appropriate intervals of time, and run into 20 ml of cold dry acetone, and remaining sodium acetate was titrated with 0.004 N hydrochloric acid using a Metrohm potentiograph E 336 A. Plots of log $(A_\infty - A_t)$ *vs.* time, where A_∞ and A_t are titers at infinity and at the given times, respectively, were uniformly linear. The slopes multiplied by -2.303 gave the pseudo-first-order rate coefficients.

Solvolysis Products from 4-OBs.—The solvents and conditions used are listed in Table II. The concentration of 4-OBs was the same as that used for the rate measurements. The ratios of retained 4-OH and inverted 8-OH in Table II were determined by vpc analysis of the reaction mixture on a Hitachi gas chromatograph Model K-53 equipped with a hydrogen flame ionization detector and a UCON R-15 capillary column; the temperature of the column was 140° and carrier gas was helium at 2 kg/cm² pressure. The products from trifluoroacetolysis were hydrolyzed by 50% aqueous methanol containing sodium carbonate and then analyzed by vpc.

Solvent was evaporated from the hydrolysis mixture under a reduced pressure and the residue was dissolved in ether. The ether solution was washed with aqueous sodium carbonate, dried, and evaporated. Treatment of the residue by thin layer chromatography as described above gave pure samples of 4-OH and 8-OH besides a mixture of hydrocarbons.

Registry No.—1-OBs, 30538-46-6; 2-OBs, 1233-41-6; 3-OBs, 30538-48-8; 4-OH, 30538-49-9; 4-OBs, 30597-76-3; 5-OH, 30538-50-2; 5-OBs, 30538-51-3; 8-OH, 30538-52-4; 2-indanyl OBs, 16384-76-2.

The Hydrolysis of 7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one[1]

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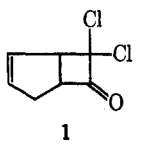
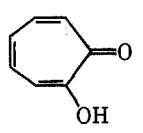
Tropolone is obtained in good yield by the sodium acetate–water–acetic acid hydrolysis of 7,7-dichlorobicyclo-[3.2.0]hept-2-en-6-one, the cycloadduct of dichloroketene and cyclopentadiene. Hydrolysis in aqueous sodium carbonate proceeds mainly with cleavage of the cyclobutanone ring, giving 1-formylcyclopentene-5-carboxylic acid, which is readily oxidized to cyclopentene-1,5-dicarboxylic acid. Structure assignments among the isomeric cyclopentenedicarboxylic acids were revised and the unreported cyclopentene-1,4-dicarboxylic acid was prepared. An improved procedure for the synthesis of 4,5-benzotropolone from the corresponding indene adduct is included.

Dichloroketene-based chemistry became the subject of extensive literature[3] following the preliminary report from this laboratory of an *in situ* generation and capture with reactive olefins to yield 2 + 2 cycloadducts. As a novel method of forming cyclobutanones it has already found considerable synthetic utility.[3g,l–o]

The initial experiments were carried out with cyclopentadiene leading to subject cycloadduct **1** which proved to be an intermediate precursor of tropolone **2**.[1a]

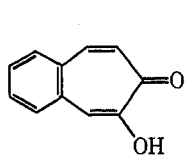


1



2

The general approach has been extended by several investigators to substituted tropolones **3**–**5** *via* the corresponding 2 + 2 cycloaddition with indene,[3d,l,o] 6,6-dimethylfulvene,[4] and 1-*tert*-butylcyclopentadiene.[5]



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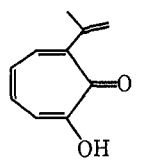

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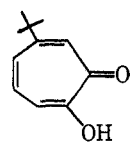

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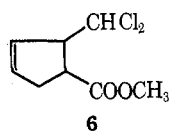
From a synthetic viewpoint, dichlorobicycloheptenone (**1**) has proven to be a useful intermediate. Reductive dechlorination provides the best source of bicyclo[3.2.0]hept-2-en-6-one, not easily accessible from ketene and cyclopentadiene.[6] Brook showed the sodium borohydride reduction of **1** to result in a mixture of endo and exo alcohols, precursors of stereoisomeric carboxaldehydes and carboxylic acids of the [3.1.0] ring system.[7] The reaction of **1** with sodium methoxide resulted in the cleavage of the cyclobutanone ring to give an isomer of **6**.[3a] Lactone **7** has recently been



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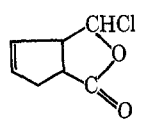


7

isolated in the triethylamine-catalyzed hydrolysis of **1** in aqueous acetone.[5] This paper deals with the unusual course of solvolytic reactions observed with **1**, leading to tropolone on one hand and cyclopentene derivatives on the other.

