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[CONTRIBUTION FROM BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

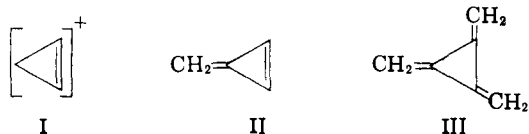
## Synthesis of Cyclopropane Derivatives. Precursors for Dimethylenecyclopropane and Trimethylenecyclopropane

BY A. T. BLOMQUIST AND DANIEL T. LONGONE<sup>1</sup>

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Two diamines, *trans*-1,2-bis-(dimethylaminomethyl)-cyclopropane and *trans*-2,3-bis-(dimethylaminomethyl)-1-methylenecyclopropane, desired as precursors for projected syntheses of dimethylenecyclopropane and trimethylenecyclopropane, respectively, have been obtained *via* the reaction sequence  $R(\text{CO}_2\text{H})_2 \rightarrow R(\text{COCl})_2 \rightarrow R(\text{CONMe}_2)_2 \rightarrow R(\text{CH}_2\text{NMe}_2)_2$ . The various transformations were effected in good yields starting from *trans*-1,2-cyclopropanedicarboxylic acid and *trans*-1-methylenecyclopropane-2,3-dicarboxylic acid (Feist's acid). Examination of the infrared spectra of some fourteen cyclopropane derivatives confirmed the view that absorption bands in the 9.8–10.0 and 11.5–11.7 $\mu$  regions are not reliable for indicating the presence of a cyclopropane system in a molecule.

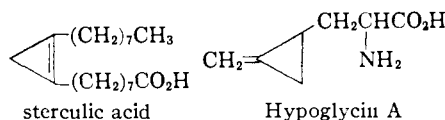
The increasing interest in the chemistry of cyclopropane derivatives is due in part to the prediction of non-classical aromatic character for certain unsaturated cyclopropyl compounds. Application of the molecular orbital (LCAO) method in the calculation of the electron delocalization energies, bond orders and free valence indices of a number of small ring compounds predicts delocalization (resonance) energies of about 34, 16 and 29 kcal. for the cyclopropene cation (I), methylenecyclopropene (II) and trimethylenecyclopropane (III), respectively.<sup>2</sup>



Since the results of these calculations are essentially qualitative due to the known limitations of the method used and the approximations introduced, the only true test of their reliability must eventually lie in the synthesis and study of the compounds in question. A derivative of I, the triphenylcyclopropenyl cation, has recently been synthesized.<sup>3</sup> The success in obtaining this relatively stable cation not only supports experimentally the reliability of the theoretical conclusions cited above but also stimulates synthetic effort toward other non-classical aromatic compounds in the cyclopropane series.

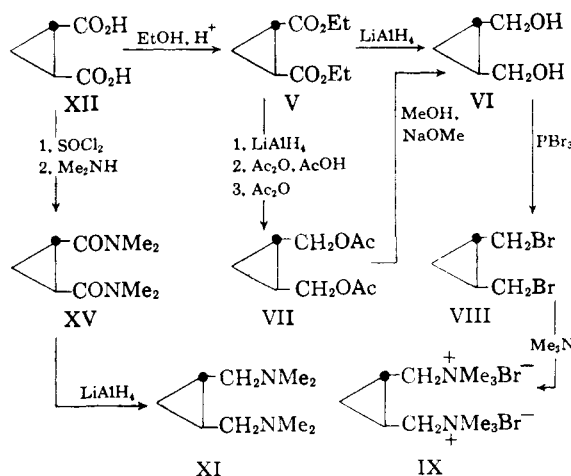
The cyclopropane compounds of particular interest are those which contain *exo* or *endo* double bonds. Besides the naturally occurring cyclopropane sterculic acid<sup>4</sup> and the methylenecyclopropane Hypoglycin A<sup>5</sup> the number of, and routes to, such cyclopropyl compounds are meager. For this

reason, a careful study of the applicability to cyclopropane systems of standard classical transformations utilized successfully in the larger, strainless-



ring homologs to convert dicarboxylic acids to diol-efins would be valuable.<sup>6</sup> This paper describes the synthesis and characterization of intermediates to be used for such a study. They are derived from two of the more readily accessible cyclopropanedicarboxylic acids, *trans*-1,2-cyclopropanedicarboxylic acid (XII) and Feist's acid (XX).

**Derivatives of *trans*-1,2-Cyclopropanedicarboxylic Acid (XII).**—The dicarboxylic acid XII, obtained from  $\alpha$ -bromoglutaric ester (IV) by the method described by Ingold,<sup>7</sup> served as the starting material for synthesis of the cyclopropane derivatives given below.



Cyclization of the bromoester IV *via* intramolecular dehydrobromination with methanolic potas-

(1) U. S. Rubber Research Fellow, 1957–1958. The work reported here was abstracted from part of the dissertation presented by Daniel T. Longone in September, 1958, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *THIS JOURNAL*, **74**, 4579 (1952).

(3) R. Breslow, *ibid.*, **79**, 5318 (1957).

(4) K. L. Rinehart, Jr., W. A. Nilsson and H. A. Whaley, *ibid.*, **80**, 503 (1958).

(5) J. A. Carbon, W. B. Martin and L. R. Swett, *ibid.*, **80**, 1002 (1958); R. S. deRopp, *et al.*, *ibid.*, **80**, 1004 (1958).

(6) (a) A. T. Blomquist and D. T. Longone, *ibid.*, **79**, 3916 (1957); (b) A. T. Blomquist, J. Wolinsky, Y. C. Meinwald and D. T. Longone, *ibid.*, **78**, 6057 (1956).

