filtrate was washed successively with dilute hydrochloric acid, dilute sodium bicarbonate solution, and water, and the solvent was evaporated. The orange residue (0.307 g.) was chromatographed over alumina (10 g.) and eluted in 12 fractions of 25 ml. each with solvents ranging from hexane–benzene (1:1) through benzene. Fractions 1–7 when pooled had m.p. 173.5–176° (0.191 g., 59%). The infrared spectra (in carbon disulfide) of the pooled material (and of individual fractions) were identical with that of authentic diacetate of phenol **17** and showed no allyl absorptions in the 995- or 920-cm.$^{-1}$ regions. Fraction 9 (0.004 g., eluted with benzene) was dissolved in a small amount of hexane, stood overnight in the refrigerator, and yielded pale yellow crystals (m.p. 172–174°) whose infrared spectrum lacked absorption at 1754 (ester carbonyl) but had bands at 1658, 1639, 995, 929, 917, 760, and 750 cm.$^{-1}$. The ultraviolet absorption in 95% ethanol was complex: λ 227 mμ (ϵ 11,700, based on a molecular weight of 362), 254 (25,700), 290 (12,600), 337 (3200), and 346 (4000). Lack of material precluded further investigation of this minor product.

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Proximity Effects in the Decomposition of Mixed Dicarboxylic–Carbonic Anhydrides

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The preparation and properties of bis(ethylcarbonic)dicarboxylic anhydrides (I) derived from a variety of dicarboxylic acids have been investigated. There is a strong tendency for these to decompose into cyclic anhydride (path A) when a five- or six-membered ring can form. When this condition is not met, the bis(ethylcarbonic)dicarboxylic anhydrides are generally stable at room temperature although a few cases of decomposition into diester *via* path B have been noted.

It has been shown that mixed carboxylic–carbonic anhydrides prepared from a monocarboxylic acid and ethyl chlorocarbonate are surprisingly stable in a number of cases.[2] These mixed anhydrides have been isolated, the course of their heat-induced decomposition has been established, and the reaction products have been characterized.[3]

We now have found that there is a consistent pattern in the stability of bisethylcarbonic anhydrides (I) derived from a variety of dicarboxylic acids. When the carboxyl groups of the diacid are sufficiently separated, the mixed anhydrides are quite stable at ordinary laboratory conditions and are analogous to the stable, mixed anhydrides of aliphatic and aromatic monocarboxylic acids studied earlier. However, when the carboxyl groups are close together, the mixed anhydrides are not stable under these same conditions and decompose spontaneously into the cyclic anhydride (II) of the dicarboxylic acid (path A). In a few cases where the carboxylic–carbonic groups were of intermediate propinquity and cyclic anhydride formation unlikely, decomposition into diester (III) according to path B occurred. This type of carboxylic–carbonic anhydride decomposition has been observed previously.[3] As we were interested only in the factors influencing the spontaneous formation of cyclic anhydrides (path A), the course of the heat-induced decomposition of those mixed anhydrides stable at room temperature and details of ester formation *via* path B were largely ignored. (See Fig. 1.)

Throughout this investigation a standard experimental procedure, similar to the one reported previously (see ref. 3c), was used in the preparation of the bis(ethylcarbonic)dicarboxylic anhydrides (I). This involved the reaction of the diacid with ethylchlorocarbonate in tetrahydrofuran at 0 to −10° using triethylamine as a hydrogen chloride acceptor and isolating the reaction products under conditions such that the temperature was never allowed above 25°. The stability of the bis(ethylcarbonic)dicarboxylic anhydride, when it did not spontaneously decompose, was determined by allowing it to stand at room temperature and noting the evolution of carbon dioxide and by periodic examination of its infrared spectrum.

The bis(ethylcarbonic)dicarboxylic anhydrides derived from suberic and sebacic acids [R = $(CH_2)_6$ and $(CH_2)_8$] were stable at room temperature for 20 days and behaved as typical stable mixed anhydrides of monocarboxylic acids. On the other hand, bis(ethylcarbonic)succinic anhydride [R = $(CH_2)_2$] was quite unstable under these same conditions and only cyclic anhydride, in 80% yield, was isolated. Bis(ethylcarbonic)glutaric anhydride [R = $(CH_2)_3$] was only moderately stable as shown by its slow decomposition after 2 days into a 55% yield of cyclic glutaric anhydride. Bis(ethylcarbonic)adipic anhydride [R = $(CH_2)_4$] proved to be considerably more stable than either the succinic or glutaric derivatives. For 10 days it remained unchanged, then carbon dioxide began to evolve. After 14 days about 50% diethyl adipate, together with polymeric anhydrides, were present.

