water at 25° was added 5 ml. (0.09 mole) of freshly distilled methyl vinyl ketone. After the exothermic reaction had subsided and the solution had become colorless, the product was precipitated with 300 ml. of methanol, filtered, dried (16.5 g., 89%), and recrystallized from 25 ml. of water to give 9.2 g. (50%) of white needles, m.p. >300° with discoloration above 200°. The infrared spectrum indicated the presence of a carbonyl group (1690) and a NH group (3300 cm.$^{-1}$).

Anal. Calcd. for $C_5H_6N_2O_7S_2K_2$: C, 17.23; H, 1.73; N, 8.04; S, 18.40. Found: C, 17.5; H, 1.7; N, 7.6; S, 17.5.

3-Acetylpyrazole-5-sulfonic Acid, Potassium Salt (VII). A.—A solution of 5 g. (0.0136 mole) of VI in 20 ml. of concentrated HCl was heated to 100° for 3.5 hr. (sulfur dioxide evolved), then evaporated to dryness, and the yellow-white residue recrystallized from 9 ml. of water to give 2.45 g. (78%) of slightly tan crystals which upon repeated crystallization from 5 ml. of water gave 1.95 g. (63%) of white crystals, m.p. >300°. The infrared spectrum showed the presence of a carbonyl group (1700) and a NH group (3200 cm.$^{-1}$).

Anal. Calcd. for $C_5H_5N_2O_4SK$: C, 26.30; H, 2.21; N, 12.27; S, 14.04. Found: C, 26.3; H, 2.3; N, 12.1; S, 13.8.

B.—To 0.85 g. (0.015 mole) of KOH in 5 ml. of water was added 5.25 g. (0.0143 mole) of VI, which caused the pH of the mixture to drop to ~8. After the addition of 5 ml. of water, the mixture was warmed until a clear solution was obtained and then cooled in ice. The crystalline deposit was filtered (2.65 g., 81%) and recrystallized from 6 ml. of water to give 2.1 g. (61%) of a white crystalline product, the infrared spectrum of which was identical with that of A.

3-Acetyl-1-methylpyrazole-5-sulfonic Acid, Potassium Salt (VIII).—To a solution of 0.46 g. (0.008 mole) of KOH in 3.5 ml. of water was added 1.42 g. (0.0062 mole) of VII and 0.6 ml. (0.0064 mole) of dimethyl sulfate. The mixture was shaken and cooled, after 30 min. warmed to complete solution, then cooled in ice. A white solid separated which was filtered, dried, (0.55 g., 36%), and recrystallized from 30 ml. of methanol to give 0.38 g. (25%) of white crystals, m.p. >300°. The infrared spectrum showed the carbonyl band (1670 cm.$^{-1}$) and no N–H band .

Anal. Calcd. for $C_6H_7N_2O_4SK$: C, 29.75; H, 2.91; N, 11.55. Found: C, 30.0; H, 2.6; N, 11.4.

3-Carbethoxy-Δ^2-pyrazoline-5,5-disulfonic Acid, Dipotassium Salt (IX).—To a stirred solution of 5 g. (0.017 mole) of I in 40 ml. of water at 25° was added 15 ml. of methanol (to increase the solubility of the olefin) and 2.5 ml. (0.027 mole) of ethyl acrylate. The mixture was colorless after 1.25 hr. and the product was precipitated with 300 ml. of methanol, filtered, and dried to give 5.9 g. (92%) of white powder. This material could not be recrystallized because of its extremely high solubility in water. Its infrared spectrum had absorption bands for ester carbonyl (1710 cm.$^{-1}$) and sulfonate groups. Further evidence for structure IX was obtained from acid treatment of the crude adduct.

Two grams (0.0053 mole) in 10 ml. of concentrated HCl was heated to 100° for 2 hr., then cooled and the resulting solid (1.18 g.) recrystallized from 3.5 ml. of water to give 0.75 g. (61%) of white needles, which were identical with compound (III) by comparison of the infrared spectra.

