

Guaiacol thiolacetate. Thioguaiacol was prepared from the diazonium salt of *o*-anisidine and potassium ethyl xanthogenate according to Mauthner.¹⁰ The mercaptan (7.3 g.) was allowed to react with acetyl chloride (3.8 ml.). A large excess of pyridine (15 ml.) was added and the mixture added to water and ice. Carbonate was added, the oil was collected, washed several times with water, dissolved in ethyl ether, the ethereal solution was dried, and the ether distilled off. The oily residue was twice distilled, b.p. (0.1 mm.) 101°. The compound is a liquid, colorless when pure; it gives a positive reaction of Raschig-Feigl.

Anal. Calcd. for C₉H₁₀O₂S: C, 58.21; H, 5.53; S, 17.58. Found: C, 58.40; H, 5.77; S, 17.77.

When the present work was in progress this thiolester was described by Charonnat and Lazelari¹¹ who report b.p. (15 mm.) 145°. However their sample was reported as being yellowish and, therefore, probably was not very pure.

Guaiacol benzoate was prepared by condensation of benzoyl chloride and guaiacol in the presence of pyridine. The mixture was treated with water, the product collected, and washed with alkali, acid, and water. The ester was twice recrystallized from methanol, m.p. 58–59°. Reported m.p. 57–58°.¹²

Guaiacol thiolbenzoate was prepared in a way similar to that used for guaiacol benzoate. This new compound is a colorless solid, which melts at 105.5–106.5°.

Anal. Calcd. for C₁₄H₁₂O₂S: C, 68.82; H, 4.95; S, 13.12. Found: C, 68.71; H, 4.99; S, 12.70.

Absorption measurements were carried out as in an earlier paper.^{1c}

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(10) F. H. Mauthner, *Ber.*, **39**, 1347 (1906).

(11) R. Charonnat and I. Lazelari, *Compt. rend.*, **238**, 119 (1954).

(12) Lange's Handbook of Chemistry, 5th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1944.

On Darling's Cyclopropene Derivative and Its Rearrangement¹

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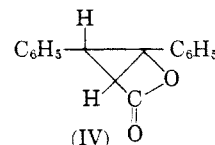
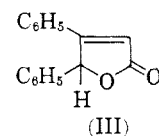
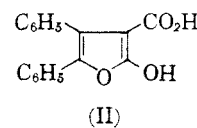
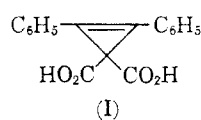
Few authentic cyclopropene derivatives are known, and the erroneous attribution of cyclopropene structures to some substances, such as Feist's acid,² seems to have led to a general distrust of all cyclopropene assignments in the earlier literature. We wish to report that the 1,2-diphenylcyclopropene-3,3-dicarboxylic acid structure (I)

(1) Part of this work was first presented at the 132nd Meeting of the American Chemical Society, New York, September 1957.

(2) See, for instance, A. S. Kende, *Chem. & Ind. (London)*, 544 (1956).

assigned by Darling³ to a compound obtained by him from vigorous alkaline treatment of a nitro-cyclopropane compound is indeed correct, and that the substance is a member of a group of rather stable derivatives of the strained cyclopropene molecule.

We have prepared Darling's compound by an alternate route, utilizing the reaction of diphenylacetylene with diazomalonic ester. After hydrolysis, an acid was obtained which melted at 205° (dec.) [Darling reports³ "about 190° (dec.)"]. As confirmation of the identity of the two substances we have prepared the dimethyl ester, m.p. 143–143.5° (reported³ 140–142°), and its dibromide, m.p. 197–198° (reported³ 194–195°). In addition, we find that the lactone from thermal decomposition of the acid has m.p. 149–151° (reported³ 149–151°).