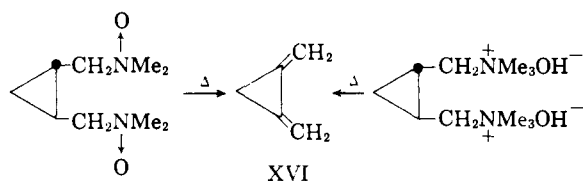
(7) C. K. Ingold, *J. Chem. Soc.*, **119**, 305 (1921).

sium hydroxide afforded the dicarboxylic acid XII (crude) from which pure liquid diethyl *trans*-1,2-cyclopropanedicarboxylate (V) was prepared (55% from IV). *trans*-1,2-Bis-(hydroxymethyl)-cyclopropane (VI) was best obtained indirectly from the ester V through methanolysis of the glycol diacetate VII. The latter compound (VII) was prepared by direct acetylation, with acetic anhydride, of the unisolated lithium aluminum hydride reduction product derived from the ester V. The yield of the glycol VI by this indirect method was 81%, whereas VI was obtained in but 55% yield when prepared directly from the ester V.

Conversion of the glycol VI to *trans*-1,2-bis-(bromomethyl)-cyclopropane (VIII) was effected with the reagent phosphorus tribromide in 51% yield. Treatment of the dibromide VIII with methanolic trimethylamine gave crude *trans*-1,2-bis-(dimethylaminoethyl)-cyclopropane dimethobromide (IX) in essentially quantitative yield. This quaternary ammonium salt IX formed a crystalline dipicrate derivative, m.p. 257–260° dec.

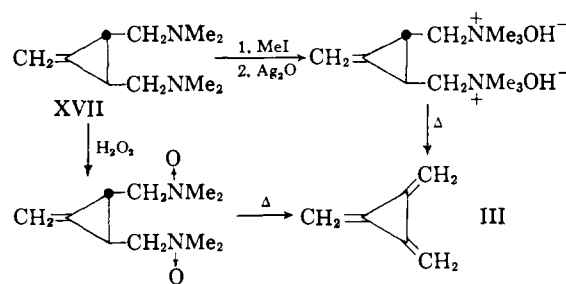
Reaction of the dicarboxylic acid XII with thionyl chloride gave *trans*-1,2-cyclopropanedicarbonyl chloride (XXI) in 77% yield. Aminolysis of XXI in benzene solution with anhydrous dimethylamine produced *N,N,N',N'*-tetramethyl *trans*-1,2-cyclopropanedicarboxamide (XXII), 88% yield, m.p. 56–58°. Lithium aluminum hydride reduction of the diamide XXII gave a 64% yield of liquid *trans*-1,2-bis-(dimethylaminomethyl)-cyclopropane (XVII). Over-all yield of the diamine XVII from the dicarboxylic acid XII was increased from 43 to 71% by carrying out the transformations described above without isolating the intermediates XXIII and XV. An alternative route to the diamine XVII, aminolysis of the ditosylate derivative of the glycol VI (X), was examined and found to be substantially inferior to the route described above.

The diamine XVII and its dimethobromide IX are being used currently as precursors for the preparation of dimethylenecyclopropane (XVI) *via* thermal decomposition of the corresponding bisamine oxide and bis-quaternary ammonium hydroxide.



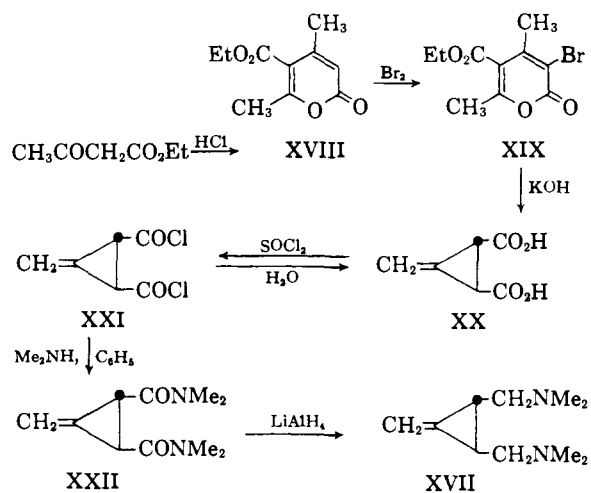
**Derivatives of Feist's Acid (*trans*-1-methylenecyclopropane-2,3-dicarboxylic Acid (XX)).**—The successful transformation of the dicarboxylic acid XII to the diamine XVII, a precursor for dimethylenecyclopropane (XVI), encouraged an examination of a similar conversion of Feist's acid (XX) to *trans*-2,3-bis-(dimethylaminomethyl)-1-methylenecyclopropane (XVII). The diamine XVII would serve as a convenient precursor for the interesting triene trimethylenecyclopropane (III), an isomer of benzene.

Of particular concern in this study was the stability of the exocyclic double bond under the reaction conditions necessary for the conversion of XX to XVII. Fortunately, the presence of this double



bond in various intermediates can be conveniently detected by the terminal methylene ( $R_2C=CH_2$ ) absorption at *ca.* 11  $\mu$  in the infrared region.

