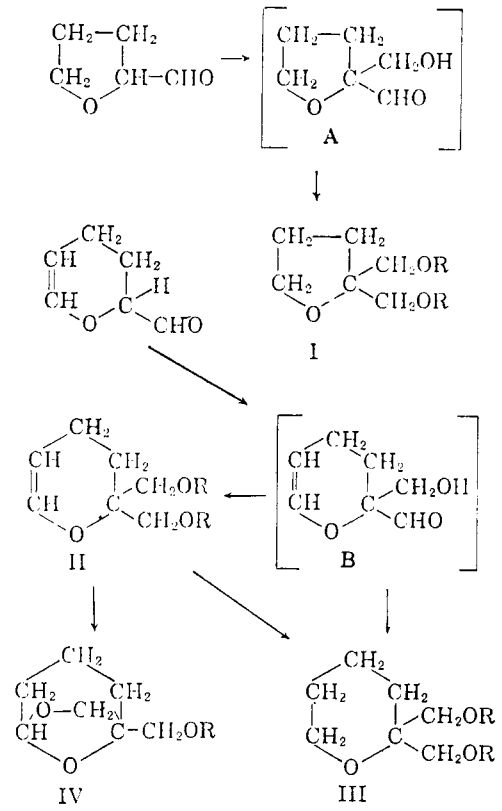
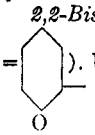


product [b.p. 77–87° (15 mm.): 53% yield] was freed from monoether by heating with phthalic anhydride and subsequent distillation.

2,2-Bis(2-tetrahydropyranoxymethyl)tetrahydrofuran (I, R = ). Using a slight modification of the procedure of Woods and Kramer[4] and an excess of 2,3-dihydro(4H)pyran, a mixture of the mono- and bis-2-pyranoxymethyl derivatives was obtained. The pure "bis" compound was obtained by careful fractionation.

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3-Cyclohexene-1-acetamide

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As part of an investigation of the nucleophilic reactions of mono- and ditosyl derivatives of *cis*- and *trans*-1,4 - cyclohexanediols we condensed ethyl malonate with *trans*-1,4-ditosyloxycyclohexane in the presence of sodium ethoxide. A product was isolated in low yield whose elementary analysis corresponded to that calculated for 7,7-dicarbethoxynorbornane. Saponification and decarboxylation of the diester followed by conversion to the amide, however, gave a monocarboxamide whose properties differed from those of norbornane-7-carboxamide. The infrared spectrum of the condensation product supported the structure of an unsaturated dicarboxylic ester and the melting point of the monocarboxamide was in the range of those reported for the known cyclohexeneacetamides[1b] rather than that of the more compact and much higher melting norbornanecarboxamides.[2]

The behavior of certain tosyl esters in nucleophilic reactions has been recorded by earlier investigators. Although primary tosyl esters undergo nucleophilic displacement rather readily[3] and in good yields, the reactivity of the tosyl esters of secondary alcohols is greatly diminished.[4,5] The influence of steric factors upon the reactivity of certain alicyclic tosyl esters has been discussed[4] and Ingold[6] has pointed out the similarity in reactivity of the tosylates of secondary alcohols to that of tertiary alkyl halides.

These considerations indicated the structure of the diester to be ethyl 3-cyclohexene-1-malonate and that of the monocarboxylic acid amide derived from it to be 3-cyclohexene-1-acetamide.

The synthesis of 3-cyclohexene-1-acetic acid and its amide *via* the Diels-Alder condensation with unactivated dienophiles, such as vinylacetic acid, requires the use of high temperature and introduces the possibility of double bond migration. The reaction of butadiene with acrylic acid to form 3-cyclohexene-1-carboxylic acid, on the other hand, can be carried out at low temperatures without isomerization. When 3-cyclohexene-1-carbonyl chloride was subjected to the Arndt-Eistert reaction 3-cyclohexene-1-acetamide was obtained in good yield.

Elementary analysis, a comparison of the infrared spectra and mixed melting point deter-

(1)(a) Present address: Shulton, Inc., Clifton, N. J.

(1)(b) Cyclohexeneacetamides: Δ^1-(m.p. 151°), O. Schnider and J. Hellerbach, *Helv. Chim. Acta*, 33, 1437 (1950); Δ^2- (m.p. 147–148°), M. Mousseron and F. Winternitz, *Compt. rend.*, 217, 428 (1943); α- (m.p. 146.5–147.5°), A. Ya. Berlin and L. V. Sokolova, *Zhur. Obshcheĭ Khim.*, 25, 347 (1955).

(2) Norbornanecarboxamides: 1- (m.p. 235–236°), 2-*endo*- (m.p. 210.5–211.5°), W. R. Boehme, *J. Am. Chem. Soc.*, 81, 2762 (1959); 2-*exo*-(m.p. 192.5–193.5°), W. R. Boehme, E. Schipper, W. G. Scharpf, and J. Nichols, *J. Am. Chem. Soc.*, 80, 5488 (1958).

(3) W. Braker, E. J. Pribyl, and W. A. Lott, *J. Am. Chem. Soc.*, 69, 866 (1947).

(4) N. K. Matheson and S. J. Angyal, *J. Chem. Soc.*, 1133 (1952).

(5) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 320 (1949).

(6) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, 1953, p. 341.

minations showed the monocarboxylic amide derived from *trans*-1,4-ditosyloxycyclohexane and ethyl malonate to be 3-cyclohexene-1-carboxamide.