(1) For preliminary communications of this work, see (a) H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965); (b) H. C. Stevens and G. M. Trenta, *Chem. Commun.*, 1407 (1970).

(2) To whom inquiries should be addressed.

(3) (a) L. Ghosez, R. Montaigne, and P. Mollet, *Tetrahedron Lett.*, 135 (1966); (b) W. T. Brady, H. G. Liddell, and W. L. Vaughn, *J. Org. Chem.*, **31**, 626 (1966); (c) D. Borrmann and R. Wegler, *Chem. Ber.*, **99**, 1245 (1966); **102**, 64 (1969); (d) R. W. Turner and T. Seden, *Chem. Commun.*, 399 (1966) (since no experimental details are given and low yields are indicated, a preparation of 4,5-benzotropolone is included in this paper); (e) R. Hull, *J. Chem. Soc.*, 1154 (1967); (f) J. Ciabottini and H. W. Anderson, *Tetrahedron Lett.*, 3377 (1967); (g) W. T. Brady and O. H. Waters, *J. Org. Chem.*, **32**, 3703 (1967); (h) R. Montaigne and L. Ghosez, *Angew. Chem.*, **80**, 194 (1968); (i) L. Ghosez, R. Montaigne, H. Vanlierde, and F. Dumay, *Angew. Chem., Int. Ed. Engl.*, **7**, 643 (1968); (j) J. M. Lavanish, *Tetrahedron Lett.*, 6003 (1968); (k) H. Knoche, *Justus Liebigs Ann. Chem.*, **722**, 232 (1969); (l) R. E. Harmon and T. R. Potts, *J. Org. Chem.*, **34**, 2792 (1969); (m) V. R. Fletcher and A. Hassner, *Tetrahedron Lett.*, 1071, 5053 (1970); (n) E. J. Corey, Z. Arnold, and J. Hutton, *ibid.*, 307 (1970); (o) L. Ghosez, private communication.

(4) T. Asao, T. Machiguchi, T. Kitamura, and Y. Kitahara, *Chem. Commun.*, 89 (1970).

(5) P. Bartlett and T. Ando, *J. Amer. Chem. Soc.*, **92**, 7518 (1970).

(6) M. Rey, J. A. Huber, and A. S. Dreiding, *Tetrahedron Lett.*, 3583 (1968).

(7) P. R. Brook, *Chem. Commun.*, 565 (1968).

Experimental Section

General.—All melting points were taken on a Fisher–Johns melting point block and are uncorrected. Infrared spectra were taken on a Perkin–Elmer 521 grating spectrometer. Nmr spectra were taken on a modified Varian DA-60-IL spectrometer in deuterioacetone unless otherwise specified. Tetramethylsilane was used as an internal standard.

7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one (1).—To a vigorously stirred solution of 30.9 g of dichloroacetyl chloride, 23.8 g of freshly distilled cyclopentadiene, and 200 ml of hexane was added 20.2 g of dry triethylamine in 200 ml of hexane over a period of 1–2 hr. A slight nitrogen pressure was maintained during the reaction. After standing overnight the reaction mixture was filtered and the filter cake was washed with hexane. The solvent was removed under vacuum on a rotary evaporator at *ca.* 40°, yielding an orange liquid residue weighing 35.6 g. Vacuum distillation of this liquid gave a colorless distillate, bp 66–68° (2.1–2.2 mm) (a forerun of *ca.* 1 ml was discarded). The yield was 85%. The product yellows on standing at room temperature: ir (neat) 1806 (C=O) and 1609 cm^{-1} (C=C); nmr ($CDCl_3$) 354 (m, 2 H, CH=CH), 246 (m, 2 H, bridgehead), 162 cps (m, 2 H, $-CH_2-$).

Anal. Calcd for $C_7H_6Cl_2O$: C, 47.5; H, 3.4; Cl, 40.1. Found: C, 47.6; H, 3.4; Cl, 39.9.

Tropolone (2).—Sodium hydroxide (8.9 g) was dissolved carefully in 50 ml of glacial acetic acid. Water (5 ml) and **1** (8.85 g) were added all at once to the stirred solution under nitrogen. The reaction mixture was held at reflux temperature for 6.0 hr. Upon cooling it was poured into a 20% solution of cupric sulfate (300 ml) and slurried well. The precipitated copper–tropolone complex was removed by filtration and the filtrate was neutralized with solid sodium carbonate. The neutralized solution was extracted with four 250-ml portions of chloroform and the chloroform extract was dried over sodium sulfate. The solid complex which had been removed by filtration was dissolved in chloroform, washed with aqueous sodium carbonate, and dried. The combined chloroform extracts were concentrated to give 6.7 g of green solid (87% yield of crude product), mp 295° dec. The crude solid was recrystallized from chloroform–hexane (mp 310° dec).[8a]

