due to free O—H stretching at 3623 cm.$^{-1}$ in lower concentration (less than 0.015*M* in carbon tetrachloride).

Lead tetraacetate cleavage was carried out according to Criegee's method,[19] $K_{20} > 1000$ for VIa and $K_{20} = 9$ for VIb.

Dehydration of VIa *and* VIb. A heterogeneous mixture of VIa (1 g.) and 10% sulfuric acid (10 ml.) was refluxed for 2 hr. The resulting oil was extracted with ether, and the ether layer was washed with water and dried over magnesium sulfate. The ether was removed and the residue was distilled to give a menthone mixture (VII) (yield 800 mg.), b.p. 103–105° (27 mm.), $[\alpha]_D^{20}$ +15° (*c*, 2 in methanol), ketone % = 98.5 (hydroxylamine method). By the same procedure, VIb yielded the same VII (yield 700 mg.).

From VII, the semicarbazone (m.p. 186–187°; yield 45%) and 2,4-dinitrophenylhydrazone (m.p. 145–147°; yield 50%) of (−)-menthone were obtained and no depression of their melting points were observed by admixture with the authentic samples.[20] The infrared spectrum of VII coincided with that of the authentic mixture of (−)-menthone and (+)-isomenthone showing the following absorptions: 1249, 1203, 1094, 1043, 865, 837, 748 (cm.$^{-1}$) for (−)-menthone[21]; and 1227, 1076, 1024, 832, 797, 768 (cm.$^{-1}$) for (+)-isomenthone.[21]

Isomerization of VIb *to* VIa. A solution of VIb (500 mg.) in 50% aqueous acetic acid (5 ml.) containing 1 drop of sulfuric acid was heated under reflux for 1 hr. and extracted with ether. From this extract, an oil was obtained which was a mixture of diols and ketones. The diols were converted to the 3,5-dinitrobenzoates. The ketones were separated from the esters by steam distillation. The esters (250 mg.) were separated by repeated recrystallization from *n*-hexane into mono-3,5-dinitrobenzoate of VIa (50 mg., m.p. 124–125°) and mono-3,5-dinitrobenzoate of VIb (100 mg., m.p. 142–143°). The ketone fraction was identified by infrared spectrum as a menthone mixture.

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KYOTO, JAPAN

(19) R. Criegee, E. Höger, G. Huber, P. Kruck, F. Marktscheffel, and H. Schellenberger, *Ann.*, **599**, 81 (1956).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Alkylation of Bimalonic Ester[1]

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Methyl 1,1,2,2-ethanetetracarboxylate (bimalonic ester) can be alkylated only once, even though it contains two acidic hydrogen atoms. Failure to undergo a second alkylation is a result of steric hindrance. Replacement of both hydrogens when a difunctional alkylating agent is used results because the second step is intramolecular.

Bimalonic ester (I) contains two acidic hydrogen atoms, and replacements of both of these by use of dihalogen compounds have been used in synthesis of several cyclic substances. For example methyl 1,1,2,2-cyclopentanetetracarboxylate (II) has been obtained by alkylation with 1,3-dibromopropane.[2]

I II

Use of monohalogen compounds has often led to low yields of poorly characterized products.[3] But it has now been found that these substances actually react quite satisfactorily, and alkylation products have been obtained using methyl iodide, ethyl iodide, *n*-butyl bromide, allyl bromide, benzyl chloride, and acrylonitrile.

It is interesting that only one of the acidic hydrogens of bimalonic ester can be replaced using these reagents. Even when a large excess of alkylating agent is used or when the monoalkylated product is isolated and treated again, a monoalkylated product is obtained.

Resistance to dialkylation might be caused by low acidity of the monoalkylated bimalonic ester. Attempts to study this factor by the method of Pearson[4] were unsuccessful because of low solu-

(1) From the Ph.D. thesis of John R. Sjolander, August 1950.