3-Cyano-3-methyl-Δ^1-pyrazoline-5,5-disulfonic Acid, Dipotassium Salt (X).—To a solution of 15 g. (0.05 mole) of I in 100 ml. of water was added 35 ml. of methanol (to increase solubility of the olefin) and then 5 ml. (0.087 mole) of methacrylonitrile. After 6 hr. stirring of the mixture at room temperature the yellow color of the diazo compound had disappeared and an almost white precipitate formed. After the addition of 350 ml. of methanol the precipitate was filtered, dried (18.4 g.), and recrystallized from water to give 15.8 g. (86%) of fine white needles m.p. >300°. The infrared and ultraviolet spectra of this product have been discussed earlier.

Anal. Calcd. for $C_5H_5N_3O_6S_2K_2 \cdot H_2O$: C, 16.53; H, 1.99; N, 11.56; S, 17.64. Found: C, 16.5; H, 1.8; N, 11.4; S, 17.4.

Bis(Δ^2-pyrazoline-3)-sulfone-5,5,5′,5′-tetrasulfonic Acid, Tetrapotassium Salt (XI).—To a stirred solution of 2.94 g. (0.01 mole) of I in 25 ml. of water at 25° was added 0.6 g. (0.005 mole) of divinyl sulfone. After 1.75 hr., the yellow color of the diazo compound had disappeared with the formation of white crystals. The product was precipitated with 225 ml. of methanol, filtered, dried (3.43 g., 96%), and recrystallized from water to give 2.9 g. (81%) of white crystals, dec. point 200–205°. The infrared spectrum showed the presence of N–H groups (3300 cm.$^{-1}$).

Anal. Calcd. for $C_6H_6N_4O_{14}S_5K_4 \cdot 2H_2O$: C, 10.13; H, 1.42; N, 7.88. Found: C, 10.3; H, 1.6; N, 7.7.

Bis(pyrazole-3-)sulfone-5,5′-disulfonic Acid, Dipotassium Salt (XII).—A mixture of 1.5 g. (0.0022 mole) of XI and 10 ml. of concentrated HCl was heated to 100° for 3.5 hr.; sulfur dioxide was evolved. White crystals separated upon cooling; they were collected, dried (0.97 g.), and recrystallized from water to give 0.63 g. (64%) of white product, m.p. >300°. The infrared spectrum showed the presence of N–H groups (3150 cm.$^{-1}$).

Anal. Calcd. for $C_6H_4N_4S_3O_8K_2 \cdot 2H_2O$: C, 15.32; H, 1.71; N, 11.92. Found: C, 15.9; H, 1.6; N, 11.7.

Configurational Stabilities in Cyclic Systems. I

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Base-Induced equilibration of a series of methyl esters of some cyclic 1,2-dicarboxylic acids has been carried out. The relative order of stability of the configurational isomers in each system has been determined and a discussion of conformational and configurational factors in three-, four-, five-, and six-membered ring systems is presented.

Although the stereochemical science of cyclohexyl systems has been highly developed, relatively little is known about the smaller carbocyclic ring systems. The present work was undertaken in an effort to examine conformational and configurational factors in the three- to five-membered ring systems and derivatives thereof.

As a relatively simple beginning, we have undertaken a study of the equilibration of *cis* and *trans* isomers of suitably substituted systems in order to ascertain substituent interactions and the effect of the ring structure and geometry on the relative stability of configurational isomers. Similar investigations[1-3] have proved to be of significant value in the determination of stereochemical factors in other systems.

The present work is a study of relative stabilities of cyclic 1,2-dicarboxylic acid esters of the cyclopropane, cyclobutane, cyclopentane, and cyclohexane ring systems.

The pure *cis*- and *trans*-dimethyl esters of the several cyclic dicarboxylic acids were prepared by conventional means and were subjected to equilibration with sodium methoxide. Equilibrium was approached from both the *cis* and the *trans* side in each case. The composition of the equilibrium mixtures were determined by v.p.c.

(1) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(2) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer; *J. Am. Chem. Soc.*, **83**, 4838 (1961).

(3) N. L. Allinger and R. J. Curby, *J. Org. Chem.*, **26**, 933 (1961).

and all runs gave essentially the same value ±1%. The equilibrium compositions of the esters studied are tabulated in Table I.