The copper–tropolone complex (2.3 g) was dissolved in chloroform (125 ml) and the solution was saturated with hydrogen sulfide. The precipitated cupric sulfide was removed by filtration and the solvent was removed. Recrystallization of the residue (1.6 g) from hexane gave pure **2** as a white, crystalline solid, mp 50–51°.[8b]

α-Chlorotropone (9).—This compound was prepared from tropolone and thionyl chloride.[8b] Refluxing **9** (1.4 g, mp 66–67°) in 10 ml of acetic acid and 1 ml of water in the presence of 1.4 g of sodium hydroxide for 5.5 hr failed to give any tropolone detectable with copper sulfate. Recovery of starting material by removal of solvent, acidification, and extraction was 88%.

4,5-Benzotropolone (3).—Triethylamine (50.6 g) in *n*-hexane (400 ml) was added to indene (233.0 g) and dichloroacetyl chloride (74.5 g) at 21–36°. Upon filtration the product solution was stripped at reduced pressure and the residue was distilled *in vacuo*, bp 95–99° (0.2 mm). 2,2-Dichlorocyclobut[*a*]indan-1-one (**8**) (mp 79–81°)[9d,1] was obtained in 59% yield. Hydrolysis of **8** (66.8 g) with 158 g of sodium acetate trihydrate in 500 ml of acetic acid and 500 ml of water was accomplished by refluxing for 48 hr. Crude **3** (40.8 g, mp 156–158°)[9] was isolated by direct crystallization from the reaction mixture.

1-Formylcyclopentene-5-carboxylic Acid (12).—A mixture of **1** (53.1 g) and 1062 ml of 1 *N* sodium bicarbonate solution was heated to 75° with stirring for 5 hr. Upon removal of a slight amount of residual oil, acidification with hydrochloric acid, and saturation with ammonium chloride, the aqueous product solution was extracted continuously with methylene chloride for several hours. The semisolid residue from the removal of the solvent contained 6–7 g of solid, which was recrystallized from cyclohexane: mp 90–91°; ir (neat) 1695 (C=O), 1665 (C=O), 1620 cm^{-1} (C=C); nmr ($CDCl_3$) 660 (s, 1 H, COOH), 588 (s, 1 H, CHO), 426 (quasi s, 1 H, C=CH), 228 (t, 1 H, –CHCOOH), 156 cps (m, 4 H, CH_2).

Anal. Calcd for $C_7H_6O_3$: C, 60.00; H, 5.72. Found: C, 59.99; H, 5.73; neut equiv 140.

About 1–2 g of crude **2**, bp 72–75° (3.5 mm), mp 46–49°, could be recovered from the oily portion of the product. Flocculent polymeric material remained in the raffinate after the extraction.

Cyclopentene-1,5-dicarboxylic Acid (13).—To 6.37 g of silver nitrate in 9.5 ml of water and 1.75 g of **11** was added dropwise with cooling 4.9 g of potassium hydroxide dissolved in 15 ml of water. After filtration, acidification, and concentration at reduced pressure, solid separated. Exhaustive ether extraction gave solid product, mp 179–182°. Repeated crystallization from ether resulted in a melting point of 181.5–182.5°; nmr 612 (s, 2 H, COOH), 416 (quasi s, 1 H, C=CH), 222 (t, 1 H, –CHCOOH), 156 cps (m, 4 H, $-CH_2-$).

Anal. Calcd for $C_7H_8O_4$: C, 53.80; H, 5.13. Found: C, 53.86; H, 5.09; neut equiv, 79.

Cyclopentene-1,5-dicarboxylic Acid Diethyl Ester (14).—The diethyl ester of **13** was prepared by heating with excess ethanol in the presence of Dowex 50W-X8. The compound was isolated by preparative-scale gc as a colorless oil: ir (neat) 1720 (C=O), 1630 cm^{-1} (C=C); nmr 412 cps (1 H, C=CH).

***cis*- and *trans*-Cyclopentane-1,2-dicarboxylic Acid Diethyl Esters (15).**—Atmospheric pressure hydrogenation of **14** in refluxing absolute ethanol using 0.2% Pd on powdered carbon (Engelhard) resulted in a liquid mixture of cis (60%) and trans (40%) esters estimated from the two cycle-separated triplet signals for CH_3- in the nmr spectrum related to authentic trans ester: ir 1735 cm^{-1} (C=O); nmr 71 (t, CH_3 cis), 73 cps (t, CH_3 trans).