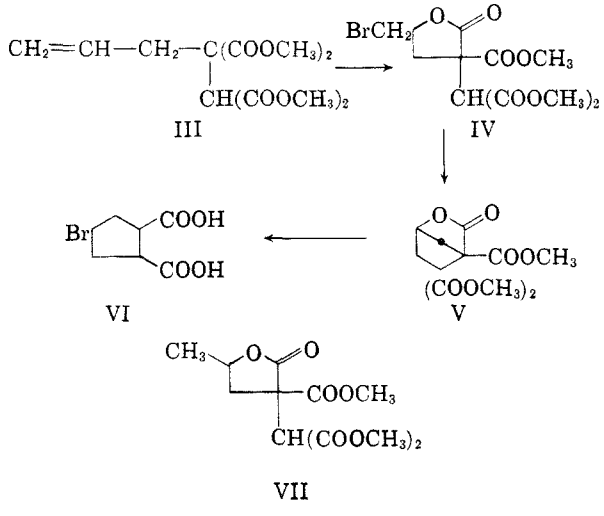
(2) A. Kötz and P. Spiess, *J. prakt. Chem.* **64**, 394 (1901). Other dihalogen compounds which yield the expected cyclic products are methylene iodide (Kötz and Spiess, *loc. cit.*), α,α'-dibromo-*o*-xylene [A. Baeyer and W. H. Perkin, *Ber.*, **17**, 448 (1884); *J. Chem. Soc.*, **53**, 1 (1888)], 2,2′-bisbromomethylbiphenyl [J. Kenner, *J. Chem. Soc.*, **103**, 613 (1913)], ethyl α,β-dibromopropionate [L. J. Goldsworthy and W. H. Perkin, *J. Chem. Soc.*, **105**, 2665 (1914)], ethyl α,β-dibromosuccinate [Y. Schibata, *Ber.*, **43**, 2619 (1910)], α,α'-dichlorodimethylsulfide [F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **123**, 1172 (1923)], β,β'-dibromodiethylether [I. Ali-Zade and B. A. Arbuzov, *J. Gen. Chem., U.S.S.R.*, **13**, 113 (1943); *Chem. Abstr.*, **38**, 352 (1944)]. 1,3-Dibromobutane, once believed to yield ethyl methylcyclopentanetetracarboxylate [R. G. Fargher and W. H. Perkin, *J. Chem. Soc.*, **105**, 1353 (1914)] has been shown to yield only ethyl 2-hexene-5,5,6,6-tetracarboxylate [R. B. Bates, E. J. Eisenbraun, and S. M. McElvain, *J. Am. Chem. Soc.*, **80**, 3413 (1958)].

(3) C. A. Bischoff and C. Rach, *Ber.* **17**, 2788 (1884); *Ann.*, **234**, 54 (1884); A. Baeyer and W. H. Perkin, *J. Chem. Soc.*, 1 (1888); C. A. Bischoff, *Ber.*, **40**, 3150 (1907); F. Bachér, *J. prakt. Chem.*, **120**, 301 (1929); O. Silberad, *J. Chem. Soc.*, 611 (1904).

(4) R. G. Pearson, *J. Am. Chem. Soc.*, **71**, 2212 (1949).

bilities of the compounds involved. But C-ethylbimalonic ester was brominated readily in presence of sodium methoxide, indicating that the ester did form an anion.

It is likely that resistance to dialkylation is simply a result of steric hindrance, for it is well known[5] that even *sec*-alkylated malonic esters are difficult to alkylate, and a monoalkylated bimalonic ester is sterically comparable to a *tert*-alkylated malonic ester. Double alkylation (cyclization) using dihalogen compounds succeeds because the second step in the reaction is intramolecular. Here steric factors are of minor importance, for the reactive centers are in approximately proper position by virtue of the geometry of the molecule. It was possible that cyclizations occurred for another reason: Energy from the first alkylation was not dissipated rapidly but served to activate the molecule for the second step. This possibility has been eliminated by carrying out typical cyclizations in two separate stages. C-Allylbimalonic ester (III) was treated with hydrogen bromide in presence of peroxide,[6] and the resulting γ-bromopropylbimalonic ester was then converted to methyl 1,1,2,2-cyclopentanetetracarboxylate by action of sodium methoxide. C-Allylbimalonic ester was also treated with bromine, and the resulting bromolactone (IV) was similarly cyclized to V. Structure of the latter product was proved by using hydrobromic acid, giving VI, a compound which furnished known *trans*-1,2-cyclopentane dicarboxylic acid when it was dehalogenated with hydrogen in presence of palladium.



EXPERIMENTAL

Bimalonic ester was obtained from methyl malonate, sodium methoxide, and bromine[7] in yields of 70–85%. Alkylations were generally carried out using an excess of both sodium methoxide and halogen compound. For example, 13.1 g. of bimalonic ester was mixed with a solution of 2.3 g. of sodium in 55 ml. of methanol, and then 19 g. of benzyl chloride was added dropwise. The mixture was boiled for 3 hr., then evaporated under reduced pressure, and steam distilled to remove excess benzyl chloride. Crystallization of the organic residue gave pure methyl 3-phenyl-1,1,2,2-propane tetracarboxylate. In all cases the alkylated products were hydrolyzed and decarboxylated by boiling for 12 hr. with excess constant-boiling hydrochloric acid, and the resulting substituted succinic acids (yields 80–90%) were identified by melting point and neutral equivalent. Results of the alkylations are given in Table I.