One of the key bits of evidence offered by Darling for the cyclopropene structure was the formation of dibenzoylmethane on oxidation, which we have confirmed. Although this would seem to leave no room for doubt, more or less reasonable arguments, which will not be detailed here, can be made for the possibility of structure II. This, apparently the only alternative to Darling's structure, is however in poor agreement with some of the experimental facts and is completely ruled out by our finding that the corresponding Δ¹-1,2-diphenylcyclopropene monocarboxylic acid, m.p. 209.5–211.5° (dec.), prepared from reaction of diazoacetic ester and diphenylacetylene, followed by alkaline hydrolysis, has an ultraviolet spectrum which is virtually identical with that of the dicarboxylic acid; the two compounds thus have similar structures. On the alternative basis its structure would have to be that of III or a tautomer, which is of course a neutral lactone.

We have prepared⁴ III and find that it is in fact identical with the neutral lactone, m.p. 149–151°, which results from pyrolysis of the cyclopropene diacid. Darling had rejected this structure in favor of IV on the basis that the hydrolysis product was not an olefin, but it is known⁵ that in base III is hydrolyzed to desylacetic acid.

The diphenylcrotonolactone III is also formed on pyrolysis of the cyclopropene monocarboxylic acid; these rearrangements are readily formulated

(3) S. F. Darling and E. W. Spanagel, *J. Am. Chem. Soc.*, **53**, 1117 (1931).

(4) J. Thiele and F. Straus, *Ann.*, **319**, 155 (1901).

(5) J. Thiele, *Ann.*, **306**, 194 (1899).

on a mechanistic basis, and presumably derive part of their driving force from the relief of ring strain. It is interesting, however, that under many other conditions the cyclopropene system in these compounds is remarkably stable. Thus, refluxing an ester of the monoacid with potassium *t*-butoxide in *t*-butyl alcohol for 60 hr. leaves the cyclopropene system intact,⁶ and even in acid, to which it is more sensitive, the compound is unaffected by 40% sulfuric acid in methanol at room temperature or by refluxing *N* methanolic sulfuric acid, although more vigorous conditions cause rearrangement to III. The stability of these compounds, which results from the heavy conjugating substitution, suggests that related cyclopropene derivatives should also be readily preparable.⁷

EXPERIMENTAL

Diphenylcyclopropenedicarboxylic acid (I). A mixture of 17 g. of diphenylacetylene with 1 g. of electrolytic copper dust was heated at 125° with stirring. Diazomalonic ester⁸ (9.3 g.) was added over 1.5 hrs. and the reaction was continued until N₂ evolution had ceased. After solution in ether and filtering, the solvent was removed and the mixture directly hydrolyzed by refluxing for 90 min. with 30 g. KOH in 200 ml. of methanol. After dilution and recovery of the diphenylacetylene by extraction the solution was acidified and the product collected with chloroform. Percolation of the extract through Florex and removal of the solvent yielded 1.5 g. of the acid after crystallization from ether/petroleum ether; m.p. 205° (dec.).

Anal. Calcd. for C₁₇H₁₂O₄: C, 72.85; H, 4.32. Found: C, 73.32; H, 4.37.

In the infrared the compound showed carbonyl absorption at 5.98 μ. In the ultraviolet spectrum it showed maxima at 306, 315, and 225 mμ (log ε 4.48, 4.38, and 4.30, respectively).

The dimethyl ester of (I) was prepared with diazomethane. Crystallized from ether/petroleum ether it had m.p. 143–143.5°.

Anal. Calcd. for C₁₉H₁₆O₄: C, 74.04; H, 5.23; mol. wt., 308. Found: C, 74.26; H, 5.30; mol. wt. (Rast, camphor), 297, 290.

In the infrared the compound absorbs at 5.90 and 5.98 μ. The ultraviolet spectrum shows maxima at 306, 322, 225, and 230 mμ (log ε 4.48, 4.40, 4.11, and 4.08 respectively).

The diester dibromide was prepared from the above compound by Darling's procedure,³ m.p. 197–198°.