The synthesis of the diamine XVII is outlined



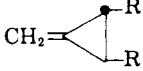
The preparation of Feist's acid (XX) from ethyl acetoacetate was carried out using essentially the procedure described by Goss, Ingold and Thorpe.<sup>8</sup> Ethyl isodehydracetate (XVIII) was obtained in 42–46% yield. The yellow crystalline bromo derivative XIX, m.p. 83–84°, was obtained smoothly (90%). Conversion of the bromopyrone XIX to Feist's acid was effected with boiling aqueous potassium hydroxide in 80% yield. This yield was realized only when the original isolation procedure<sup>8</sup> was modified as described in the Experimental Part. The modified procedure gave quite pure acid XX directly, m.p.'s 194–195° and 195–196°. One crystallization of this crude product from ether gave Feist's acid of m.p. 200–201° (cor.), reported<sup>8</sup> m.p. 200°.

Treatment of the acid XX with thionyl chloride gave *trans*-1-methylenecyclopropane-2,3-dicarboxylic acid (XX) (93%). Hydrolysis of the latter afforded an acid identical with the original acid XX. Aminolysis of the acid chloride XXI with anhydrous dimethylamine in benzene produced *N,N,N',N'*-tetramethyl-*trans*-1-methylenecyclopropane-2,3-dicarboxamide (XXII), m.p. 70–71°, in 80% yield. Finally, lithium aluminum hydride reduction of the amide XXII afforded *trans*-2,3-bis-(dimethylaminomethyl)-1-methylenecyclopropane (XVII) in 57% yield.

(8) F. R. Goss, C. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, **123**, 327 (1923).

**Infrared Absorption Spectra of Cyclopropane Derivatives.**<sup>9</sup>—The spectra of fourteen cyclopropane derivatives were obtained. Most of the compounds possessed carbonyl or other functional groups adjacent to the cyclopropane ring. The absorption bands of particular interest are those due to the terminal methylene group in Feist's acid and its derivatives at *ca.* 11  $\mu$ , the carbonyl absorption in the 5.6–6.1  $\mu$  region and bands at 9.8 and 11.6  $\mu$  attributed to the cyclopropane system. The data are presented in Tables I and II.


TABLE I  
INFRARED ABSORPTIONS OF FEIST'S ACID DERIVATIVES<sup>a</sup>



R	>C=O	>C=CH <sub>2</sub>	9.8- $\mu$ region	11.6- $\mu$ region
-CO <sub>2</sub> H) (KBr)	5.88s	11.00s	9.75w	...
-COCl	5.60s	10.83m	9.68, 9.96m	...
-CONHC <sub>6</sub> H <sub>5</sub> (KBr)	6.04s	11.09m	9.73, 9.97w	...
-CONMe <sub>2</sub> (Nujol)	6.07s	10.96s	.....	...
-CH <sub>2</sub> NMe <sub>2</sub>	...	11.28m	9.81w	...

<sup>a</sup> w = weak, m = medium, s = strong.

TABLE II  
INFRARED ABSORPTIONS OF *trans*-1,2-CYCLOPROPANEDI-CARBOXYLIC ACID DERIVATIVES



R	>C=O	9.8- $\mu$ region	11.6- $\mu$ region
-CO <sub>2</sub> H (KBr)	5.90s	....	11.66m
-CO <sub>2</sub> Et	5.78s	....	11.60m
-COCl	5.61s	9.80s	11.65m
-CONHC <sub>6</sub> H <sub>5</sub> (KBr)	6.05s	9.74w	....
-CONMe <sub>2</sub> (Nujol)	6.07s	....	11.55w
-CH <sub>2</sub> OAc	5.78s	9.69m	....
-CH <sub>2</sub> OH	...	9.78s	11.61w
-CH <sub>2</sub> OTs	...	9.81m	....
-CH <sub>2</sub> NMe <sub>2</sub>	...	....	....

(1) **Carbonyl Absorption.**—The carbonyl vibration absorption is normal<sup>10</sup> for all carbonyl derivatives in both cyclopropane series. The exocyclic methylene group in the Feist's acid series does not affect the carbonyl absorption as evidenced by the fact that corresponding derivatives in the two series absorb at essentially identical wave lengths.

(2) **Terminal Methylene Absorption.**—Asymmetric disubstituted ethylenes, R<sub>2</sub>C=CH<sub>2</sub>, absorb strongly at *ca.* 11.2  $\mu$ . This absorption is due to the hydrogen out-of-plane deformations in olefins of this particular structure. When the double bond is not conjugated the location of this peak varies by less than one-tenth of a micron, the quoted range

(9) A Perkin-Elmer double beam infrared spectrophotometer, model 21, was used to obtain the spectra. A sodium chloride prism was used. Liquid samples were on sodium chloride windows whereas solid samples were examined as potassium bromide pressings or Nujol mulls.

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954.

being 11.22–11.27  $\mu$ .<sup>10</sup> In four of the five methylenecyclopropane derivatives listed in Table I this peak has been shifted to abnormally high frequencies, the range being 10.8–11.1  $\mu$ . This interesting phenomenon must be due to some type of interaction involving the  $\alpha,\beta$ -unsaturated group (carbonyl) present in each of the four structures. It is clear that this shift is not due to the strained cyclopropane structure. Methylenecyclopropane<sup>11</sup> and substituted methylenecyclopropanes<sup>5</sup> containing no  $\alpha,\beta$ -unsaturated groups all absorb normally at *ca.* 11.25  $\mu$ . The one compound listed in Table I that has no  $\alpha,\beta$ -unsaturated group absorbs normally at 11.28  $\mu$ . It is also clear that the interaction involved is probably not that of conjugation as the  $\alpha,\beta$ -unsaturated group (carbonyl) absorbs at normal wave lengths in all cases. An inductive effect due to the electronegative carbonyl group and transmitted through the ring appears to be operating. That this may be the case is evidenced by the fact that the most electronegative functional group, the acid chloride, is associated with the greatest shift in frequency of the absorption peak in question. The remaining compounds having carbonyl-containing functional groups of decreased electronegativities have smaller frequency shifts. Although the cyclopropane ring probably does not transmit electrical effects between two  $\alpha,\beta$ -unsaturated groups,<sup>12</sup> the possibility of such an effect when one of the unsaturated groups is an exocyclic double bond (as in the Feist's acid derivatives) has not been investigated at all.

