected, and there is no basis on which one could assign the cyclopropane structure to either of the compounds from the available infrared data.

EXPERIMENTAL

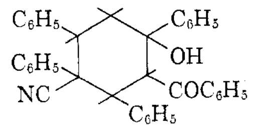
Incidental to the investigation of infrared absorptions characteristic of the cyclopropane ring, the spectra have been most useful in confirming functional group substitutions, in establishing the homogeneity of stereoisomeric forms, and in revealing the components of mixtures of such forms. Thus, in the highly substituted 2-benzoyl-1-carboxamido-1,3-diphenylcyclopropane (XVII), the presence of the carboxamido group could be readily confirmed, although this was difficult to do chemically. Also, as noted in the following section, stereoisomers of two of the compounds which had been reported previously could be eliminated as being mixtures.

Preparation of materials. Acetylcyclopropane,[21] dicyclopropyl ketone,[22] ethyl chrysanthemumate,[22] carboxycyclopropane,[23] and α-hydroxyethylcyclopropane[24] were obtained from commercial sources and redistilled where necessary, by using a 10-inch glass-packed column with a variable take-off head, and taking a fraction with constant boiling point and refractive index. Acetylcyclopropane, b.p. 110°, n_D^{25} 1.4200; ethyl chrysanthemumate, b.p. 218°, n_D^{25} 1.4581; dicyclopropyl ketone, b.p. 162°, n_D^{25} 1.4632; cyclopropanecarboxylic acid, n_D^{25} 1.4353. The infrared spectrum of dicyclopropyl ketone was the same as that recently reported.[25] The two stereoisomeric forms of 1,2-dibenzoyl-3-phenylcyclopropane[26] and its dioxime, m.p. (corr.) 175°, were newly prepared.* Most of the others were the original analytical samples;[27, 28] however, the two higher-melting stereoisomeric forms [m.p. (corr.) 169.5, 176.5] of 2-benzoyl-1-cyano-1,3-diphenylcyclopropane[21, 29] were also freshly prepared, in an unsuccessful attempt to secure more of the low-melting (143°) isomer. The only product in this range was a mixture of the two other forms; this conclusion was confirmed by the infrared absorptions. Since none of the original sample was available, and since its isolation could not be repeated, its existence must now be regarded as doubtful.

Similarly, the present work on 2-benzoyl-1-cyano-1-(4-nitrophenyl)-3-phenylcyclopropanes (XVIII, XIX) has shown that the isomer previously reported as melting at 144°[27] was a mixture of the other two.

2-Benzoyl-1-cyano-1,3-diphenylcyclopropane. The procedure was improved over the original[29] by using a continuous reactor[30] for the first two steps, for preparing the δ-ketonic nitrile and two bromo derivatives. In the general form of the apparatus, at the rate of one mole per hour, the yield of adduct from benzyl cyanide and benzalacetophenone is 87.7%, of which 95% is the higher-melting form and 5% is the "trimolecular product." The former has two polymorphic modifications, m.p. 118.5° and 120.5°, which can be interconverted by suitable manipulation; their infrared spectra are different in Nujol mulls which are different from their solution.

The trimolecular product is now believed to be the cyclohexane (XXII), since infrared assay indicated the presence of tertiary OH, CN, and only 47% of the extinction of the $\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\text{—C—}}$ that would be expected from the open-chain form (which has two carbonyl groups).



XXII

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* All melting points are corrected.

(21) Eastman Kodak Co.

(22) Aldrich Chemical Co.

(23) *Org. Syntheses*, **Coll. Vol. 3**, 221 (1956).

(24) Tennessee Eastman Co., kindness of E. B. Towne. Methyl cyclopropyl ketone was hydrogenated at 100° and 2000 p.s.i. over barium-promoted copper chromite catalyst. The carbinol, b.p. 120–120.9° (727 mm.), n_D^{20} 1.4312, is known [V. A. Slabey and P. H. Wise, *J. Am. Chem. Soc.*, **71**, 3252 (1949)].

(25) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.*, **78**, 112 (1956).

(26) Table I, Ref. c.

