(d) *With dilute sulfuric acid.*[10] The oxime (25 g.) was boiled for 1 hr. with a solution of 5 ml. of 36*N* sulfuric acid in 125 ml. of water and worked up in the manner of the reference cited to give a nitrile indistinguishable in its infrared and proton resonance spectra from that described above. No attempt at isolation of the lactam was made.

Hydrolysis of the nitrile. A mixture of 10 g. of the nitrile derived from the reaction of fenchone oxime with dilute sulfuric acid, 10 g. of potassium hydroxide, 25 ml. of methanol, and 10 ml. of water was heated under reflux for 60 hr. The methanol was removed by distillation at reduced pressure, water (50 ml.) was added, the mixture was cooled to 0°, and the oily solid which precipitated was filtered and recrystallized from benzene–petroleum ether (b.p. 30–60°) to give 4.8 g. (43%) of *dl*-α-fencholenamide as white platelets, m.p. 85–86.5°. An analytical specimen was prepared by sublimation at 100°/1 mm.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.84; H, 10.25; N, 8.38. Found: C, 71.71, 71.75; H, 10.22, 10.43; N, 8.42, 8.51.

Evaporation of the mother liquor from the recrystallization of the amide produced a liquid residue (3.2 g.) which was shown by its infrared spectrum to be largely unchanged starting material containing a small amount of the amide as evidenced by the amide carbonyl band.

The alkaline solution from the hydrolysis was cooled in ice and acidified with hydrochloric acid. The amber liquid which separated was removed and the aqueous phase was extracted with ether. The organic solutions were combined, dried with anhydrous magnesium sulfate, and the solvent was removed by distillation from a steam bath at 10 mm. The crude acidic product obtained in this manner was a viscous yellow-brown oil which was identified as containing largely α-fencholenic acid by the presence of a band for vinyl hydrogen in its proton resonance spectrum and vapor phase chromatography which indicated the crude acid was at least 80% one component.

The crude acid (0.8 g.) was heated under reflux for 2 hr. with 15 ml. of oxallyl chloride. The mixture was concentrated by distillation from the steam bath, and the brown oily residue was treated with 30 ml. of 30% aqueous ammonia to produce a brown solid. This product was twice recrystallized from benzene-petroleum ether (b.p. 30–60°) to give 0.3 g. of slightly yellow platelets identical in infrared spectrum, melting point and mixed melting point with the amide obtained directly from hydrolysis of the nitrile.

The Ritter reaction of the unsaturated nitrile.[13] The nitrile obtained from the above reactions (50 g., 0.33 mole) was added cautiously, with stirring, to 50 ml. of 36*N* sulfuric acid. The mixture was cooled in an ice bath throughout the addition to maintain the reaction temperature below 25°. When the addition of the nitrile was completed, the reaction mixture was allowed to stand in the ice bath for an additional 0.5 hr. and then warmed to room temperature, whereupon the temperature rose spontaneously to 60° and the mixture turned red and foamed slightly. The flask was then stoppered loosely and allowed to stand overnight.

The dark brown resinous mixture was poured into an ice cold solution of 80 g. of sodium hydroxide in 500 ml. of water and the aqueous suspension was extracted four times with a total of 1 l. of ether. The ethereal extract was dried over anhydrous magnesium sulfate and concentrated to dryness to give an oily brown residue which was triturated with petroleum ether (b.p. 30–60°) to remove the unsaturated nitrile.

The crude product was worked up in the usual manner to give 10 g. of unchanged nitrile and *ca.* 0.5 g. of lactam which was shown to be identical with the product obtained directly from the oxime in melting point, mixed melting point, and infrared spectrum. (As in the sulfuric acid catalyzed rearrangement, a large amount of resinous material was formed.)

Dehydration of the lactam.[20] A mixture of 3.24 g. of the lactam, 3.4 g. of phosphorus pentachloride and 35 ml. of petroleum ether (b.p. 30–60°) was allowed to stand for 48 hr. with periodic shaking and then heated for 1 hr. on a steam bath. The mixture was worked up in the manner described for the Beckman rearrangement with phosphorus pentachloride to give 1.9 g. of nitrile which was identical with that derived directly from the oxime in infrared spectrum and inseparable from the latter in vapor phase chromatography.