(3) **Absorption in the 9.8- $\mu$  Region.**—Absorption between 9.8 and 10.0  $\mu$ , assigned to a ring deformation,<sup>13</sup> has often been cited as indicative of the cyclopropane structure. Recently, Allen, *et al.*,<sup>14</sup> have concluded that this band is unreliable for such structural characterization.

An examination of the data in Tables I and II shows that of the 14 cyclopropane derivatives prepared here only three have moderate or moderately strong absorption peaks in the range 9.8 to 10.0  $\mu$  while two others absorb weakly in this narrow region. If the range is broadened to include the 9.7 to 10.0  $\mu$  region, then five compounds have moderate or moderately strong absorptions while four others have weak absorptions. The strong absorption at 9.78  $\mu$  in the case of the glycol in Table II cannot be assigned to the cyclopropane structure, but to the carbon-oxygen stretching mode or the hydrogen-oxygen deformation mode.<sup>15</sup>

Thus, the spectra of the cyclopropane derivatives examined here further confirm the unreliability of the 9.8 to 10.0  $\mu$  range for the indication of the presence or absence of the cyclopropane structure.

(4) **Absorption in the 11.6- $\mu$  Region.**—Some cyclopropane derivatives have a strong absorption band near 11.6  $\mu$ .<sup>16</sup> This absorption has been as-

(11) J. T. Grayson, K. W. Greenlee, J. M. Durfer and C. E. Boord, *THIS JOURNAL*, **75**, 3344 (1953).

(12) E. N. Trachtenberg and G. Odian, *ibid.*, **80**, 4018 (1958).

(13) Hs. H. Günthard, R. C. Lord and T. K. McCubbin, Jr., *J. Chem. Phys.*, **26**, 768 (1956).

(14) C. F. H. Allen, T. J. David, W. J. Humphlett and D. W. Stewart, *J. Org. Chem.*, **22**, 1291 (1957).

(15) L. J. Bellamy, *ref. 10*, p. 94.

(16) J. M. Derfer, E. E. Pickett and C. E. Boord, *THIS JOURNAL*, **71**, 2482 (1949).

signed to a ring methylene ( $\text{CH}_2$ ) wagging vibration.<sup>13</sup> Since the five Feist's acid derivatives in Table I all lack the annular methylene group, the peak attributed to this group should be absent. As expected, none of the compounds absorb between 11.5 and 11.7  $\mu$ .

On the other hand, the annular methylene group is present in each of the compounds listed in Table II. However, of the nine compounds tabulated only three absorb moderately to strongly in the 11.5 to 11.7  $\mu$  range while two others absorb weakly.

The inconsistent appearance of this peak in the compounds reported here and elsewhere<sup>16</sup> leads to the conclusion that, as in the case of absorption in the 9.8 to 10.0  $\mu$  region, the region 11.5 to 11.7  $\mu$  is of little value for the characterization of cyclopropane derivatives. In addition to the inconsistency of this absorption, there is the added factor of interference due to other functional groups. Trisubstituted olefins, substituted aromatics and alkyl and aryl aldehydes all have moderate or strong absorption maxima in this region due to carbon-hydrogen deformations.

(5) **Absorption in Other Regions.**—The use of the carbon-hydrogen stretching bands at 3.23 and 3.32  $\mu$  has been suggested for the identification of methylene groups in the cyclopropane system.<sup>17</sup> For optimum results in this region a spectrometer employing a sodium chloride prism does not afford sufficient resolution. For this reason a careful examination of this region was not warranted in this study. Allen, *et al.*, have shown that in addition to interferences from vinyl, aromatic and heterocyclic carbon-hydrogen absorptions these peaks are also inconsistent and therefore of little value.<sup>14</sup>

#### Experimental Part<sup>18</sup>

**Diethyl  $\alpha$ -Bromoglutarate (IV).**—The procedure previously described<sup>7</sup> was followed except that no illumination was used during the addition of bromine. From 748 g. (5.67 moles) of technical grade glutaric acid there was obtained 761 g. (50%) of the bromoester IV which had b.p. 113–115° (2 mm.) and  $n_{\text{D}}^{25}$  1.4546–1.4553. In repetitive preparations, distilled fractions of IV showed a refractive index range as broad as  $n_{\text{D}}^{25}$  1.4533–1.4666, presumably due to the presence of sulfur which codistills with the product. The product was yellow in color, to a variable degree depending on the amount of sulfur present, and on long standing at room temperature small amounts of sulfur would crystallize from the product. The b.p. range and infrared spectra of distilled fractions were used as a measure of product yield rather than refractive indices.

**Diethyl *trans*-1,2-Cyclopropanedicarboxylate (V).**—The bromoester IV (267 g., 1.00 mole) was added dropwise with stirring over a 5-hr. period to 1 l. of boiling 8 *M* methanolic potassium hydroxide. The mixture was gently refluxed and stirred overnight. The precipitated salts were dissolved in 600 ml. of water and the solution obtained was evaporated to near dryness by heating with steam *in vacuo*. Concentrated hydrochloric acid (*ca.* 700 ml.) was added to the residual slurry until the resulting solution was strongly acidic. The insoluble potassium bromide was removed by filtration and the acidic filtrate exhaustively extracted with ether continuously over 10 days.