Bis(ethylcarbonic)terephthalic anhydride (R = p-C_6H_4–) was stable at room temperature but bis(ethylcarbonic)phthalic anhydride (R = o-C_6H_4–) decomposed on isolation to give a 75% yield of phthalic anhydride.

A study of two pairs of dicarboxylic acids derived from bicyclo[2.2.2]octane and bicyclo[2.2.2]octene (IV and VI, R = H) gave added evidence to the importance of the proximity of the carboxyl groups in determining the course of the decomposition of their bis(ethylcarbonic)dicarboxylic anhydrides. In the two

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[2] D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, **23**, 1149 (1958).

[3] (a) T. B. Windholz, *ibid.*, **23**, 2044 (1958). (b) D. S. Tarbell and F. J. Longosz, *ibid.*, **24**, 774 (1959). (c) T. B. Windholz, *ibid.*, **25**, 1703 (1960). (d) For important contributions toward the understanding of the mechanisms involved, see F. J. Longosz and D. S. Tarbell, *ibid.*, **26**, 2161 (1961); C. J. Michejda, D. S. Tarbell, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **84**, 4113 (1962).

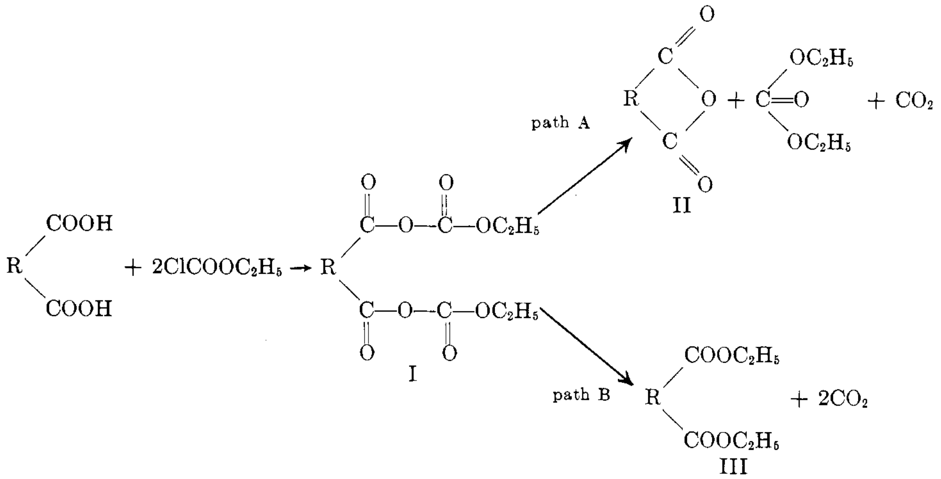

Figure 1.

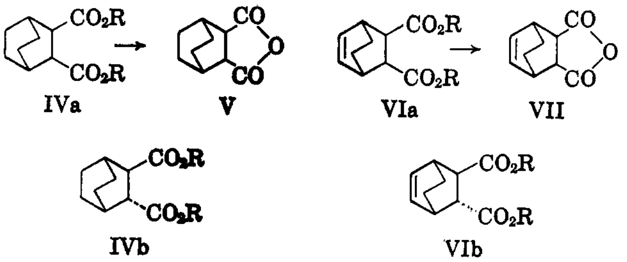

Figure 2.

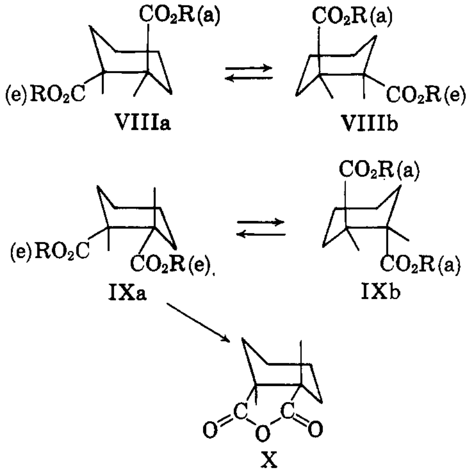

Figure 3.