Acknowledgment. The author wishes to express his thanks to Mr. John A. Ray for assistance with the experimental work, Miss Ruth A. Staszesky for infrared spectra, and Dr. W. D. Phillips for assistance in the interpretation of the proton magnetic resonance data.

WILMINGTON, DEL.

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[20] G. Schroeter, *Ber.*, **44**, 1201 (1911).

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, KYOTO UNIVERSITY]

Synthesis of Two Isomeric *p*-Menthane-3,4-diols and Their Pinacolic Dehydration to a Menthone Mixture[1]

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Two isomeric *p*-menthane-3,4-diols, (+)-*cis*-4-hydroxymenthol (VIa) and (−)-*trans*-4-hydroxyneoisomenthol (VIb), were prepared by lithium aluminum hydride reduction of two isomeric *p*-menthane-4,8-epoxy-3-ols (Va) and (Vb) which were derived from (+)-pulegone. With 10% sulfuric acid, VIa and VIb were dehydrated to a menthone mixture (VII) which was composed of 65% (−)-menthone and 35% (+)-isomenthone.

The pinacolic dehydration of *p*-methane-3,4-diol (VI) to a menthone mixture[2–4] appears to be significant for the industrial production of synthetic menthol, because VI can be easily prepared from

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[1] Presented at the meeting of the Kansai Branch of the Agricultural Chemical Society of Japan, Nara, Japan, October 17, 1959.

[2] S. Tanaka, *J. Chem. Soc. Japan*, **53**, 668 (1932); *Mem. Coll. Sci. Kyoto Univ.*, 22A, 97 (1939).

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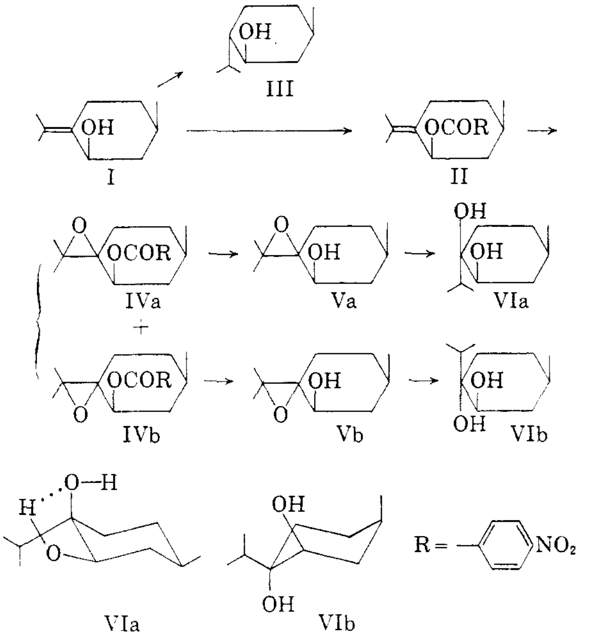
[4] Y. R. Naves, *Helv. Chim. Acta*, **42**, 1174 (1959).

terpinene-1-ol-4,α-terpineol, limonene, or α-pinene via 3-*p*-menthene. According to Klyne,[5] the course of a pinacolic rearrangement depends on whether an axial or an equatorial hydroxyl group is eliminated. Therefore, the information regarding the predominant conformation of isomeric VI may contribute to the understanding of the stereochemistry of the above reaction. From this viewpoint the results hitherto obtained[2-4] are not considered to be satisfactory because of the uncertainty about the relationship between the C_1-methyl group and other substituents in VI.

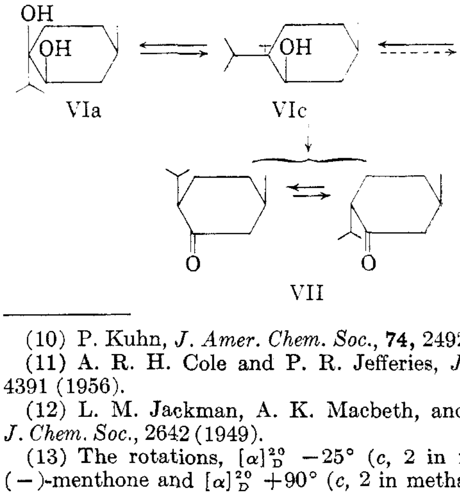
(+)-*cis-4-Hydroxymenthol* (VIa) *and* (−)-*trans-4-hydroxyneoisomenthol* (VIb). Usually VI is prepared by the oxidation of 3-*p*-menthene[2-4,6-8] but this oxidation yields theoretically four geometrical isomers. Consequently the assignment of configuration may be difficult. Another possible route starting from 4-bromomenthone was examined by Jefferies and Milligan[8] but the product was *p*-menthane-2,3-diol.