TABLE I
EQUILIBRIUM MIXTURE COMPOSITION AT 65°

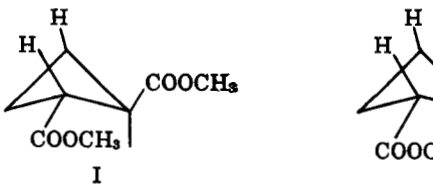
Compound (dimethyl ester)	% *trans* isomer	% *cis* isomer
1,2-Cyclopropanedicarboxylic acid	99	1
1,2-Cyclobutanedicarboxylic acid	90	10
1,2-Cyclopentanedicarboxylic acid	90	10
1,2-Cyclohexanedicarboxylic acid	93	7

It is of interest to note the small variation in relative configurational stability in the four-, five, and six-membered ring systems. The cyclopropyl system is a bit unique in that the *trans* configuration is overwhelmingly preferred.

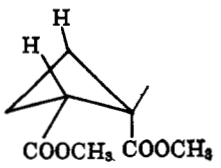
A reasonable interpretation based on simple structural considerations allows correlation of these data. The value for the cyclohexyl system is quite in line with similar stabilities of substituted cyclohexyl systems.[1]

The relative stabilities of the cyclohexyl and cyclopentyl systems might be expected to be quite similar since the probably preferred "envelope" conformation of the substituted cyclopentane strongly resembles the normal cyclohexane conformation. The conformational energy minima in substituted cyclopentyl systems are probably not so low as in cyclohexyl systems.[1] Thus the conformational energy differences are probably smaller in cyclopentanes than in cyclohexanes. The differences in order of stabilities is however too small to attribute to any significant differences in over-all structural factors.

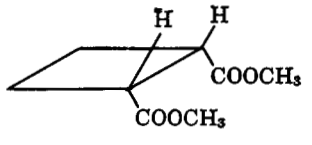
If cyclobutane were planar one would expect a fairly severe 1,2 repulsion between the adjacent carbomethoxy groups, yet the order of relative stability is the same as found in the cyclopentyl system. Since it appears reasonably certain that cyclobutyl systems prefer a nonplanar conformation[4,5] one may plausibly rationalize the configurational data in terms of such structures. Such nonplanar conformations as I and II may be considered for the *trans* and *cis* isomers, respectively, of the dimethyl esters of cyclobutane-1,2-dicarboxylic acid. In the case of the *cis* isomer, II, the nonplanar conformation should significantly reduce the interaction of the adjacent carbomethoxy groups as compared to the planar conformation III.



I



II



III

(4) A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961).

(5) J. M. Conia, J. L. Ripoll, L. A. Tushaus, C. L. Neumann, and N. L. Allinger, *J. Am. Chem. Soc.*, **84**, 4982 (1962).

The 1,3 nonbonded interaction of the two *cis*-hydrogens indicated in II, may be moderately severe although models suggest it to be no worse than a 1,3-diaxial hydrogen interaction as found in cyclohexyl systems.

The cyclopropyl system, by rules of elementary geometry, is constrained to have a planar conformation. It is quite reasonable that this would result in full eclipsing of carbomethoxy groups in the *cis* isomer and only carbomethoxy-hydrogen eclipsing in the *trans* isomer, assuming bond deformation does not occur. Thus it seems reasonable that the configurational equilibrium should lean overwhelmingly toward the *trans* isomer.

It appeared of interest to compare the diester configurational stabilities with those of the corresponding dimethyl derivatives of the same cyclic systems. Such a comparison is shown in Table II. As is evident,

TABLE II
COMPARISON OF CONFIGURATIONAL STABILITIES

Ring system	ΔF, dicarboxylic acid dimethyl ester (340°K.), kcal./mole[a]	ΔF, dimethyl deriv. (298°K.), kcal./mole
Cyclopropane-1,2	3.1	1.1[b]
Cyclobutane-1,2	1.5	
Cyclopentane-1,2	1.5	1.8[c]
Cyclohexane-1,2	1.7	1.6[d]

[a] Present work. [b] M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.* (London), **257**, 122 (1960). The values of ΔF was estimated by Curtin, ref. 2. [c] J. N. Haresnape, *Chem. Ind.* (London), 1091 (1953). [d] J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer, and F. D. Rossine, *J. Res. Natl. Bur. Std.*, **39**, 523 (1947).

there appears to be no major difference in relative stabilities with the exception of the cyclopropyl system. It appears likely, however, that the extremely low ΔF of −1.1 kcal. for *cis*- and *trans*-1,2-dimethylcyclopropane is incorrect. The relative stabilities of *cis*- and *trans*-1,2-diphenylcyclopentane have been determined by Curtin[2] and the ΔF of −2.3 kcal. appears reasonable from consideration of the factors involved.