cases where the carboxyl groups are *cis* (IVa and VIa, R = H) and consequently close to each other, the mixed anhydrides (IVa and VIa, R = $CO_2C_2H_5$) decomposed spontaneously into good yields of cyclic anhydrides (V and VII). As was expected, no cyclic anhydrides resulted from the *trans*-mixed anhydrides (IVb and VIb, R = $CO_2C_2H_5$). The saturated, *trans*-mixed anhydride (IVb, R = $CO_2C_2H_5$) was isolated and proved to be stable at room temperature. The unsaturated analog (VIb, R = $CO_2C_2H_5$), however, decomposed spontaneously according to path B to give the corresponding diethyl ester (VIb, R = C_2H_5). This difference in behavior is not fully understood. (See Fig. 2.)

The above results indicate that there is a strong tendency for bis(ethylcarbonic)dicarboxylic anhydrides to decompose according to path A whenever a five- or six-membered cyclic anhydride can form. When this condition is not met, the mixed anhydrides are either stable or decompose according to path B to give the corresponding diethyl esters.

The great effect that the proximity of dicarboxylic acid groups exerts on the stability of their mixed anhydrides was demonstrated using *cis*- and *trans*-cyclohexane-1,2-dicarboxylic acid. *cis*-Bis(ethylcarbonic)-cyclohexane-1,2-dicarboxylic anhydride (VIII, R = $CO_2C_2H_5$) was stable for 10 days but *trans*-bis(ethylcarbonic)cyclohexane-1,2-dicarboxylic anhydride (IX, R = $CO_2C_2H_5$) decomposed spontaneously into a 75% yield of cyclic *trans*-cyclohexane-1,2-dicarboxylic anhydride (X) (see Fig. 3).

The stability of the *cis* mixed anhydride (VIII, R = $CO_2C_2H_5$) can probably be explained by the steric disposition of the reacting anhydride groups. In the known conformational equilibrium (VIIIa $\leftrightarrows$ VIIIb), the reactive groups are probably far enough apart to confer reasonable stability to the molecule.

The case of the *trans* mixed anhydride is somewhat more complicated. If we again assume the same sort of conformational equilibrium (IXa $\rightleftarrows$ IXb) for the mixed anhydride, it can be seen that form IXa brings the anhydride groups close together, thus permitting decomposition into cyclic anhydride X to occur readily. This would require preference for an equatorial–equatorial disposition, and such an arrangement has generally been discounted with regard to 1,2-*trans*-cyclohexanedicarboxylic acids and their derivatives.[4] Nevertheless, we feel that decomposition of form IXa to X offers a reasonable explanation for the results observed.

Experimental

All melting points are corrected. Microanalyses are by Mr. Grant Gustin of our analytical department. Infrared spectra were determined with a Perkin-Elmer Infracord, Model 137. Aliphatic dibasic, phthalic, and terephthalic acids were commercially available materials. *cis*- and *trans*-Cyclohexane-1,2-dicarboxylic acid were prepared according to Smith.[5] The bicyclo[2.2.2]octane- and bicyclo[2.2.2]octenedicarboxylic acids

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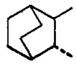
[4] (a) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 20; (b) H. A. Smith, *J. Am. Chem. Soc.*, **78**, 4000 (1956); (c) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., 1959, p. 243; (d) see, however, N. B. Chapman, J. Shorter, and K. J. Toyne, *J. Chem. Soc.*, 2543 (1961).

[5] H. A. Smith and F. P. Byrne, *J. Am. Chem. Soc.*, **72**, 4406 (1950), and ref. 4b.

TABLE I

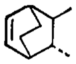
BIS(ETHYLCARBONIC)DICARBOXYLIC ANHYDRIDES
STABLE AT ROOM TEMPERATURE
$C_2H_5OCOOCORCOOCOOC_2H_5$

R	Infrared bands, cm.$^{-1}$	Derivative, m.p., °C.
$(CH_2)_6$	1835, 1767	Dianilide, 198[a,b]
$(CH_2)_8$	1850, 1781	Dianilide, 185–186[b,c]
p-C_6H_4	1810, 1748	Dianilide, 333–335[b,d]
	1780, 1730	Dianilide, 272–273[e]

[a] C. R. Barnicoat, *J. Chem. Soc.*, 2927 (1927); m.p. 200°. [b] The diethyl ester was also prepared by the directed decomposition of the mixed anhydride using boron trifluoride etherate as previously described (ref. 3c). In each case the infrared spectrum was identical with that of authentic diethyl ester. [c] See ref. *a;* m.p. 182°. *Anal.* Calcd. for $C_{20}H_{24}N_2O_2$: N, 8.95. Found: N, 8.88. [d] K. W. Rosenmund and F. Zetzsche, *Ber.*, **54**, 2892 (1921); m.p. 334–337°. [e] *Anal.* Calcd. for $C_{22}H_{26}N_2O_2$: N, 8.06. Found: N, 7.95.