***cis*- and *trans*-Cyclopentane-1,2-dicarboxylic Acid (16).**—The mixture of diethyl esters **15** was hydrolyzed by heating in the presence of Dowex 50W-X8. Upon filtration and water removal a solid of wide melting range remained. Some impure trans acid could be isolated by addition of concentrated hydrochloric acid. Exclusively trans acid, mp 160–161°, was obtained from the isomeric mixture by refluxing with acetic anhydride[10] followed by hydrolysis of the vacuum-stripped residue with boiling water. Mixture melting points with authentic *trans*-cyclopentane-1,2-dicarboxylic acid showed no depression.

Cyclopentene-1,4-dicarboxylic Acid Diethyl Ester (17).—*cis,cis,cis*-2-Chloro-1,4-cyclopentanedicarboxylic acid, mp 177–178°, prepared from *endo*-5-chloro-2-norbornene[11a] by oxidation with sodium permanganate,[11b] was esterified by refluxing with absolute alcohol in the presence of a few drops of sulfuric acid. The liquid ester was isolated by preparative-scale glc, ir (neat) 1735 cm^{-1}. Upon heating with quinoline[12] to 210° for 15 min dehydrochlorination was complete. After removal of the quinoline by extraction with dilute hydrochloric acid, the diester **17** was isolated by preparative-scale glc as an oil: $n^{20}D$ 1.4664; ir (neat) 1740 (C=O), 1633 cm^{-1} (C=C); nmr 396 cps (m, –CH=C).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.09, 62.15; H, 7.46, 7.63.

Cyclopentene-1,4-dicarboxylic Acid (18).—Hydrolysis of **17** by heating in the presence of Dowex 50W-X4 with agitation resulted in the disapperance of all oily material. After filtration and ether extraction a solid product was recovered. Recrystallization from ether gave a solid, mp 180–182° with darkening. Alkali hydrolysis of **17** resulted in a cleaner product of equal melting point. Twice recrystallized from water, the melting point was 182.5–183.5°; ir (mull) 1685 (C=O), 1612 cm^{-1} (C=C); nmr 569 (s, 2 H, –COOH), 400 (m, 1 H, –CH=C<), 198 (m, 1 H), 170 (m, 4 H), 122 cps (m, 2 H).

Anal. Calcd for $C_7H_8O_4$: C, 53.85; H, 5.16 Found: C, 53.63; H, 5.27.

Cyclopentene-1,3-dicarboxylic Acid Diethyl Ester (19).—*cis*-2-Chloro-*cis*-1,3-dicarboxylic acid was prepared from *syn*-7-chloro-*exo*-norborneol[11b] by oxidation with potassium permanganate: mp 194–194.5° (lit.[11b] 186–187°); nmr 602 (s, 2 H), 290 (t, 1 H), 207 (m, 2 H), 128 cps (m, 2 H). The diethyl ester was obtained by refluxing with excess absolute ethanol in the

(8) (a) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **73**, (1951); (b) *ibid.*, **74**, 5683 (1952).

(9) D. S. Tarbell, G. P. Scott, and A. D. Kemp, *ibid.*, **72**, 379 (1950), give mp 158.5–160°.

(10) (a) W. H. Perkin, *J. Chem. Soc.*, **65**, 572 (1894); (b) R. C. Fuson and W. Cole, *J. Amer. Chem. Soc.*, **60**, 1237 (1938).

(11) (a) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950); (b) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *ibid.*, **76**, 5698 (1954).

(12) H. C. Stevens and O. Grummitt, *ibid.*, **74**, 4876 (1952).

presence of sulfuric acid. Dehydrochlorination was observed as a side reaction. The mixed esters were heated in the presence of quinoline to 175° for 1 hr. The desired diethyl ester was obtained in nearly quantitative yield as an oil: $n^{20}D$ 1.4667; assay 99.9% by glc; ir (neat) 1725 (C=O), 1633 cm^{-1} (C=C); nmr 399 cps (m, -CH=O<).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.38; H, 7.47.

Cyclopentene-1,3-dicarboxylic Acid (20).—Hydrolysis of **19** in either aqueous sulfuric acid or dilute sodium hydroxide led to the dibasic acid, which was recrystallized from an ether–pentane mixture: mp 150–151° (lit.[13a] 150.5°); ir (mull) 1685 (C=O), 1625 cm^{-1} (C=C); nmr 630 (s, 2 H, COOH), 406 (m, 1 H, -HC=C), 227 (m, 1 H, HCCOOH), 146 cps (m, 4 H, CH_2).

Anal. Calcd for $C_7H_8O_4$: C, 53.85; H, 5.16. Found: C, 54.01; H, 5.11, 5.26.

