spontaneous and exothermic reaction between thiosalicylic acid and a carbodiimide in the absence of a solvent. Compound I is quite stable.

On prolonged boiling with dilute acid, the corresponding dione (II) is formed. Alkaline hydrolysis of I causes ring rupture with formation of the *sym*-disubstituted urea. Compound II is stable to prolonged treatment with acid or permanganate.

When thiosalicylic acid is replaced by its ester, the reaction product is a complex mixture containing some I.

The structures of I and II, assigned on the basis of elemental analysis, spectra, and postulated mechanism of formation, have been confirmed by the recently reported[2] synthesis of II *via* cyclization of the carbamate of thiosalicylic acid.

A study of the reduction of I and II and the reaction of carbodiimides withs alicylic, anthranilic, and β-mercaptopropionic acids is in progress.

Experimental[3]

3-Cyclohexyl-2-cyclohexylimino-2,3-dihydro-4H-1,3-benzothiazin-4-one (I, R = cyclohexyl).—To 20.6 g. (0.1 mole) of dicyclohexylcarbodiimide (Aldrich Chemical Co.) was added 7.7 g. (0.5 mole) of thiosalicylic acid. There was an immediate exothermic reaction and 20–25 ml. of dry benzene was added to make the thickening mixture more fluid. The suspension was left at room temperature for 3 hr. and then heated on a steam bath for 20 hr. The insoluble solid was filtered and proved to be dicyclohexylurea (10 g., 88% yield, m.p. 225–230°; lit.,[4] m.p. 229–230°). The filtrate was concentrated *in vacuo* and the resulting oil slowly crystallized, m.p. 80–83°. The solid was recrystallized from ethanol, m.p. 81–84°, yield 9.6 g. (56%).

Anal. Calcd. for $C_{20}H_{26}N_2OS$: C, 70.14; H, 7.65; N, 8.18. Found: C, 70.26; H, 7.81; N, 8.25.

When the reaction was carried out by adding thiosalicylic acid to a solution of carbodiimide in benzene, the yield was very low.

3-Cyclohexyl-2H-1,3-benzothiazine-2,4(3H)-dione (II, R = cyclohexyl).—A 2-g. sample (0.0058 mole) of II (R = cyclohexyl) in 20 ml. of 10% sulfuric acid and enough ethanol to dissolve the solid was refluxed for 5 hr. The solution was concentrated *in vacuo* to yield a solid which was separated by filtration, m.p. 140–145°. It was recrystallized from ethanol to give 0.95 g. of product, m.p. 150–152°, 62% yield (lit.,[2] m.p. 148°).

Anal. Calcd. for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36. Found: C, 64.72; H, 5.58; N, 5.36.

Base-Catalyzed Hydrolysis of II (R = cyclohexyl).—A solution of 2 g. of the imino compound (I) in dilute aqueous–alcoholic potassium hydroxide was refluxed for 1.5 hr. On cooling 0.7 g. (54% yield) of a white solid separated, m.p. 220–223°; a mixed melting point determination with dicyclohexylurea did not show any depression. A small amount of unidentified oil was also isolated from the filtrate.

3-Isopropyl-2-isopropylimino-2,3-dihydro-4H-1,3-benzothiazine (I, R = isopropyl).—The procedure described for the preparation of the cyclohexyl analog was followed using 15.4 g. (0.1 mole) of thiosalicylic acid and 25.2 g. (0.2 mole) of diisopropylcarbodiimide (Aldrich Chemical Co.). After the diisopropylurea had been separated by filtration, (m.p. 185–190°, 14 g., 97% yield), the filtrate was concentrated *in vacuo* to yield an oil which slowly solidified and was recrystallized from a mixture of ethanol–water, m.p. 51–52°, 11 g. (42%).

Anal. Calcd. for $C_{14}H_{18}N_2OS$: C, 64.09; H, 6.92; N, 10.68. Found: C, 63.92; H, 6.74; N, 10.83.

3-Isopropyl-2H-1,3-benzothiazine-2,4(3H)-dione (II, R = isopropyl).—The hydrolysis of the isopropylimine was carried out as described for the cyclohexyl analog, using 10% ethanolic sulfuric acid. The product was isolated as a white solid which was recrystallized from a mixture of ethanol and water, m.p. 67–68° (lit.,[1] m.p. 67°) 0.9 g. (28%).

Anal. Calcd. for $C_{11}H_{11}NO_2S$: C, 59.71; H, 5.01; N, 6.33. Found: C, 60.00; H, 4.74; N, 5.86.

(2) K. Hasspacher, U.S. Patent 2,978,449 (1961).

(3) Analyses were carried out by Mrs. D. Rolston and her staff of these laboratories.

(4) A. Skita and H. Rolfes, *Ber.*, **53B**, 1242 (1920).