The residue, crude *trans*-1,2-cyclopropanedicarboxylic acid (XII), was esterified by the azeotropic method using 240 ml. of absolute ethanol and 180 ml. of toluene. After the usual work-up there was obtained 93 g. (50%) of the diester V, b.p. 107–115° (9–10 mm.),  $n_{\text{D}}^{25}$  1.4309–1.4369. In a repetitive azeotropic esterification of crude XII with benzene and ethanol the distilled di-ester V showed b.p. 111–113° (10 mm.) and  $n_{\text{D}}^{25}$  1.4374–1.4378.

(17) S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

(18) All m.p.'s and b.p.'s are uncorrected unless otherwise stated.

*Anal.* Calcd. for  $\text{C}_9\text{H}_{14}\text{O}_4$ : C, 58.05; H, 7.58. Found: C, 58.19; H, 7.45.

***trans*-1,2-Bis-(hydroxymethyl)-cyclopropane (VI).** (A) From V.—Lithium aluminum hydride (55.2 g., 1.46 moles) was added to 1 l. of dry ether. After this mixture had been stirred for 0.5 hr. at room temperature and chilled with an ice-bath, the di-ester V (91.1 g., 0.488 mole) was added to it dropwise over 1 hr. After the addition of V was complete, the mixture was refluxed gently and stirred for 5 hr. Excess water was then added cautiously to the chilled mixture. The hydrolyzed mixture was filtered and the collected salts copiously washed with ether. The combined filtrate and ether washes were dried over calcium sulfate and the ether removed to give crude glycol VI. The inorganic salts from above were dissolved in concentrated hydrochloric acid and the solution obtained was exhaustively extracted with ether for three days. The crude glycol VI obtained by this extraction was about equal to that isolated previously. Distillation of the combined crude glycol gave 27.3 g. (55%) of VI which had b.p. 95–103° (1 mm.) and  $n_{\text{D}}^{25}$  1.4630–1.4702.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{10}\text{O}_2$ : C, 58.80; H, 9.87. Found: C, 58.00; H, 9.68.

(B) From VII.—Transesterification of 78.9 g. (0.423 mole) of *trans*-1,2-bis-(acetoxymethyl)-cyclopropane (VII, *vide infra*) was effected by heating with 100 ml. of absolute methanol and 1.5 g. of sodium methoxide. The methanol-methyl acetate azeotrope distilled at 53°. Transesterification was considered to be complete when pure methanol distilled from the mixture at 63°. After removal of the excess methanol (distillation *in vacuo*) there was obtained 39.8 g. (92%) of the glycol VI which had b.p. 103–105° (1.1 mm.) and  $n_{\text{D}}^{25}$  1.4698–1.4703.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{10}\text{O}_2$ : C, 58.80; H, 9.87. Found: C, 59.54; H, 10.15.

***trans*-1,2-Bis-(acetoxymethyl)-cyclopropane (VII).**—Diester V (90.0 g., 0.483 mole) was added dropwise with stirring over 2.5 hr. to a mixture of 55 g. (1.45 moles) of lithium aluminum hydride and 1 l. of dry ether which had previously been stirred under reflux for 0.5 hour. After completion of the addition of V, the reaction mixture was stirred and refluxed gently for 9 hr. and then 250 ml. of acetic anhydride was added. Following this addition, 460 ml. of glacial acetic acid was added and finally another 250 ml. of acetic anhydride was added. It was then necessary to add additional acetic anhydride to facilitate stirring of the viscous mixture. After the ether had been removed by distillation the residual mixture was refluxed 24 hr. This mixture was filtered and the filtrate distilled to give 79.6 g. (88%) of pure diacetate VII, b.p. 113–115° (7.2 mm.),  $n_{\text{D}}^{25}$  1.4368–1.4381.

*Anal.* Calcd. for  $\text{C}_9\text{H}_{14}\text{O}_4$ : C, 58.05; H, 7.58. Found: C, 58.37; H, 7.39.

***trans*-1,2-Bis-(bromomethyl)-cyclopropane (VIII).**—Using the procedure described for the preparation of 1,2-bis-(bromomethyl)-cyclohexane<sup>6</sup> from 24.2 g. (0.237 mole) of the glycol VI there was obtained 27.8 g. (51%) of distilled dibromide VIII, b.p. 86–88° (7 mm.),  $n_{\text{D}}^{25}$  1.537–1.540.

*Anal.* Calcd. for  $\text{C}_3\text{H}_5\text{Br}_2$ : C, 26.34; H, 3.54; Br, 70.12. Found: C, 26.41, 26.33; H, 3.70, 3.60; Br, 70.10.

**1,2-Bis-(dimethylaminomethyl)-cyclopropane Dimethobromide (IX).**—A mixture of 42 g. (0.71 mole) of trimethylamine, 26.3 g. (0.115 mole) of VIII and 25 ml. of methanol was kept in a sealed Pyrex bomb at room temperature for one week. Evaporation of the reaction mixture to dryness *in vacuo* gave the bis-quaternary ammonium bromide (96%). A portion of the product was converted to its *dipicrate derivative* which was recrystallized from 90% ethanol, m.p. 257–260° dec.

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_{14}$ : C, 42.99; H, 4.71; N, 17.44. Found: C, 43.60; H, 4.81; N, 17.32.