2-Cyanocyclopentenecarboxylic Acid (21).—Dehydrochlorination of 1-chloro-1-cyano-2-cyclopentanecarboxylic ester[13b] with aqueous potassium hydroxide at room temperature resulted in an exothermic reaction. Upon acidification and extraction with ether, 2-cyanocyclopentenecarboxylic acid was obtained in nearly quantitatve yield as a white solid. Recrystallized from hot water the acid showed mp 114.0–114.5°; nmr 628 (s, 1 H), 166 (t, 4 H), 124 cps (m, 2 H).

Anal. Calcd for $C_7H_7NO_2$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.13; H, 5.01; N, 10.15.

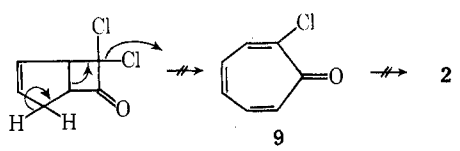
Cyclopentene-1,2- and -1,5-dicarboxylic Acids (22 and 13).—Refluxing of **21** in 30% potassium hydroxide solution for several hours followed by acidification and extraction with ether gave a mixture of dibasic acids. Some of the 1,2 isomer **22**[14] could be isolated by fractional crystallization: mp 176.5–177.5°; nmr 726 (s, 2 H), 169 (t, 4 H), 115 cps (m, 2 H). The bulk of the product was comprised of a eutectic mixture: mp 144–146°; nmr 666 (s), 416 (m), 222 (m), 170 (t), 115 cps (m).

Anal. Calcd for $C_7H_8O_4$: C, 53.85; H, 5.16. Found: C, 53.54; H, 4.97.

Signal ratios indicated a slight predominance of **13** over **22**.

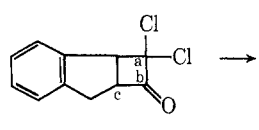
Discussion

The unique course of the solvolysis followed by cyclopentadiene–dichloroketene adduct **1** has been the subject of recent papers by Kitahara's group[4,15] as well as by Bartlett and Ando.[5] For the acetate hydrolysis to tropolone, a direct proton abstraction by base with subsequent collapse to α-chlorotropone could be ruled out from the outset when the latter failed to give tropolone under the conditions of the solvolysis.



9

The introduction of a substituent into the cyclopentadiene component proved to be the key to the most salient feature of the mechanism. In the conversion of indene to 4,5-benzotropolone the mechanistic clue afforded by the substituent was not recognizable due to the fortuitous equivalence of two benzotropolone structures.



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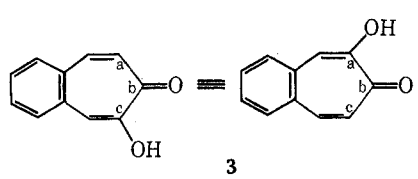
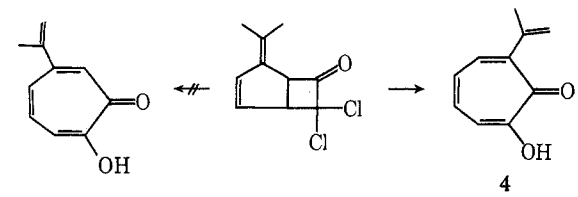


3

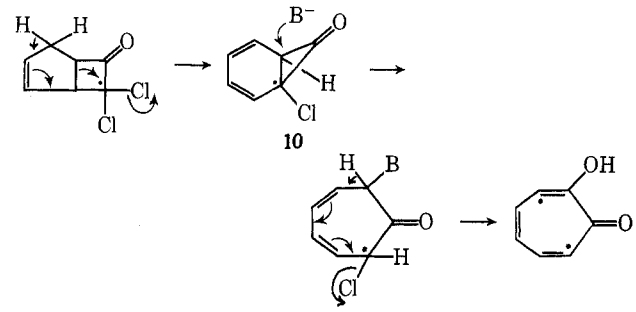
In an attempted synthesis of 4-isopropenyltropolone from the corresponding cycloadduct of dimethylfulvene, Kitahara's group[4] unexpectedly found the isopropenyl substituent in the resulting tropolone adjacent to either of the oxygen-carrying carbon atoms. Bartlett and Ando[5] similarly found the corresponding adduct from



4

1-*tert*-butylcyclopentadiene and dichloroketene to be opened to β-*tert*-butyltropolone (**5**) rather than the γ isomer, establishing the same "rearrangement" for a saturated substituent.

Examining the synthesis of tropolone itself by isotopic labeling with ^{14}C of the dichloroketene carbon and degradation of the resulting tropolone, the Japanese investigators[15] established unequivocally that neither of the two oxygen functions stemmed from the original $=CCl_2$ group. Their mechanistic interpretation involved a proton abstraction at the methylenic 4 position with formation of a norcaradienone intermediate **10**, followed by base attack and a 1,6-conjugate dehydrochlorination as follows.