The Synthesis of 4-Substituted Cyclopentenes from 1,4-Dibromobutene-2

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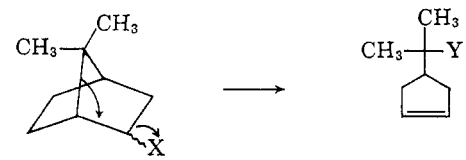
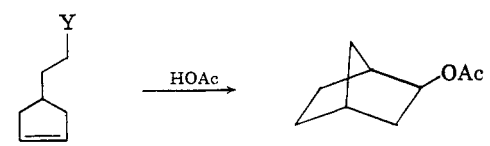
In studying the reactions of 2-substituted bicyclo[2.1.1]hexanes (I), we encountered a monocyclic, unsaturated product which appeared to arise *via* opening of the four-membered ring in the bicyclic system, giving a 4-substituted cyclopentene (II) (equation 1). To confirm the structure of II, as well as to provide material for the study of the



(1)

Ia. X = N_2^+ IIa. Y = OAc
b. X = OTs b. Y = OH

possible reclosure of II to the original bicyclic system, in analogy to the closure of III to *exo*-norbornyl acetate (IV) (equation 2) reported independently by Lawton[4] and by Bartlett and Bank,[5] we have sought a convenient method for the synthesis of compounds of this type. The results of this search are reported below.



(2)

III. Y = OTs or *p*-$O_3SC_6H_4NO_2$ IV

Several approaches to 4-substituted cyclopentenes are reported in the literature.[6-9] Of these

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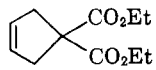
(3) National Institutes of Health Predoctoral Fellow.

(4) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

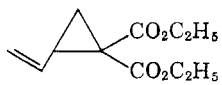
(5) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

published techniques, only one appeared attractive; this involved the cycloalkylation of malonic ester with 1,4-dibromobutene-2 (equation 3) to give the diester V.[8] Although this scheme appears straightforward, there are several reasons for viewing its reported success with skepticism. First of all, no evidence in support of structure V for the product was presented. Secondly, *trans* - 1,4 - dibromobutene-2 was used, rather than the *cis* isomer, so that cyclization to a cyclopentene would be sterically unfavorable. Finally, Kierstead, Linstead, and Weedon showed, without comment on the earlier work, that the reaction between *trans*-1,4-dibromobutene-2 and sodiomalonic ester yields the vinyl cyclopropane VI, *via* an internal S_N2' type of displacement.[10] The properties of VI are in good agreement with those reported earlier for V, and it therefore seems reasonable to conclude that the synthesis of V remains to be realized.

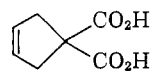
$$Br{-}CH_2{-}CH{=}CH{-}CH_2Br + Na^+\bar{C}H(CO_2Et)_2 \longrightarrow \quad (3)$$



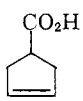
V



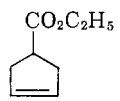
VI



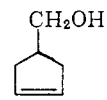
VII



VIII



IX



X

We have now carried out the condensation of *cis*-1,4-dibromobutene-2 with malonic ester and have obtained V in 54% yield. Alkaline hydrolysis of V gives a crystalline malonic acid VII whose n.m.r. spectrum shows peaks at −0.1, 4.55, and 7.00 τ of relative intensity 1:1:2, in good agreement with expectations for the carboxylic, olefinic, and allylic protons of VII, respectively.[11] This acid is decarboxylated by heating to 170° to give cyclopentene-4-carboxylic acid (VIII) in 30% yield. This acid was converted directly into its ethyl ester IX by treatment with diazoethane. Hydrogenation of IX gave the ethyl ester of cyclopentane carboxylic acid, thus confirming the cyclopentenoid nucleus.

Finally, the conversion of IX into the corresponding primary alcohol X was brought about by reduction with lithium aluminum hydride. An alternative synthesis of X was carried out by treating the Grignard reagent derived from 4-bromocyclopentene[12] with formaldehyde. The low yield in preparing the 4-bromocyclopentene, however, made this route unattractive.

Methylmagnesium iodide reacted smoothly with IX to give the tertiary alcohol IIB. In contrast, the Grignard reagent derived from 4-bromocyclopentene gave very poor results with acetone.[13] On the basis of these observations, the malonic ester route to cyclopentenes of this type appears to be the most convenient now available.

(6) M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **212**, 581 (1941).

(7) U.S. Patent No. 2,454,047 (*Chem. Abstr.*, **43**, 5416 C).

(8) G. S. Skinner, G. Limperosa, and R. Pettibone, *J. Am. Chem. Soc.*, **72**, 1648 (1950).

(9) E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 25 (1960).