***trans*-1,2-Bis-(tosyloxymethyl)-cyclopropane (X).**—To a solution of 14.9 g. (0.146 mole) of the glycol VI in 92.4 g. of pyridine (reagent grade, dried over barium oxide) cooled to 5° there was added in small portions with stirring 61.3 g. (0.321 mole, 10% excess) of tosyl chloride. This mixture was stirred for 3 hr. at 5–10° and then 500 ml. of chilled dilute hydrochloric acid was added in small portions. After this acidified mixture had been shaken thoroughly it was extracted with ether. The ethereal solution was dried

and the ether removed to leave 36.1 g. (60%) of the crude tosylate X. This crude X could not be crystallized and it set to a glass on storage in the refrigerator. The infrared spectrum of this X showed absorption at 7.38 and 8.4  $\mu$ , characteristic of the tosylate group.

**trans-1,2-Cyclopropanedicarbonyl Chloride (XIII).**—The crude dicarboxylic acid XII described above was recrystallized from ether and then showed m.p. 178–178.5° (lit.<sup>19</sup> m.p. 175.5–178°). A mixture of 31.3 g. (0.240 mole) of this recrystallized XII and 86 g. (0.72 mole, 50% excess) of thionyl chloride was heated at 60–70° for two days or for 7 hr. when stirred vigorously. Excess thionyl chloride was removed *in vacuo* over steam and the residue distilled. There was obtained 30.8 g. (77%) of pure diacid chloride XIII, b.p. 67–68° (5 mm.),  $n_D^{25}$  1.4931 (reported<sup>19</sup> b.p. 80° (6 mm.)). The pure XIII had m.p. between 5 and 20° as it formed colorless crystals in the refrigerator which quickly melted on warming to room temperature.

Treatment of this XIII (0.95 g.) with water at 100° gave 0.51 g. of the dicarboxylic acid XII, m.p. 177–179°, which had m.p. 179–179.5° after recrystallization from ether. The infrared spectra of this XII and authentic XII were identical.

The dianilide derivative of XII was obtained as colorless crystals, m.p. 310.5–311° from ethanol. After a second recrystallization from ethanol it showed m.p. 311.0–311.5° (reported<sup>19</sup> m.p. 299–301°).

*Anal.* Calcd. for  $C_{17}H_{16}O_2N_2$ : C, 72.84; H, 5.75; N, 9.99. Found: C, 73.12; H, 5.84; N, 9.69.

**N,N-Dimethyl-trans-2-carboxycyclopropanecarboxamide (XIV).**—The diacid chloride XIII (25.7 g., 0.154 mole) was added dropwise with stirring to 50 ml. of 33% aqueous dimethylamine chilled in an ice-bath. The solution was then stirred for 4 hr. and allowed to stand overnight. The aqueous solution was extracted thoroughly with ether. Concentration of the dried ethereal extracts gave a total of 13.9 g. (58%) of crystalline amide-acid XIV which after recrystallization from ether had m.p. 82–83°. The infrared spectrum of this product showed absorption at 5.85  $\mu$  (acid carbonyl) and at 6.24  $\mu$  (amide carbonyl).

*Anal.* Calcd. for  $C_7H_{11}O_3N$ : C, 53.49; H, 7.05; N, 8.91. Found: C, 53.31, 53.59; H, 7.05, 7.10; N, 8.64, 8.89.

**N,N,N',N'-Tetramethyl-trans-1,2-cyclopropanedicarboxamide (XV).**—Gaseous dimethylamine was passed into a solution of 22.3 g. (0.134 mole) of the diacid chloride XIII in 350 ml. of benzene with continuous stirring and intermittent cooling with tap water. Introduction of the dimethylamine was interrupted from time to time when the reaction mixture was cooled. Reaction was considered to be complete when heat was no longer evolved upon the introduction of the amine. The mixture was then filtered after it had been stirred at room temperature an additional 2 hr. The filtered salts were washed with benzene and the washings combined with the original benzene filtrate. The dried solid residue obtained after removal of the benzene was recrystallized from ether after treatment with a small amount of Norit. There was isolated 21.7 g. (88%) of the diamide XV as colorless needles, m.p. 56–58°. The infrared spectrum of this product had but one band (6.07  $\mu$ ) in the carbonyl region.

*Anal.* Calcd. for  $C_9H_{16}O_2N_2$ : C, 58.67; H, 8.75; N, 15.21. Found: C, 58.62; H, 8.74; N, 14.90.

**trans-1,2-Bis-(dimethylaminomethyl)-cyclopropane (XI).** (A) From XV.—To a suspension of 7.01 g. (0.184 mole) of lithium aluminum hydride in 100 ml. of dry ether which had been stirred at reflux for 1 hr. there was added dropwise a solution of 22.5 g. (0.122 mole) of the diamide XV in 250 ml. of ether. After this addition, which required 2 hr., the mixture was stirred at reflux temperature another 3 hr. Finally, after stirring for 2.5 hr. at room temperature, the mixture was cooled in an ice-bath and hydrolyzed by the successive dropwise addition of 7 ml. of water, 7 ml. of 15% sodium hydroxide solution and 21 ml. of water. The mixture was brought to room temperature and filtered. The dried ethereal filtrate was distilled to give 12.2 g. (64%) of the diamine XI, b.p. 104–105° (55 mm.),  $n_D^{25}$  1.4420.

*Anal.* Calcd. for  $C_8H_{20}N_2$ : C, 69.17; H, 12.90; N, 17.93. Found: C, 68.96; H, 13.23; N, 17.76.

The dipicrate derivative of XI was prepared and showed m.p. 138–139° after recrystallization from ethanol.

*Anal.* Calcd. for  $C_{21}H_{26}N_8O_{14}$ : N, 18.24. Found: N, 18.06.