10

While this mechanism fully accounts for the "rearrangement" observed with substituted adducts as well as the result of the isotopic labeling experiment, the valence tautomeric relationship of the norcaradienone intermediate **10** to chlorotropone (**9**), shown to be stable under the solvolysis conditions, argues against it.

An alternate mechanistic path involves an initial base attack at the "enolic" bridgehead carbon. Some qualitative indication as to the lability of this hydrogen was gained from nmr-monitored solvolysis experiments in a deuterioacetate system.[16] While a Favorskii intermediate would seem excessively strained, displacement of one of the α chlorines by a π-participated ionization mechanism[17] might reduce to a question of p-orbital overlaps in the dichlorocyclobutanone ring. Since the removal of one chlorine would result in substantially reduced strain, a transition state with much sp^2 character of the $-CCl_2$ carbon may be conceivable as the chloride departs.

(13) (a) B. L. Nandi, *J. Indian Chem. Soc.*, **11**, 277 (1934); (b) *ibid.*, **11**, 213 (1934).

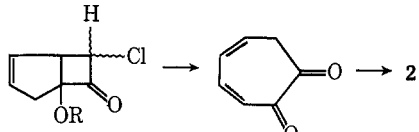
(14) E. Haworth and W. H. Perkin, *J. Chem. Soc.*, 987 (1894).

(15) T. Asao, T. Machiguchi, and Y. Kitahara, *Bull. Chem. Soc. Jap.*, **43**, 2662 (1970).

(16) Unpublished results by K. R. Fountain, Wisconsin State University, LaCrosse, Wis.

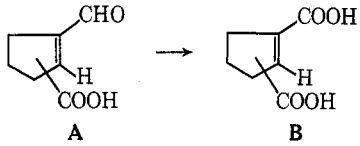
(17) F. G. Bordwell, R. G. Scameborn, and W. R. Springer, *J. Amer. Chem. Soc.*, **91**, 2087 (1969), and preceding papers.

In extensive work with dichloroketene adducts of diolefins other than cyclopentadiene, Bartlett, *et al.*,[18] as well as Ghosez, *et al.*,[19] observed a facile rearrangement of one chlorine to the "enolic" bridgehead position in the presence of base or by thermal means. Although this rearrangement is not observed in the case of **1**, it nevertheless suggests a pathway to tropolone. As formulated by Bartlett and Ando[5] it involves the intermediacy of isomeric acetates **11a**, which were successfully isolated and hydrolyzed to tropolone with great facility. The second elimination of hydrogen chloride with collapse of the central bond was attributed to the hydrolysis of acetates **11a** and ketonization of tertiary alcohols **11b**. This mechanism for the formation of tropolone appears consistent with all the experimental evidence.



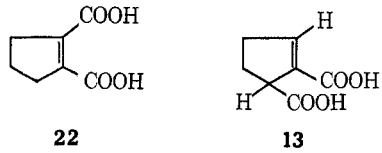
11a, R = Ac
b, R = H

Strongly basic reagents such as methoxide or *tert*-butoxide failed to convert **1** to tropolone or tropolone derivatives, instead causing a facile opening of the cyclobutanone ring.[3a,5] The reaction receiving close scrutiny in this study was the aqueous hydrolysis of **1** with sodium carbonate or bicarbonate. Unexpectedly, only minor quantities of tropolone were formed (<5%). The main course of the reaction involved ring opening of the dichlorocyclobutanone. Aside from polymeric products, a solid was isolated in yields up to 15% whose functionality was established from nmr evidence as a formylcyclopentenecarboxylic acid of type A. Oxidation with silver oxide led to dibasic acid B, mp 182°. Identification of B, *i.e.*, the position of the carboxyl group, could not be made from the existing literature and in fact required a complete reassessment of the structure assignments among the cyclopentenedicarboxylic acids.[1b]



A **B**

To be consistent with the [3.2.0] structure of the adduct **1**, the carboxylic groups were expected on adjacent carbons. Isomer **22**, mp 178°, was ruled out due to the absence of a vinylic proton. Compound **13**, reported by three different sources,[13a,20] had an alleged melting point in the range of 144–147°.



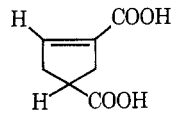
22 **13**

(18) P. D. Bartlett, H. Knoche, H. Griengl, and T. Ando, unpublished work.

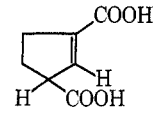
(19) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971); see also R. Montaigne, Ph.D. Thesis, Universite Catholique de Louvain, Louvain, Belgium, 1968.