(10) R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 3610 (1952).

(11) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, 1959.

(12) The authors are indebted to Professor Paul D. Bartlett for providing the details for this preparation.

Experimental

4,4-Dicarbethoxycyclopentene (V).—Diethyl malonate (26.2 g.) was added to a cold solution of 7.80 g. of sodium in 165 ml. of absolute alcohol. The resulting suspension of monosodio diethylmalonate was added dropwise to 35.0 g. of *cis*-1,4-dibromobutene-2 with stirring at 0°. The reaction mixture was stirred for 2 hr. at 0°, 16 hr. at room temperature, and 2.5 hr. at 50–55°. The solution was then diluted with ether and filtered to give 33.6 g. of inorganic salts (97% based on the theoretical yield of sodium bromide). The filtrate was washed thoroughly with water and dried over anhydrous magnesium sulfate. Removal of the drying agent and solvent gave 30.4 g. of crude product. This material was fractionally distilled to yield 18.7 g. (54%) of V, b.p. 85.5–87.5° (21 mm.), $n^{26}D$ 1.4510.

Redistillation gave an analytical sample, $n^{26}D$ 1.4512.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.12; H, 7.71.

4,4-Dicarboxycyclopentene (VII).—A mixture of 54.3 g. of V, 50 ml. of water, 20 ml. of ethanol, and 55 g. of potassium hydroxide was heated to reflux for 4.5 hr. The reaction mixture was cooled and extracted with ether. The aqueous solution was saturated with sodium chloride and acidified with dilute hydrochloric acid. The product was immediately extracted with ether. After drying over anhydrous magnesium sulfate and removal of the solvent, there remained 39.3 g. (98%) of crude VII, m.p. *ca.* 100–130°.

Two recrystallizations from benzene followed by sublimation gave an analytical sample, m.p. 165.0–165.5°.

Anal. Calcd. for $C_7H_8O_4$: C, 53.84; H, 5.16. Found: C, 54.09; H, 4.88.

4-Carbethoxycyclopentene (IX).—Five grams of crude VII were pyrolyzed at 170° and 1 mm. pressure, the product being collected in a Dry Ice–acetone trap. The crude monoacid (VIII) was immediately esterified with diazoethane. The ethereal solution of the ester was dried over anhydrous magnesium sulfate, filtered, and the ether removed under reduced pressure. The residue was fractionally distilled to yield 1.34 g. (30%) of IX, b.p. 89–93° (40 mm.), $n^{21}D$ 1.4445.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.75; H, 8.64.

An anilide of VIII was prepared as follows: One gram of VII was decarboxylated in the usual manner to give 0.52 g. of crude VIII. This was immediately dissolved in 20 ml. of dry benzene and 1 ml. of oxalyl chloride was added. After standing for 1 hr., the reaction mixture was concentrated to *ca.* 10 ml. on a flash evaporator and was treated with 1 ml. of aniline, added dropwise. The solid aniline hydrochloride was removed by filtration, and the solvent removed from the filtrate. The residue was recrystallized

twice from ethanol–water (Norit) to give shiny white plates of anilide, m.p. 139–140° (lit. m.p. 140°).[6]

Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.80; H, 7.03; N, 7.53.

Carbethoxycyclopentane.—Cyclopentane carboxylic acid (1.50 g.) was treated with diazoethane and distilled to give 1.72 g. (92%) of carbethoxycyclopentane, b.p. 87–90° (45 mm.), $n^{24}D$ 1.4325 (lit.[14] b.p. 89.3° (45 mm.), $n^{20}D$ 1.4360).

Carbethoxycyclopentane by Reduction of IX.—4-Carbethoxycyclopentene (IX) (140 mg.) was hydrogenated over 10% palladium on charcoal. Sixty-four milligrams of the saturated ester, $n^{23}D$ 1.4332, was isolated by preparative vapor phase chromatography. The infrared spectrum was identical to that of an authentic sample, and retention times on vapor phase chromatography were the same.

4-Hydroxymethylcyclopentene (X) A.—A solution of 2.68 g. of IX in 20 ml. of dry ether was added dropwise, with stirring and cooling, to a slurry of 1.50 g. of lithium aluminum hydride in 20 ml. of dry ether. The reaction mixture was stirred overnight and was then hydrolyzed by the addition of 6 ml. of water dropwise with cooling and stirring followed by stirring for an additional hour. The organic salts were removed by filtration and were dried over anhydrous magnesium sulfate. After removal of the drying agent and solvent, the residue was distilled to yield 1.63 g. (87%) of X, b.p. 98–99° (57 mm.), $n^{22}D$ 1.4670. An analytical sample was prepared by preparative vapor phase chromatography.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.16; H, 10.37.