(B) From the Dicarboxylic Acid XII.—The over-all yield of diamine XI from the dicarboxylic acid XII was greatly improved and the preparative time decreased by carrying out the conversion without isolation of the intermediates XIII and XV. The dicarboxylic acid (25.0 g., 0.192 mole) was converted to the diacid chloride XIII as described above. The crude XIII obtained in 350 ml. of benzene was treated with dimethylamine as described above to give the crude diamide XV. This XV, in 150 ml. of ether, was reduced with 11 g. (ca. 50% excess) of lithium aluminum hydride in 200 ml. of ether. Total time of reflux, after the addition of XV, was increased to 20 hr. From this reduction mixture there was obtained 24.0 g. of crude, light yellow diamine XI,  $n_D^{25}$  1.4440, from which there was obtained on distillation 21.2 g. (71% from XII) of pure XI, b.p. 92–93° (28 mm.),  $n_D^{25}$  1.4419.

(C) From the Tosylate X.—Aminolysis of the crude tosylate X in benzene with anhydrous dimethylamine was carried out at room temperature in a sealed Pyrex tube. The usual work-up afforded crude diamine XI in low yield. The infrared spectrum of this crude XI indicated that it was identical with XI obtained by the reduction of XV.

**5-Carboethoxy-4,6-dimethyl-2-pyrone (XVIII).**—Using the procedure previously described,<sup>8</sup> from 1504 g. (11.5 moles) of reagent grade ethyl acetoacetate there was obtained 519 g. (46%) of the distilled pyrone XVIII having b.p. 132–140° (2 mm.),  $n_D^{25}$  1.5110–1.5130. The center cut in the distillation, comprising most of the product, had b.p. 139–139.5° (2 mm.),  $n_D^{25}$  1.5129,  $d_4^{25}$  1.1619 (reported<sup>8</sup> b.p. 160–190° (20 mm.)).

*Anal.* Calcd. for  $C_{10}H_{12}O_4$ : C, 61.21; H, 6.17;  $M_D$ , 48.6. Found: C, 61.66; H, 6.25;  $M_D$ , 50.7 (no correction for exaltation due to ring and conjugation).

**3-Bromo-5-carboethoxy-4,6-dimethyl-2-pyrone (XIX).**—Using the procedure previously described,<sup>8</sup> from 589 g. (3.00 moles) of the pyrone XVIII there was obtained 739 g. (90%) of recrystallized XIX, m.p. 83.5–84.5° (reported<sup>8</sup> m.p. 87°).

**trans-1-Methylenecyclopropane-2,3-dicarboxylic Acid. Feist's Acid (XX).**—The addition of fused XIX to boiling 7 *M* potassium hydroxide was carried out in the manner previously described.<sup>8</sup> However, a modified work-up procedure was developed which involved a reduction in isolation time and, in our hands, gave an excellent yield (80%) of product. The inorganic salts from the acidified reaction mixture (from 119.5 g., 0.434 mole, of XIX and 600 ml. of 7 *M* base) was filtered with suction and washed thoroughly with ether. The aqueous filtrate, dark red in color, was extracted repeatedly with ether until light yellow in color. The combined ethereal washings and extracts were dried over magnesium sulfate, the drying agent removed and the solution concentrated to incipient precipitation using a water aspirator. After standing in a refrigerator overnight the slurry of crude product and ethereal solution was filtered with suction and the product washed with a small amount of ether, and then air-dried to give 27.1 g. of powdery diacid XX, m.p. 194–196°, yellow-brown in color. The filtrate was treated with a small amount of Norit, refluxed for a few minutes and filtered. The precipitation procedure described above was repeated to give a second crop, 20.2 g., m.p. 195–196°, and finally a third crop, 2.3 g., m.p. 193–195°. The filtrate from the third crop gave only a viscous residue on concentration and was discarded. Recrystallization of a portion of the product from ether gave fine colorless crystals which formed needles which had m.p. 200–201° (corrected) and decomposed with gas evolution just above the m.p. (reported<sup>8</sup> m.p. 200°).

**trans-1-Methylenecyclopropane-2,3-dicarbonyl Chloride (XXI).**—This preparation was carried out essentially as described for the preparation of the diacid chloride XIII. From 19.8 g. (0.139 mole) of crude Feist's acid (XX) and 49.5 g. (0.417 mole, 50% excess) of thionyl chloride heated at 70° for ca. 18 hr. there was obtained, after distillation, 23.1 g. (93%) of the pure diacid chloride XXI, b.p. 85–86° (9.9 mm.),  $n_D^{25}$  1.5102.

Hydrolysis of XXI with water at 90–100° regenerated Feist's acid (XX), m.p. 195–196° from ether, whose infrared spectrum was identical with the spectrum of authentic Feist's acid.

(19) D. G. Markees and A. Burger, *THIS JOURNAL*, **70**, 3329 (1948).

The dianilide derivative of the diacid chloride XXI was prepared in benzene. It was obtained as colorless crystals from absolute ethanol, m.p. 244.5–245°.

*Anal.* Calcd. for  $C_{18}H_{16}O_2N_2$ : C, 73.95; H, 5.52; N, 9.58. Found: C, 73.80; H, 5.33; N, 9.46.

*N,N,N',N'*-Tetramethyl-*trans*-1-methylenecyclopropane-2,3-dicarboxamide (XXII) was obtained by the procedure used to prepare the diamide XV. From 16.54 g. (0.0924 mole) of the diacid chloride XXI in 250 ml. of benzene, there was obtained *in toto* 14.48 g. (80%) of the diamide XXII. The first crop of crystals (11.23 g.) which deposited in the final crystallization from ether had m.p. 70–71°.