Consideration of the first and second dissociation constants of the cyclopropane and cyclobutane 1,2-dicarboxylic acids leads to additional support for the assignment of a nonplanar conformation to the cyclobutyl system. As shown in Table III the rather large K_1/K_2

TABLE III

Dicarboxylic acid	K_1/K_2 *cis*	K_1/K_2 *trans*
Cyclopropane-1,2[a]	1210	19.4
Cyclobutane-1,2[b]	200	72
Cyclopentane-1,2[c]	138	104
Cyclohexane-1,2[c]	267	56

[a] Values from L. L. McCoy and G. W. Nachtigall, *J. Am. Chem. Soc.*, **85**, 1321 (1963). [b] Values from H. Bode, *Ber.*, **67B**, 332 (1934). [c] Values from tables compiled by G. S. Hammond, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 431–433; see ref. *a*, p. 1323, footnote 16b, for commentary on the probable correctness of the presently listed K_1/K_2 values.

ratio found in the case of *cis*-1,2-cyclopropanedicarboxylic acid no doubt reflects the close proximity of the first formed carboxylate ion to the undissociated second carboxyl group. Since cyclopropyl systems can only

be planar there is no way in which such close interaction can be relieved in the *cis* configuration. The *cis*-1,2-cyclobutanedicarboxylic acid on the other hand shows a much smaller K_1/K_2 ratio which is of the same order as that found in the cyclopentane analog. Simple geometrical considerations would suggest that if the cyclobutyl system were planar one would observe a K_1/K_2 ratio of the same order of magnitude as found in the cyclopropyl case.

Further studies of the conformational factors involved in the chemistry of cyclobutane systems and the general stereochemistry of the small ring systems are being undertaken.

Experimental

Vapor phase chromatographic analytical data were obtained with both a Beckman GC-2A gas chromatographic instrument using a 6-ft. column of May-Baker silicone oil on C-22 firebrick and with an F and M flame ionization gas chromatograph, Model 609 using a 6-ft. Carbowax packed column. All the starting diesters used in equilibrations runs were shown to contain less than 1% of the other isomer as a contaminant. All the ester mixtures obtained from equilibrations were completely resolved and analysis of standard reference mixtures showed that no significant correction factors were needed for the analytical procedure. Component peak areas were measured with an automatic disk integrator. A minimum of three equilibrations of each ester gave equilibrium compositions which varied by not more than 1%.

Cyclopentane-1,2-dicarboxylic Acid.—The *trans* isomer was prepared by the method of Fuson and Cole.[6] The *cis* isomer was prepared by converting the *trans* acid to the *cis* anhydride by prolonged reflux with acetyl chloride and hydrolysis of the anhydride with water. The *trans* acid had m.p. 160–161° (lit.[6a] m.p. 161°); the anhydride had m.p. 72–73° (lit.[6a] m.p. 74.5–75°); and the *cis* acid had m.p. 140–141° (lit.[6] m.p. 139°).

Cyclobutane-1,2-dicarboxylic Acids.—The *cis* acid was prepared by the method described by Buchman[6b] and afforded material m.p. 136–138° (lit.[6b] m.p. 139–140°). The *trans* acid was prepared by equilibration of the dimethyl ester of the *cis* acid followed by hydrolysis of the mixed esters with hydrochloric acid. The crude acid was recrystallized repeatedly to afford a 70% yield of *trans* acid, m.p. 129–130° (lit.[6b] m.p. 130–131°).

Cyclopropane-1,2-dicarboxylic Acids.—The *cis* and *trans* acids were prepared by the method described by McCoy.[7] The *trans* acid had m.p. 178° (lit.[7] m.p. 177–177.5°). The acid could be isolated in two crystalline modifications, prisms which change to needles at about 165° and the needle form, m.p. 178°. The *cis* acid had m.p. 140–142° (lit.[7] m.p. 139–142°).