(27) Table I, Ref. g.

(28) Table I, Ref. a, b, d (cpd. XIV; kindness of J. B. Shohan), f.

(29) Table I, Ref. e.

(30) C. F. H. Allen, J. R. Byers, W. J. Humphlett, and D. D. Reynolds, *J. Chem. Educ.*, **32**, 394 (1955), Fig. 1.

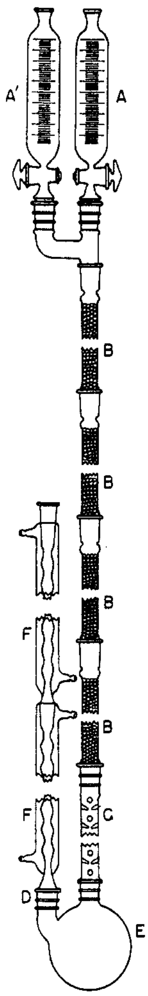

FIG. 4. APPARATUS FOR CONTINUOUS BROMINATION.

Bromination of the adduct by using a form of the continuous reactor[30] modified for bromination (Fig. 4), gives a 95% yield of mixed isomers (m.p. 173°; 131°) in the ratio of 3:2; there is none of the gummy by-product that always appears in a batch procedure. The column is made up of five 20- × 1-inch sections (B-C); the upper four (B) are packed with glass helices and the lower (C) is a Vigreux. Each is wrapped with 0.5-inch heating tape and is covered, in turn, with 0.5-inch asbestos paper tape. Hydrogen bromide escapes at the top of two reflux condensers (F), which are cooled with circulating ice water. A 25% solution of the nitrile in acetic acid, and an equal volume of acetic acid containing the required amount of bromine, were admitted from A, A'. With the Variacs set at 60, the capacity was 165 grams of product per hour. Since this is a very rapid bromination, only two sections (B) suffice.

Methyl 3-phenylcyclopropane-1,1,2,2-tetracarboxylate. The necessary methyl benzalmalonate was prepared in a large (4-inch diameter), continuous reactor (general form).[30] On using 6.1 moles each of benzaldehyde and methyl malonate, 16 min. were required for the addition, with Variacs set at 85 (bottom) and 55 (top). The yield was 952 g. (75%). It was fractionated through an 8-inch Vigreux column and had b.p. 115–116° at 0.4 mm.; n_D^{25} 1.5552 (unchanged on refractionation). The methyl benzaldimalonate[31] melted at 77° (lit. 64–65° uncorr.).

Anal. Calcd. for $C_{17}H_{20}O_8$: C, 57.9; H, 5.7. Found: C, 58.2; H, 5.8.

The new monobromoester, m.p. 103.5°, was obtained in a yield of 93% on bromination in chloroform in the usual fashion.[23, 31]

Anal. Calcd. for $C_{17}H_{19}O_8Br$: C, 47.3; H, 4.4. Found: C, 47.5; H, 4.7.

Methyl cyclopropane-1,1,2,2-tetracarboxylate, m.p. 87°, was obtained from the monobromoester by the usual procedure,[31] and treatment with alcoholic potassium acetate.

Anal. Calcd. for $C_{17}H_{18}O_8$: C, 58.3; H, 5.2. Found: C, 58.2; H, 5.0.

The mixed melting point of a 1:1 mixture of methyl benzaldimalonate and the tetracarboxylic methyl ester was 62.5°–63.5°.

The ethyl ester is known.[32] Both methyl and ethyl esters are hydrolyzed and decarboxylated to the same 3-phenylcyclopropane-1,2-dicarboxylic acid,[32] m.p. 174°; neut. equiv. Calcd., 103. Found, 103.

Acknowledgment. We are pleased to acknowledge the technical assistance of A. L. Geddes, for the infrared spectra obtained by using a lithium fluoride prism and of Messrs. W. Blum, J. R. Byers, Jr., and D. D. Reynolds, all of these Laboratories.

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[31] H. Meerwein, *Ann.*, **360**, 344 (1908).

[32] A. Kötz and P. Spiess, *J. prakt. Chem.*, [2], **68**, 163 (1903).