For the starting compound, we prepared pure (−)-*cis*-pulegol (I), which has a higher melting point and higher optical rotation than reported by Macbeth and Shannon[9] for an impure specimen. Because hydrogenation of I over palladium-charcoal yields quantitatively (−)-menthol (III), the *cis* relationship between the C_1-methyl and C_3-hydroxyl group in I is established. The infrared spectrum indicates that the double bond in I is of the isopropylidene type.[9] Epoxidation of (−)-*cis*-pulegyl-*p*-nitrobenzoate (II) with perbenzoic acid yields two isomeric epoxides (IVa) and (IVb) in the ratio 1:1.3 with traces of triol mono-*p*-nitrobenzoate. The epoxides (IVa)(m.p. 134–135°) and (IVb)(m.p. 128–129°) are hydrolyzed to the corresponding *p*-menthane - 4,8 - epoxy - 3 - ols (Va) (m.p. 73–75°) and (Vb)(an oil) without opening the oxide ring. In ether, IVa is reduced with lithium aluminum hydride to (+)-*cis*-4-hydroxymenthol (VIa)(m.p. 80–81°), whereas IVb resists the reduction giving only Vb. In tetrahydrofuran, however, all of the isomers of IV and V are reduced with lithium aluminum hydride to the corresponding diols, VIa and (−)-*trans*-4-hydroxyneoisomenthol (VIb)(m.p. 75–76°).

The *cis* and *trans* relationships between the two hydroxyl groups in VIa and VIb are determined by the fact that VIa is cleaved faster than VIb with lead tetraacetate. Such relationships are also deduced from the infrared spectra of VIa and VIb in dilute solution (carbon tetrachloride). In VIa an intramolecular hydrogen bonded O—H stretching absorption[10,11] is observed at 3584 cm.$^{-1}$ besides a free O—H stretching absorption at 3636 cm.$^{-1}$, whereas in VIb only the latter absorption is observed at 3623 cm^{-1}. From the absence of hydrogen bonding in VIb, the predominant conformation of VIb is considered as such that the comparatively large isopropyl group takes an equatorial position and this forces the hydroxyl groups to take a diaxial conformation. The isopropyl group in VIa may also take an equatorial conformation, because such conformation seems to be more energetically favored than an axial conformation.

Pinacolic dehydration of VIa and VIb. With 10% sulfuric acid, VIa and VIb are dehydrated to a menthone mixture (VII). The infrared spectrum of VII corresponds to that of a mixture of (−)-menthone and (+)-isomenthone. The composition of VII can be calculated[12,13] from the optical rotation of VII ($[\alpha]_D^{20}$ +15°) as composed of 65%



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(6) G. Wagner, *Ber.*, **27**, 1640 (1894).

(7) H. Hock and S. Lang, *Ber.*, **75**, 300 (1942).

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(10) P. Kuhn, *J. Amer. Chem. Soc.*, **74**, 2492 (1952).

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(12) L. M. Jackman, A. K. Macbeth, and J. A. Mills, *J. Chem. Soc.*, 2642 (1949).

(13) The rotations, $[\alpha]_D^{20}$ −25° (*c*, 2 in methanol) for (−)-menthone and $[\alpha]_D^{20}$ +90° (*c*, 2 in methanol) for (+)-isomenthone, were used for this calculation.

(−)-menthone and 35% (+)-isomenthone. From VII, the semicarbazone and 2,4-dinitrophenylhydrazone of (−)-menthone are isolated. The corresponding derivatives of (+)-isomenthone are not obtained.