TABLE II

BIS(ETHYLCARBONIC)DICARBOXYLIC ANHYDRIDES
OF INTERMEDIATE STABILITY

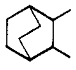
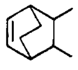
R	Infrared bands, cm.$^{-1}$	Stability	Dec. product (%)
$(CH_2)_3$	1812, 1761	2 days	Glutaric anhydride (55) m.p. 56°
$(CH_2)_4$[a]	1827, 1776	10–14 days	Diethyl adipate (50), b.p. 244°,[b,c] plus mixture of anhydrides
cis-C_6H_{10}	1810, 1775	10 days	Complex mixture containing no anhydride
	1815, 1755	1 day	Diethyl ester[b]

[a] The freshly prepared mixed anhydride was decomposed with boron trifluoride etherate to give 85% diethyl adipate and the theoretical amount of CO_2, according to path B. [b] The infrared spectra of these esters were identical with that of authentic diethyl esters. [c] Dianilide, m.p. 241° [E. Bödtker, *Ber.*, **39**, 2765 (1906); m.p. 240°].

were prepared according to Diels and Alder,[6] Alder and Stein,[7] and Clements.[8]

TABLE III

BIS(ETHYLCARBONIC)DICARBOXYLIC ANHYDRIDES
SPONTANEOUSLY DECOMPOSING INTO CYCLIC ANHYDRIDES

R	Cyclic anhydride, % (m.p., °C.)
$(CH_2)_2$	Succinic, 80 (119)[a]
o-C_6H_4–	Phthalic, 71 (130)[a]
$trans$-C_6H_{10}	*trans*-Cyclohexane-1,2-dicarboxylic, 74 (140–141)[a,b]
	Bicyclo[2.2.2]octane-2,3-dicarboxylic, 76 (187–188)[a,c]
	Bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic, 80 (147–148)[a,d]

[a] Mixture melting point with authentic material was not depressed. [b] Authentic material by A. Baeyer, *Ann.*, **258**, 145 (1890). [c] Authentic material by O. Diels and K. Alder, *Ann.*, **478**, 137 (1930). [d] Authentic material by O. Diels and K. Alder, *ibid.*, **460**, 98 (1928).

General Procedure.—To a cold, stirred solution of 0.010 mole of dibasic acid, 0.022 mole of dry triethylamine, and 25 ml. of dry tetrahydrofuran, was slowly added a cold solution of 0.021 mole of ethyl chlorocarbonate in 10 ml. of tetrahydrofuran. The reaction temperature was controlled at 0 to −10° during the addition and for a further 45 min. The separated triethylamine hydrochloride was filtered, washed with cold tetrahydrofuran, and dried. At least 95% of the theoretical amount was recovered in all cases. The filtrate was evaporated under reduced pressure using no external heat. In cases where the bis(ethylcarbonic)-dicarboxylic anhydrides were stable, the resulting oils were characterized by infrared absorption. A few diethyl esters were prepared by boron trifluoride etherate induced decomposition,[3c] and a few anilides were prepared[3b] for further characterization.

In cases where the cyclic anhydrides formed spontaneously, the resulting crystalline mush was triturated with petroleum ether (b.p. 40–60°) and the solid was filtered and dried. In cases where the mixed anhydrides were of intermediate stability the resulting oils were characterized by infrared absorption and the course of their decomposition was followed by this means. In many cases the ultimate product (ester or cyclic anhydride) was identified by physical constants. Pertinent data are collected in Tables I, II, and III. Because of solubility difficulties, tetrahydrofuran could not be used to prepare the mixed anhydride of terephthalic acid. Chloroform was the solvent in this case and the triethylamine hydrochloride was removed by washing with water. The chloroform solution was dried over sodium sulfate, then worked up as above.

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(6) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

(7) K. Alder and G. Stein, *ibid.*, **514**, 1 (1934).

(8) J. B. Clements, *J. Org. Chem.*, **26**, 2595 (1961).