*Anal.* Calcd. for  $C_{10}H_{16}O_2N_2$ : C, 61.20; H, 8.22; N, 14.28. Found: C, 61.47; H, 8.45; N, 14.47.

*trans*-2,3-Bis-(dimethylaminomethyl)-1-methylenecyclopropane (XVII).—The procedure used here was essentially the same as that followed in the reduction of the diamide XV to the diamine XI. From 13.6 g. (0.0693 mole) of the diamide XXII and 3.90 g. (0.1028 mole, *ca.* 50% excess) of lithium aluminum hydride there was ultimately isolated 6.65 g. (57%) of the colorless liquid diamine XVII, b.p. 77–79° (9.5 mm.),  $n_D^{25}$  1.4600.

*Anal.* Calcd. for  $C_{10}H_{20}N_2$ : C, 71.37; H, 11.98; N, 16.65. Found: C, 71.54; H, 11.93; N, 16.75.

The dipicrate derivative of the diamine XVII was prepared and recrystallized from 95% ethanol, m.p. 167–169°.

*Anal.* Calcd. for  $C_{22}H_{26}N_2O_{14}$ : C, 42.17; H, 4.18; N, 17.89. Found: C, 42.31; H, 4.10; N, 17.84.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

## The Reactions of Resonance Stabilized Anions. I. Neutralization of the $\alpha, \alpha$ -Dimethylbenzyl Carbanion

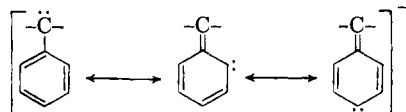
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Reaction of  $\alpha, \alpha$ -dimethylbenzylpotassium with deuterium oxide, carbon dioxide or dimethyl sulfate yields only the product of alpha attack ( $\alpha$ -deuteriocumene, *t*-butylbenzene, dimethylphenylacetic acid). Reaction of the anion with deuterium chloride in diethyl ether solution yields cumene containing deuterium in the  $\alpha$ -, *o*- and *p*-positions and containing 0, 1, 2 and 3 atoms of deuterium per molecule. This result is interpreted in terms of the anion reacting with deuterium chloride at the  $\alpha$ -, *o*- and *p*-positions to yield  $\alpha$ -deuteriocumene or an unstable isopropylidenecyclohexadiene which in the presence of base or acid can rearrange to cumene containing deuterium in the ring. The effect of heterogeneity and of solvating power of ethereal solvents upon the products of the reaction with deuterium chloride are discussed.

### Introduction

A number of highly colored benzyl-type carbanions are known which do not react readily with ethyl ether. The color and unreactivity of these carbanions is commonly attributed to resonance stabilization. If this is the case direct evidence



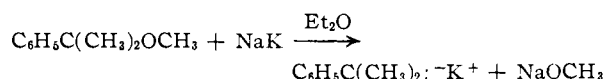
for this resonance stabilization should be forthcoming from the reactions of these carbanions, preferably in the simplest of their reactions, *i.e.*, neutralization.

The neutralization of  $\alpha, \alpha$ -dimethylbenzylpotassium (potassium cumyl) has been studied by the use of various deuterio-acids. The results indicate that weak acids, such as deuterium oxide, react with the cumyl anion to produce only  $\alpha$ -deuteriocumene. With strong acids, such as deuterium chloride in ethyl ether solution, neutralization involves attack of deuterium on the *o*- and *p*-positions of the anion. This finding presents direct chemical proof of the commonly accepted resonance stabilization mentioned previously.

### Results

Potassium cumyl, a blood-red carbanion, is readily prepared by the reaction of sodium-potassium alloy with cumyl methyl ether in the presence of ethyl ether<sup>2</sup> or other diluents. In ethyl ether the anion has a solubility of about 0.07 *M*. Treatment of a filtered solution of the anion with hydrogen chloride yields potassium chloride con-

taining less than 0.1% sodium chloride. There is therefore no question that the cleavage reaction should be formulated



Neutralization of the anion in ethyl ether solution 7 hours after the cleavage reaction had commenced (cleavage temperature, 25°) with > 99.5% deuterium oxide gave a deuteriocumene containing 90.8% *d*<sub>1</sub>-cumene and 9.2% *d*<sub>0</sub>-cumene (from mass spectra at reduced ionizing potential). Deuterium atoms in the *o*-, *m* or *p*-positions were absent as judged from the lack of infrared absorption at 15.8, 15.0 and 16.4  $\mu$  (the ring deuterated cumenes were found to have intense absorptions at these wave lengths). After storage for 161 hours a sample of the anion gave upon neutralization a cumene containing 74.4% *d*<sub>1</sub>-cumene and 25.6% *d*<sub>0</sub>-cumene. Ring deuteration was again absent. These results indicate that abstraction of a proton from ethyl ether by this anion must be extremely slow. For 0.1 mole of the anion in the presence of 700 ml. of ethyl ether, hydrogen abstraction cannot exceed 0.1% per hour and possibly is considerably less.

The formation of exclusively  $\alpha$ -deuteriocumene from the reaction of deuterium oxide with potassium cumyl is in agreement with the previous report of Ziegler and Schnell that carbonation of the anion yields only dimethylphenylacetic acid.<sup>2</sup> Moreover, treatment of the anion with dimethyl sulfate at 0° gave *t*-butylbenzene whereas *p*-cymene could not be detected by gas-liquid chromatography. The ratio of *t*-butylbenzene to

(1) Department of Chemistry, Iowa State College, Ames, Iowa.

(2) K. Ziegler and B. Schnell. *Ann.*, **437**, 222 (1934).