According to Klyne,[5] *trans* geometry between a departing and a migrating group determines the reaction course of the pinacolic dehydration of cyclohexane diols. But such *trans* geometry is not possible in the dehydration of VIb to VII. The present result can be explained well by assuming an intermediate carbonium ion,[14,15] which is logical as VIb is partly isomerized into VIa in aqueous acetic acid. Both VIa and VIb would form the same carbonium ion (VIc), which would rearrange to (−)-menthone or to (+)-isomenthone. In this case, the preponderance of (−)-menthone does not necessarily mean that the rearrangement of VIc is favored with the formation of (−)-menthone, because an equilibration will occur between two isomeric menthones in acid media and (−)-menthone will dominate in the equilibration mixture.[16]

EXPERIMENTAL[17]

(−)-cis-Pulegol (I) *and (−)-cis-pulegyl-p-nitrobenzoate* (II).[9] (+)-Pulegone [isolated from pennyroyal oil as a sodium sulfite addition compound, b.p. 80° (4 mm.), $[\alpha]_D^{19}$ +22.8° (homogeneous)] was reduced with lithium aluminum hydride in anhydrous ether to give a crude pulegol mixture which was then converted to the *p*-nitrobenzoate. The ester was repeatedly recrystallized from petroleum ether (b.p. 40–60°) to give II (yield 60%), m.p. 60–61°, $[\alpha]_D^{20}$ −110° (*c*, 2 in chloroform) (reported[9]: $[\alpha]_D^{20}$ −104°), and this was then hydrolyzed (by the potassium hydroxide–methanol-ether method[9]) to give I, b.p. 84–85° (3 mm.), m.p. 34–35°, $[\alpha]_D^{20}$ −104° (*c*, 2 in methanol) (reported[9]: $[\alpha]_D^{18}$ −85°). The yield of *trans* isomer separated as the 3,5-dinitrobenzoate (m.p. 102–103°) was lower than 10%.

Hydrogenation of I. Hydrogenation of I over 10% palladium-charcoal in methanol yielded crude (−)-menthol (III) (yield 93%), $[\alpha]_D^{20}$ −45° (*c*, 2 in methanol). The crude product gave (−)-menthyl-3,5-dinitrobenzoate (yield 90%), m.p. 154–155°, and no depression of the melting point was observed by admixture with the authentic sample.[18]

Epoxidation of II *with perbenzoic acid*. Into a cold solution of II 83 g. (0.274 mole) in chloroform (100 ml.) was added dropwise under stirring the chloroform solution of perbenzoic acid (590 ml., containing the peracid, 0.270 mole), and then the reaction mixture was left for 20 hr. at room temperature. This reaction mixture was washed with 10% sodium carbonate and water, dried over magnesium sulfate, and then the solvent was removed. The resulting crude crystals (m.p. 85–105°) were separated into three fractions by repeated recrystallization from *n*-hexane.

The first fraction (IVa) was the *p*-nitrobenzoate of *p*-menthane-4,8-epoxy-3-ol, hardly soluble in hot *n*-hexane and stout yellow rods, m.p. 134–135°, $[\alpha]_D^{20}$ −65° (*c*, 2 in chloroform), yield 30 g.

Anal. Calcd. for $C_{17}H_{21}O_5N$: C, 63.93; H, 6.63; N, 4.39. Found: C, 64.13; H, 6.67; N, 4.09.

The second fraction (IVb) was an isomer of IVa, soluble in hot *n*-hexane and pale yellow needles, m.p. 128–129°, $[\alpha]_D^{20}$ −16° (*c*, 2 in chloroform), yield 40 g.

Anal. Found: C, 63.78; H, 6.72; N, 4.69.

The third fraction was the mono-*p*-nitrobenzoate of *p*-methane-3,4,8-triol, insoluble in hot *n*-hexane, m.p. 151–153° (recrystallized from methanol), yield 3 g.

Anal. Calcd. for $C_{17}H_{23}O_6N$: C, 60.51; H, 6.87; N, 4.15. Found: C, 60.93; H, 6.88; N, 4.10.

p-Menthane-4,8-epoxy-3-ols (Va) *and* (Vb). The epoxides IVa and IVb were hydrolysed (by the potassium hydroxide–methanol-ether method[9]) to the corresponding *p*-menthane-4,8-epoxy-3-ols (Va) and (Vb), yield 90%.

Va, colorless needles, was recrystallized from petroleum ether (b.p. 40–60°), b.p. 103–105° (6 mm.), m.p. 73–75°, $[\alpha]_D^{20}$ +34° (*c*, 2 in methanol).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.42; H, 10.64.