Acrylonitrile (5 ml.) and a few crystals of quinone were added to a solution of 2.6 g. of bimalonic ester in 15 ml. of *t*-butyl alcohol that had been saturated with potassium hydroxide. The mixture was boiled for 20 hr., then filtered, and diluted with water. Crystallization from methanol, then benzene-ligroin gave 1.2 g. (66%) of pure methyl 4-cyano-1,1,2,2-butane tetracarboxylate, m.p. 84–86°.

Anal. Calcd. for $C_{13}H_{17}NO_8$: C, 49.5; H, 5.44. Found: C, 49.8; H, 5.67.

Hydrolysis of the cyano compound gave β-carboxyadipic acid, crystals, from nitromethane, m.p. 116–118° in agreement with reported values.

Allylbimalonic ester and hydrogen bromide. A solution of 7 g. of allylbimalonic ester in 10 ml. of toluene was cooled to 0° for 45 min. while hydrogen bromide was passed in. The solution was kept at room temperature for a few hours, then warmed under reduced pressure to remove hydrogen bromide and toluene. Trituration with ether-ligroin and crystallization from methanol gave about 4 g. of the *lactone trimethyl ester of 4-hydroxy-1,1,2,2-pentanetetracarboxylic acid,* colorless rhombs m.p. 75–77°. The infrared spectrum showed sharp absorption bands at 1740 (ester) and 1770 cm.$^{-1}$ (five-membered lactone) allowing assignment of structure VII.

Anal. Calcd. for $C_{12}H_{16}O_8$: C, 50.0; H, 5.60. Found: C, 50.3; H, 5.86.

When 12 g. of allyl bimalonic ester in 20 ml. of toluene containing 0.5 g. of benzoyl peroxide was treated with hydrogen bromide in the same way, the product (10 g.) was an oil, b.p. 185–195° at 3–4 mm. A 6.5-g. portion of this γ-bromopropylbimalonic ester was dissolved in 25 ml. of methanol containing 0.4 g. of sodium and boiled for 4 hr. Fractionation of the product gave 1.7 g. of methyl 1,1,2,2-cyclopentanetetracarboxylate, b.p. 155–170° at 3–4 mm., which gave 0.3 g. of *trans*-1,2-cyclopentane dicarboxylic acid, m.p. 157–159° alone or mixed with an authentic sample.

Allylbimalonic ester and bromine. A solution of 8.25 g. of allylbimalonic ester in 50 ml. of chloroform was treated with 4.7 g. of bromine in 25 ml. of chloroform, and the solvent was then removed by distillation. Crystallization of the residue from dilute methanol gave 6.8 g. of the *lactone trimethyl ester of 5-bromo-4-hydroxy-1,1,2,2-pentanetetracarboxylic acid,* colorless rhombs m.p. 87–89°. The infrared spectrum contained absorption bands at 1740 and 1770 cm.$^{-1}$, indicating structure IV.

Anal. Calcd. for $C_{12}H_{15}BrO_8$: C, 39.3; H, 4.12. Found: C, 39.5; H, 4.34.

When 18.5 g. of this bromolactone was boiled with a solution of 1.15 g. of sodium in 25 ml. of methanol for 4 hr., the solution became neutral. There was obtained 3.1 g. of the *lactone trimethyl ester of 4-hydroxy-1,1,2,2-cyclopentane tetracarboxylic acid* (V), long flat needles from water, m.p. 110–112°.

Anal. Calcd. for $C_{12}H_{14}O_8$: C, 50.4; H, 4.93. Found: C, 50.7; H, 5.07.

A solution of 2 g. of V in 25 ml. of 48% hydrobromic acid was boiled for 1 hr., the spent acid was then removed by distillation and replaced with 25 ml. of concd. material. After another hour of boiling, the mixture was concentrated to about 5 ml. and cooled, giving 0.95 g. of *4-bromo-1,2-*

(5) A. C. Cope, W. H. Hartung, E. M. Hancock, and F. S. Crossley, *J. Am. Chem. Soc.*, **62**, 314 (1940).

(6) In absence of peroxide, hydrogen bromide simply causes interaction of the double bond with an ester group. Methyl bromide is eliminated, and VII is formed.

(7) J. Walker and J. R. Appleyard, *J. Chem. Soc.*, **67**, 768 (1895).