Cyclohexane-1,2-dicarboxylic Acids.—The *cis* acid was prepared by hydrolysis of the anhydride[8] in water and had m.p. 192–193° (lit.[8] m.p. 192°). The *trans* acid was prepared by equilibration of the *cis* dimethyl ester followed by hydrolysis with hydrochloric acid. Repeated recrystallization of the acid mixture thus obtained afforded an 80% yield of pure *trans* diacid m.p. 223° (lit.[9] m.p. 221°).

Preparation of Methyl Esters.—The dimethyl esters were prepared from the pure diacids by reaction with diazomethane according to the following general procedure.

A solution of diazomethane in ether was prepared from N-nitrosomethylurea[10] and added to a slurry of the dicarboxylic acid in ether. When no further consumption of diazomethane was apparent the solution was evaporated and the residual diester was distilled. All the diesters thus prepared were found to be free of contaminating materials by v.p.c. analysis.

Equilibration of Dimethyl Esters.—The equilibrations of the pure isomeric diesters were conducted according to the following general procedure.

About 0.01 mole of pure ester was added to a freshly prepared solution of about 0.08 g.-atom of sodium metal dissolved in 100 ml. of anhydrous methanol. The solution was refluxed for a period of 2 to 14 hr. (Runs of various times were made in each case to assure attainment of equilibrium.) All cases studied had reached essential equilibrium in 2 hr. though a 4-hr. reflux period was needed for the cyclopropyl system. The cooled equilibration solution was poured into 1 l. of ice–water containing 10 ml. of concentrated hydrochloric acid. The ester was isolated by ether extraction and simple transfer distillation of the ether extract to separate the solvent from the ester and the ester from traces of high-boiling colored substances. A wide boiling cut was taken in each case to assure that no fractionation of esters had taken place. The yield of recovered equilibrated ester averaged 90% or more after such transfer distillation indicating little loss of material through condensation or hydrolysis reactions in the course of equilibration. V.p.c. analysis of both the crude equilibration product and the distilled ester mixture gave identical results. The equilibration compositions are indicated in Table I.

(6) (a) R. C. Fuson and W. Cole, *J. Am. Chem. Soc.*, **60**, 1237 (1938); (b) E. R. Buchman, A. O. Reims, T. Skei, and M. Schlatter, *ibid.*, **64**, 2696 (1942).

(7) L. McCoy, *ibid.*, **80**, 6568 (1958).

(8) C. C. Price and M. Schwarcz, *ibid.*, **62**, 2733 (1940).

(9) W. Huchel and E. Goth, *Ber.*, **58**, 449 (1925).

(10) W. E. Beckman and W. S. Struve, "Organic Syntheses," Coll. Vol. I, John Wiley and Son, Inc., New York, N. Y., 1942, p. 50.

The Free-Radical Chemistry of Cyclic Ethers. V. β-Hydrogen Atom Abstraction from Epoxides and a Thioepoxide

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Further studies in the *t*-butyl peroxide-induced free-radical reactions of epoxides have shown that, in the absence of olefin, abstraction of a hydrogen atom beta to the oxygen atom occurs in addition to the previously reported abstraction of a hydrogen atom alpha to the oxygen atom. The intermediate formed from this β-hydrogen atom abstraction rearranges by the opening of the epoxide ring to form an unsaturated alkoxy radical. Various chain termination steps, which can lead to the observed products, are outlined. The same reaction with propylene sulfide resulted in the formation of products similar to those observed for propylene oxide.

Previously it was reported that in the free-radical chemistry of cyclic ethers, the chain transfer atom is the hydrogen atom alpha to the oxygen atom.[2] The epoxy radicals formed from this α-abstraction were found to rearrange to α-keto radicals which yielded ketonic products. The abstraction and rearrangement steps, as suggested for propylene oxide, are shown (p. 3438, col. 1).

The first objective of the present work was to ascertain whether a free radical would abstract a hydrogen atom beta to the oxygen atom (allylic to the epoxide ring) and to determine the products formed from such

(1) Abstracted from the Ph.D. thesis (1963) of E. C. S., M. W. Kellogg Co., Jersey City, N. J.

(2) T. J. Wallace and R. J. Gritter, *Tetrahedron*, **19**, 657 (1963).