Vb was an oil, b.p. 103–106° (6 mm.), $[\alpha]_D^{20}$ +1° (*c*, 2 in methanol).

Anal. Found: C, 69.90; H, 10.65.

Reduction of IVa, IVb, Va, *and* Vb *with lithium aluminum hydride*. a). *In anhydrous ether*. Because IVa is slightly soluble in ether, IVa (4 g.) was placed in a continuous extractor and transferred to a stirred suspension of lithium aluminum hydride (2 g.) in anhydrous ether (200 ml.). The reflux of ether was regulated to avoid a vigorous reaction. The reaction mixture was stirred 4 hr., then decomposed with water, and filtered. The red ethereal filtrate was dried over magnesium sulfate, the solvent was removed, and the residue was distilled to give pale red camphorous crystals (1.8 g.), b.p. 135–137° (16 mm.). This crude product was recrystallized from petroleum ether (b.p. 40–60°) to give colorless needles, (+)-*cis*-4-hydroxymenthol (VIa), m.p. 80–81°, $[\alpha]_D^{20}$ +13° (*c*, 2 in methanol).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.51; H, 11.76.

Mono-3,5-dinitrobenzoate, m.p. 124–125°, was recrystallized from *n*-hexane.

Anal. Calcd. for $C_{17}H_{22}O_7N_2$: C, 55.73; H, 6.05. Found: C, 55.62; H, 6.23.

VIa showed three infrared absorptions due to O—H stretching at 3636 cm.$^{-1}$, 3584 cm.$^{-1}$, and 3527 cm.$^{-1}$ in higher concentration, but in lower concentration (less than 0.015*M* in carbon tetrachloride) the latter absorption (3527 cm.$^{-1}$) disappeared.

Under the same reduction conditions, IVb yielded only Vb.

b). *In anhydrous tetrahydrofuran*. IVa, IVb, Va, and Vb were all reduced to the corresponding diols, VIa and (−)-*trans*-4-hydroxyneoisomenthol (VIb). As an example, the reduction of Vb is described.

A solution of Vb (7 g.) in anhydrous tetrahydrofuran (50 ml.) was dropped into the stirred suspension of lithium aluminum hydride (2 g.) in anhydrous tetrahydrofuran (50 ml.) and this was refluxed for 3 hr. After decomposition with water, the reaction mixture was filtered and concentrated under reduced pressure. The resulting oil was dissolved in ether and the ether solution was washed with water and dried over magnesium sulfate. From this ether solution, VIb (5.8 g.) was obtained, b.p. 106–108° (2 mm.), m.p. 75–76° (recrystallized from petroleum ether (b.p. 40–60°)), $[\alpha]_D^{20}$ −6° (*c*, 2 in methanol).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.61; H, 11.90.

Mono-3,5-dinitrobenzoate, m.p. 143–144°, was recrystallized from *n*-hexane.

Anal. Calcd. for $C_{17}H_{22}O_7N_2$: C, 55.73; H, 6.05. Found: C, 55.83; H, 5.92. VIb showed only one infrared absorption

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(15) R. F. Brown, J. B. Nordmann, and M. Madoff, *J. Amer. Chem. Soc.*, **74**, 432 (1952).

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(17) All melting and boiling points were uncorrected.

(18) H. Ueda and T. Mitsui, *J. Agr. Chem. Soc. Japan*, **28**, 945 (1954).

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

Acknowledgment. The authors wish to express their sincere thanks to Dr. T. Hashizume, Messrs. Z. Kumazawa, and T. Fujita of Kyoto University, Kyoto, Japan, for their helpful suggestions.

KYOTO, JAPAN

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

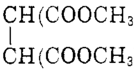
Alkylation of Bimalonic Ester(1)

C. F. KOELSCH AND J. R. SJOLANDER

Received March 7, 1960

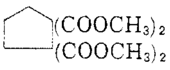
Methyl 1,1,2,2-ethanetetracarboxylate (bimalonic ester) can be alkylated only once, even though it contains two acidic hydrogen atoms. Failure to undergo a second alkylation is a result of steric hindrance. Replacement of both hydrogens when a difunctional alkylating agent is used results because the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



$$\begin{array}{l}\mathrm{CH(COOCH_3)_2}\\ |\\ \mathrm{CH(COOCH_3)_2}\end{array}$$

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-

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(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)].

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