Anal. Calcd. for C₁₉H₁₆O₄Br₂: Br, 34.2. Found: Br, 34.19.

The compound showed absorption in the ultraviolet at 220 mμ, (log ε_{max} 3.9). The dibromide was not affected by treatment with potassium permanganate solution in acetone at room temperature.

The neutral lactone (III). This compound, prepared by melting (I) according to Darling,³ had m.p. 149–151°; in the infrared it had a strong band at 5.77 μ, and in the ultraviolet it absorbed at 272 mμ (log ε 4.26), and had strong end absorption.

α,β -Diphenylcrotonolactone was prepared by the method of Thiele.⁴ The m.p. of 150–152° (reported 152°) was undepressed on mixture with the above lactone, and their infrared and ultraviolet spectra were identical in all respects.

1,2-Diphenylcyclopropene-3-carboxylic acid was prepared in a similar manner to that of the dicarboxylic acid, but the

ethyl diazoacetate was added dropwise to the diphenylacetylene at 135–140° over 2.5 hr. The product, crystallized from acetone, had m.p. 209–211° (dec.) (23% yield).

Anal. Calcd. for C₁₆H₁₂O₂: C, 81.33; H, 5.12. Found: C, 81.29; H, 5.27.

The ultraviolet spectrum of the compound had maxima at 306, 323, 225, and 232 mμ (log ε 4.52, 4.42, 4.34, and 4.28 respectively). On heating at 220–230°, the acid was converted to (III), m.p. 149–152° (20% yield), as evidenced by identity of spectra.

The methyl ester, m.p. 83–85°, had maxima in the ultraviolet at 306, 323, 224, and 232 mμ (log ε 4.53, 4.42, 4.34, and 4.29 respectively). This spectrum was unaffected by refluxing with 1 *N* sulfuric acid in methanol for 24 hr. or by standing with 40% methanolic sulfuric acid for 12 hr., although on refluxing of this latter solution for 19 hr the compound was converted into (III), m.p. 152–154°, in 40% yield. Both the monoacid and its methyl ester show the expected carbonyl absorption in the infrared.

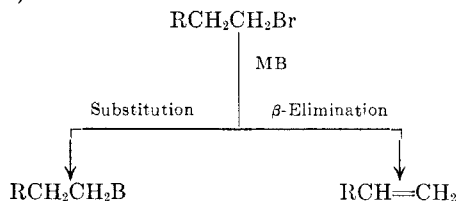
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Influence of Metallic Cation on Substitution versus Elimination Reactions of Alkyl Halides with Alkali Bases¹

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An alkyl halide may undergo with an alkali base (MB) the substitution and β -elimination reactions,



Although variations in the basic strength of the anion B⁻ are known to influence the relative extents of these two courses of reaction,³ variations in the metallic cation associated with the basic anion in alcohol appears to have no appreciable effect on the two courses. Thus, no significant difference in the ratio of the substitution and elimination products was observed by Newman and Evans⁴ on treatment of 2-ethylhexyl bromide with lithium, sodium, and potassium ethoxides in ethanol solution.

However, differences in the ratio of the two types of products have been observed on varying the alkali cation associated with certain stronger

(1) Supported by a grant from the Duke University Research Council.

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(3) See C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, pp. 451–452; E. E. Royals, *Advanced Organic Chemistry*, Prentice-Hall, Inc., New York, N. Y., 1954, p. 299.

(4) M. S. Newman and F. J. Evans, Jr., *J. Am. Chem. Soc.*, **76**, 4187 (1954).

(6) R. Breslow and M. Battiste, *Chem. & Ind. (London)*, 1143 (1958).

(7) For one example, cf. R. Breslow, *J. Am. Chem. Soc.*, **79**, 5318 (1957).

(8) H. Lindemann, A. Wolter, and R. Groger, *Ber.*, **63**, 702 (1930).