(20) (a) A. Hassel and C. K. Ingold, *J. Chem. Soc.*, 1465 (1926); (b) S. Fujise, H. Uda, T. Ishikawa, H. Obaia, and A. Fujino, *J. Chem. Soc. Jap.*, **81**, 1071 (1960).

In view of a possible retro aldol–realdolization sequence involving A, the 1,3-dicarboxylic acids **18** and **20** were also considered. No literature reference was found for **18**. The synthesis of **20**, mp 150.5°, had been reported by Nandi.[13a]

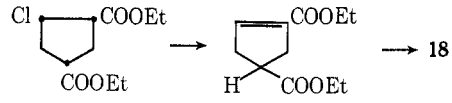


18



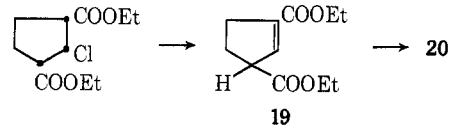
20

Unknown isomer **18** was prepared stereospecifically by the quinoline-catalyzed dehydrochlorination of all *cis*-3-chlorocyclopentane-1,4-dicarboxylic ester followed by hydrolysis. Both the diethyl ester **17** and acid **18** were spectrally distinguishable from B and its diethyl ester, although the melting points of the two acids were within one degree of each other.



17

Starting with all *cis*-2-chloro-1,3-dicarboxylic ester, isomer **20** was prepared in an analogous fashion *via* the diethyl ester **19**. The reported structure and melting point[13a] were confirmed.



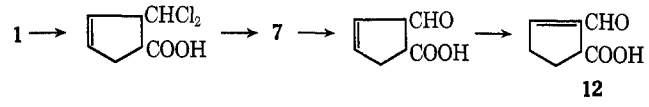
19

The only remaining compound consistent with generic structure B was **13**. This isomer was first reported by Hassel and Ingold[20a] and later by Nandi[13b] and Fujise, *et al.*[20b] The methods used by these investigators were essentially based on the alkali-catalyzed rearrangement of **22** to **13**. In our approach *via* the alkaline hydrolysis of 2-cyanocyclopentenecarboxylic acid (**21**), we indeed isolated product in the reported melting range of 144–147° in addition to unrearranged **22**. However, nmr analysis clearly indicated the "eutectic" material to be comprised of mixtures of **22** and B, whose structure was thus established as **13**. Final confirmation was afforded by the catalytic hydrogenation of the diethyl ester of B to a 60:40 mixture of *cis*- and *trans*-cyclopentane-1,2-dicarboxylic acid esters, which were characterized by hydrolysis, purification *via* the anhydride,[21] and comparison to authentic trans 1,2-dibasic acid.

The hydrolytic pathway followed by **1** in the presence of alkali carbonates thus entails cleavage of the cyclobutanone ring and displacement of the chlorines, possibly involving the newly formed carboxyl function. The shifting of the double bond into conjugation with the

(21) The conversion of the trans 1,2-acid to the cis anhydride by heating with acetic anhydride is well documented.[10a,b] However, the exclusive formation of trans acid in the acid hydrolysis of the anhydride is at best implied by inference; Perkin observed the isomerization of the cis to trans diacid by heating with hydrochloric acid.

formyl substituent would be expected in the alkaline environment. The extensive formation of polymers is



attributed to condensation reactions of the aldehydic species.

Registry No.—**1**, 5307-99-3; **12**, 30758-76-0; **13**, 3128-16-3; **14**, 30698-29-4; *cis*-**15**, 30758-77-1; *trans*-**15**, 30689-38-4; **17**, 30689-39-5; **18**, 3296-49-9; **19**, 30689-41-9; **20**, 30689-42-0; **21**, 30689-43-1; **22**, 3128-15-2.

Acknowledgment.—The authors are indebted to Professor P. D. Bartlett for many helpful discussions throughout the course of this work.

A New Pyridine Synthesis *via* 4-(3-Oxoalkyl)isoxazoles[1]