B.—A Grignard reagent was prepared by adding 4.12 g. of 4-bromocyclopentene[12] dissolved in 20 ml. of dry ether to 0.85 g. of magnesium turnings in 10 ml. of dry ether. The entire reaction was carried out under nitrogen with vigorous mechanical stirring. After the addition was complete, stirring was continued for 0.5 hr. At this point the nitrogen flow was diverted through a flask containing 3.0 g. of paraformaldehyde which had previously been dried over phosphorus pentoxide. This flask was immersed in an oil bath at 180°, causing the paraformaldehyde to depolymerize, yielding gaseous, monomeric formaldehyde which was swept into the Grignard solution by the nitrogen stream. After a good excess of formaldehyde had been introduced, the reaction mixture was stirred for an additional 0.25 hr. and then poured into ice–dilute hydrochloric acid. This mixture was extracted thrice with ether and the combined ether extracts were washed with sodium carbonate solution, then water, and dried over anhydrous magnesium sulfate. The drying agent and solvent were removed and the residue was distilled to give 1.04 g. (38%) of *X*, b.p. 105–108°, $n^{24}D$ 1.4697. This material had an infrared spectrum identical with that of the product obtained above in part **A**.

4-Dimethylhydroxymethylcyclopentene (IIB).—One gram of IX in 20 ml. of dry ether was added dropwise to the Grignard reagent prepared from 1.00 g. of magnesium, 3.00 g. of methyl iodide, and 50 ml. of anhydrous ether. The reaction mixture was stirred at room temperature for 0.5 hr., followed by hydrolysis with saturated ammonium chloride solution. The ethereal layer was removed and dried over anhydrous sodium carbonate. After removal of the drying agent and solvent, the product was isolated by preparative vapor phase chromatography to give 0.36 g. (40%) of IIB, $n^{28}D$ 1.4640.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.82; H, 11.21.

(13) Similar results were obtained by G. S. Skinner and F. P. Florentine, *J. Am. Chem. Soc.*, **76**, 3200 (1954), who observed that cyclopentylmagnesium bromide gave only 10% of the corresponding tertiary alcohol on treatment with acetone.

(14) F. C. Whitmore, J. M. Crosby, W. S. Sloatman, and D. G. Clarke, *J. Am. Chem. Soc.*, **64**, 1801 (1942).

Acknowledgment.—The authors are grateful to the General Aniline and Film Corporation for a generous gift of *cis*-but-2-ene-1,4-diol, and to the National Science Foundation for partial support of this work.

On the Structures of α-Dolabrinol and Isopygmaein

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During a paper chromatographic investigation[1] of the tropolones from a number of wood species in the family Cupressaceae we encountered five new tropolonic compounds, and recently[2,3] we determined the structures of two of them: pygmaein and α-thujaplicinol. This report deals with the isolation and structure determination of two further compounds, previousy designated as T-10 and T-0.1.

Preparative paper chromatography was applied to the mixture of α-thujaplicinol and the T-10 tropolone from *Cupressus pygmaea* (Lemm.) Sarg. Thick S&S 470 paper impregnated with dimethyl sulfoxide[4] was used, with isoöctane as eluent. The pure T-10 tropolone was obtained as a colorless oil and was purified by evaporative distillation.

The isolated T-10 material gave a red complex with ferric chloride solution, a green complex with copper acetate, and a yellow salt with sodium hydroxide. Its formula was $C_{10}H_{10}O_3$, with molecular weight (Rast) of 165 ± 10%. It exhibited a typical tropolonic electronic spectrum, similar to that of α-thujaplicinol and a typical infrared spectrum. Its n.m.r. spectrum also agreed with the tropolonic structure and indicated the presence of an isopropenyl side chain.

Hydrogenation of the isolated material, with palladium on charcoal as catalyst, indicated the presence of one double bond; the hydrogenated material was identical to α-thujaplicinol. The T-10 tropolone, accordingly, should possess the formula of 3-isopropenyl-7-hydroxytropolone, or α-dolabrinol (structure I).

So far only two natural tropolones with isopropenyl side chains—β-dolabrin and procerin[5,6]—

(1) E. Zavarin, R. M. Smith, and A. B. Anderson, *J. Org. Chem.*, **24**, 1318 (1959).

(2) E. Zavarin and A. B. Anderson, *ibid.*, **26**, 1679 (1961).

(3) E. Zavarin, A. B. Anderson, and R. M. Smith, *ibid.*, **26**, 173 (1961).

(4) C. A. Wachmeister and B. Wickberg, *Acta Chem. Scand.*, **12**, 1335 (1958).

(5) T. Nozoe, K. Takase, and M. Ogata, *Chem. Ind.* (London), 1070 (1957).

(6) J. Runeberg, *Acta Chem. Scand.*, **15**, 645 (1961).