TABLE I

ALKYLATION PRODUCTS OF BIMALONIC ESTER, $RC(COOCH_3)_2$ / $CH(COOCH_3)_2$

RX	Yield, %	M.P. (B.p.°/mm.)	Formula	Calcd. C	Calcd. H	Found C	Found H
CH_3I	74	(142–145/5)[a]	$C_{11}H_{16}O_8$	47.8	5.84	47.8	6.14
C_2H_5I	82	54–56 (150/3)	$C_{12}H_{18}O_8$	49.6	6.25	49.5	6.42
n-C_4H_9Br	30[c]	67–70	$C_{14}H_{22}O_8$	52.8	6.97	52.5	7.22
CH_2=$CHCH_2Br$	89[d]	(151/3)[b]	$C_{13}H_{18}O_8$	51.7	6.00	51.8	6.20
$C_6H_5CH_2Cl$	79	98–100	$C_{17}H_{20}O_8$	57.9	5.68	58.0	5.97

[a] n_D^{22} 1.4468. [b] n_D^{25} 1.4589. [c] 50% of bimalonic ester recovered, 11 hr. reaction time. [d] Hydrolysis and decarboxylation using hydrochloric acid gave the known lactone of 4-hydroxy-1,2-pentanedicarboxylic acid, m.p. 66–68°.

cyclopentanedicarboxylic acid (VI), crystals from ether-ligroin, m.p. 146–148°.

Anal. Calcd. for $C_7H_9BrO_4$: C, 35.5; H, 3.83; N.E., 118.5. Found: C, 35.8; H, 4.02; N.E., 120.

Hydrogenolysis of VI (0.6 g.) by shaking with palladium on barium sulfate in water for 3 hr. consumed 85% of the calculated amount of hydrogen and gave 0.18 g. of 1,2-cyclopentanedicarboxylic acid, m.p. 159–160° alone or mixed with an authentic sample.

Bromination of C-ethylbimalonic ester. A solution of 0.23 g. of sodium in 25 ml. of methanol was treated with 2.9 g. of C-ethylbimalonic ester, and then with 1.6 g. of bromine in 16 ml. of methanol, resulting in immediate reaction. Methanol was removed and replaced with ether, and the product was washed with water, and dried. There was obtained 2.88 g. of crude or 1.5 g. of pure methyl 1-bromo-1,1,2,2-butanetetracarboxylate, colorless crystals from dilute methanol, m.p. 106–107°.

Anal. Calcd. for $C_{12}H_{17}BrO_8$: C, 39.0; H, 4.64. Found: C, 39.3; H, 4.97.

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MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Condensed Cyclobutane Aromatic Compounds. XIII. An Attempted Synthesis of 1,2-Diphenylbenzocyclobutene

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The synthesis of 1,3-diphenyl-1,3-dihydroisothianaphthene-2,2-dioxide (IV), starting from *o*-dibenzoylbenzene, is described. Pyrolysis of IV at 250° gives 9-phenyl-9,10-dihydroanthracene (XII), rather than the expected 1,2-diphenylbenzocyclobutene (V). The existence of the intermediary quinodimethane (XV) was demonstrated by a Diels-Alder trapping reaction.

Since the pyrolysis of 1,3-dihydroisothianaphthene-2,2-dioxide (I) yields either benzocyclobutene (II) or 1,2,5,6-dibenzocyclooctadiene (III), depending on the conditions used,[1] the pyrolysis of 1,3-diphenyl-1,3-dihydroisothianaphthene-2,2-dioxide (IV) was investigated as a possible route to 1,2-diphenylbenzocyclobutene (V).

Sulfone IV, m.p. 200–201°, was obtained by the peracetic acid oxidation of the known sulfide, VI.[2] Methods are described in the literature for each of the preceding synthetic steps, *viz.*, the reduction of *o*-dibenzoylbenzene (VII) to 1,3-diphenylisobenzofuran (VIII);[3] the conversion of VIII to 1,3-diphenylisothianaphthene (IX) by phosphorus pentasulfide;[4] and the reduction of IX to the sulfide, VI. However, since we experienced considerable difficulty in obtaining reproducible results in all three of these reactions, modified preparations of VI and IX were developed, and these are reported in the Experimental section In addition, a new method is reported for the conversion of *o*-dibenzoylbenzene (VII) into furan VIII by the partial reduction of VII with potassium borohydride, followed by treatment of the primary reduction product (X) with acid. The success of this procedure is probably due to the tendency of the intermediary ketoalcohol, X, to exist mostly as the phthalan (XI)[5] in the basic reduction medium. Even so, good yields of VIII could be ob-

(1) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959), paper VI of this series.

(2) A. Bistrzycki and B. Brenken, *Helv. Chim. Acta*, **5**, 20 (1922). The precursor of VI (compound IX) is described incorrectly in this paper as "*phenylmesothioanthracendihydrid.*" See ref. 4 for the clarification of this point.

(3) R. Adams and M. H. Gold, *J. Am. Chem. Soc.*, **62**, 56 (1940).

(4) C. Dufraisse and D. Daniel, *Bull. soc. chim.*, [5] **4**, 2063 (1937).

(5) A. Guyot and J. Catel, *Compt. rend.*, **140**, 1348 (1905).