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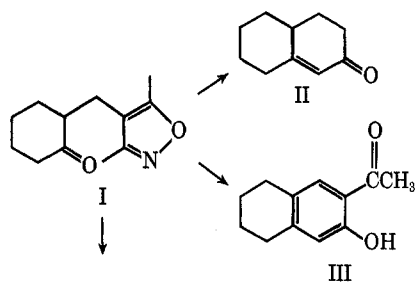
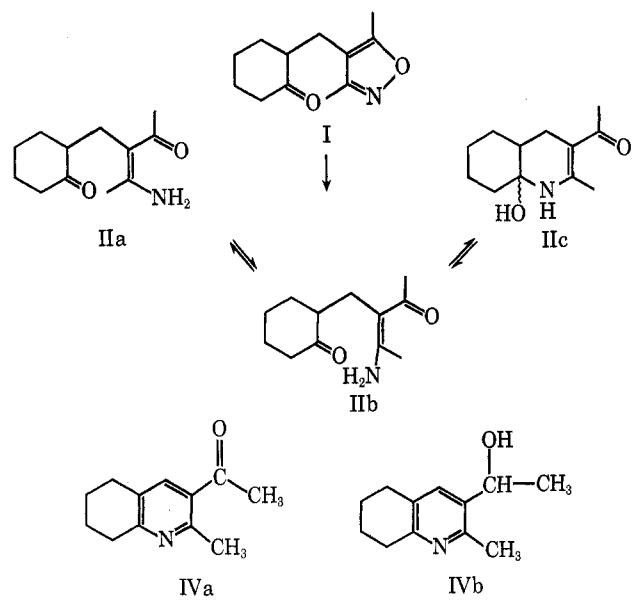
A general synthesis of β-acylpyridines *via* 4-(3-oxoalkyl)isoxazoles has been devised, based on the fact that these isoxazoles afford cyclic carbinolamines by reductive cleavage of their N–O linkage. Pyridines can be obtained in high yields from these carbinolamines by dehydration and oxidation.

We have developed a new synthetic method for the synthesis of β-acylpyridines *via* the transformation of suitably substituted isoxazoles. Although 3-substituted isoxazoles are stable under a variety of chemical conditions, their nitrogen–oxygen linkage exhibits high lability under special conditions, such as catalytic hydrogenation[3] or electron impact.[4] It is this lability which made possible our use of isoxazoles as masked



keto alkyl functions in synthesis and which is the basis of the new methods of annelation[5] (*e.g.*, I → II) and of benzene ring construction[6] (*e.g.*, I → III) *via* 4-(3-oxoalkyl)isoxazoles. The latter are easily prepared by the alkylation of ketones with the readily available 4-chloromethyl-3-methyl-5alkylisoxazoles.[7] We had noted during our previous investigation of the isoxazole annelation[5] that catalytic hydrogenation of 2-(3,5-dimethyl-4-isoxazolylethyl)cyclohexanone (I) gave an equilibrium mixture (IIa + IIb + IIc) which, upon heating with base, furnished a small amount of pyridines IVa and IVb in addition to the major product, $\Delta^{1,9}$-octalone-2 (II). It became clear that, if dehydration of the cyclic tautomer IIc took place faster than various hydrolytic reactions, the corresponding β-acylpyridine should be formed in high yield by mild oxidation of the dehydration product.



Dehydration under basic conditions would be expected to be particularly easy when a carbonyl group is present in the β position to the hydroxyl group of the carbinolamines. We have examined such cases, VIa and VIb, derived from acetylacetone and ethyl acetoacetate, respectively, and have substantiated this anticipation.

Condensation of acetylacetone and 3,5-dimethyl-4-chloromethylisoxazole (V) in the presence of potassium carbonate gave, in 61% yield, the oily diketone VIa, whose structure was confirmed by the typical isoxazole fragmentation pattern in the mass spectrum[4] and by the formation of bis(3,5-dimethyl-4-isoxazolyl)methane (VII)[4] through its reaction with hydroxylamine. Catalytic hydrogenation of VIa in the presence of palladium/charcoal in triethylamine–ethyl acetate (1:1)

(1) A part of this work was announced in a short communication: M. Ohashi, H. Kamachi, H. Kakisawa, and G. Stork, *J. Amer. Chem. Soc.*, **89**, 5460 (1967).

(2) Department of Material Science, University of Electrocommunications, Chofu-Shi, Tokyo, Japan.

(3) N. K. Kochetkov and S. D. Sokolov, *Advan. Heterocycl. Chem.*, **2**, 416 (1963).

(4) M. Ohashi, H. Kamachi, H. Kakisawa, A. Tatematsu, H. Yoshizumi, H. Kano, and H. Nakata, *Org. Mass. Spectrom*, **2**, 195 (1969); *Tetrahedron Lett.*, 379 (1968).

(5) G. Stork, *Pure Appl. Chem.*, **9**, 931 (1964); G. Stork, S. Danishefsky, and M. Ohashi, *J. Amer. Chem. Soc.*, **89**, 5459 (1967); G. Stork and J. E. McMurry, *ibid.*, **89**, 5463, 5464 (1967).

(6) M. Ohashi, T. Maruishi, and H. Kakisawa, *Tetrahedron Lett.*, 719 (1968).

(7) G. Stork and J. E. McMurry, *J. Amer. Chem. Soc.*, **89**, 5461 (1967); N. K. Kochetkov, E. D. Khomutova, and M. V. Brazilesky, *J. Gen. Chem. USSR*, **28**, 2376 (1958).