EXPERIMENTAL[7]

Ethyl 3-cyclohexene-1-malonate. One-tenth mole (16.0 g.) of ethyl malonate was added to a solution of 4.6 g. (0.2 mole) of sodium in 100 ml. of absolute ethanol. Most of the solvent was removed by distillation under reduced pressure on the steam bath and a suspension of 42.4 g. (0.1 mole) of *trans*-1,4-ditosyloxycyclohexane[5] in 350 ml. of anhydrous benzene was added. The mixture was refluxed with stirring for 20 hr., cooled, and poured into water. The benzene phase was washed with water, dried over anhydrous potassium carbonate, and the solvent distilled on the steam bath. The residual oily solid was extracted with hexane which left a residue of 6.5 g. of unchanged ditosylate. Evaporation of the hexane extract gave a pale yellow oil which was distilled slowly at a bath temperature not exceeding 145°. Following a forerun of 7.4 g. of recovered ethyl malonate there was obtained 3.3 g. (14%) of a colorless liquid, b.p. 86–95°/0.08 mm. For analysis it was redistilled yielding 2.4 g. b.p. 106–110°/0.2 mm., n_D^{25} 1.4580.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.91; H, 8.48.

3-Cyclohexene-1-malonic acid. A solution of 2.2 g. of the dicarboxylic ester above in 20 ml. of 90% ethanol containing 4.0 g. of potassium hydroxide was refluxed for 4 hr. An equal volume of water was added and the solution was distilled to dryness under reduced pressure on the steam bath. The solid residue was taken up in 40 ml. of water and acidified slightly with dilute hydrochloric acid. The colorless plates which separated were extracted with ether and the extracts were dried over anhydrous calcium chloride. Evaporation of the solvent gave 1.6 g. (95%) of a solid melting with decomposition at 151–153°. Recrystallization from toluene gave 1.2 g. of colorless plates, m.p. 151–153° dec.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.90; H, 6.53.

3-Cyclohexene-1-acetic acid. The above dicarboxylic acid (1.1 g.) was heated for 30 min. at a bath temperature of 180° when gas evolution ceased. Distillation of the residue under reduced pressure gave 0.45 g. (54%) of colorless liquid, b.p. 140–142°/15 mm. It was redistilled for analysis giving 0.35 g., b.p. 138–140°/13 mm., n_D^{25} 1.4802.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.70; H, 8.73.

3-Cyclohexene-1-acetamide. (a) The above monocarboxylic acid (0.30 g.) was dissolved in 2.0 ml. of chloroform and 0.3 ml. of thionyl chloride. The solution was allowed to stand overnight and refluxed for 1 hr. Chloroform and excess thionyl chloride were removed by distillation on the steam bath under reduced pressure and the residue of 3-cyclohexene-1-acetyl chloride was taken up in 10 ml. of anhydrous ether. A gentle stream of anhydrous gaseous ammonia was passed into the solution for 1 hr. The resulting suspension was evaporated and the solid residue was recrystallized from 15 ml. of boiling water. The colorless plates (0.19 g., 63%) which separated on cooling melted at 142–143°. Recrystallization from water gave 0.095 g., m.p. 141–142°.

Anal. Calcd. for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.21; H, 9.32; N, 9.91.

(b) An ethereal solution of diazomethane was prepared by adding 25.0 g. (0.17 mole) of *N*-nitroso-*N*-methyl-*N'*-nitroguanidine ("Diazald") in small portions to a stirred mixture of 40 ml. of 50% aqueous potassium hydroxide and 250 ml. of ether with ice bath cooling. The ethereal layer was separated and dried for several hr. over solid potassium hydroxide. A solution of 7.25 g. (0.05 mole) of 3-cyclohexene-1-carbonyl chloride[8] in 30 ml. of anhydrous ether was added dropwise with stirring to the ice-cold solution of diazomethane. When the evolution of nitrogen ceased the solvent and excess diazomethane were distilled at room temperature under reduced pressure. The residual yellow liquid diazoketone was dissolved in a solution of 150 ml. of purified dioxane[9] and 40 ml. of concd. ammonia and warmed to 60°. Five milliliters of 10% aqueous silver nitrate solution, 0.5 g. of silver oxide, and 1 ml. of methanol were added. Heating at 55–60° with stirring was continued for 1 hr. when an aliquot no longer liberated nitrogen with concd. hydrochloric acid. The suspension was then acidified slightly with dilute hydrochloric acid, filtered, and the filtrates were evaporated to dryness under reduced pressure. Recrystallization of the solid residue from boiling water gave 4.9 g. (71%) of colorless plates, m.p. 139–141°. The analytical sample melted at 141–142° (from water).

Anal. Calcd. for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.27; H, 9.26; N, 9.96.

Norbornane-7-carboxylic acid. This acid (m.p. 78.5–79.5°) was obtained by a modification of the method of Kwart and Kaplan[10] in 59% yield from carefully fractionated 7-bromonorcamphane (b.p. 58–59°/8 mm., n_D^{20} 1.5178). The hydrocarbon byproduct of the reaction (m.p. 108–110°, reported 107–109°[10] gave an elementary analysis corresponding to that calculated for 7,7'-binorcamphane and thus confirms the structural speculations of these authors.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.62; H, 11.50.

Norbornane-7-carboxamide. A solution of 1.9 g. of norbornane-7-carboxylic acid in 15 ml. of chloroform and 1.5 ml. of thionyl chloride was allowed to stand at room temperature for 3 hr. and refluxed for 2 hr. The solvent and excess thionyl chloride were removed by distillation under reduced pressure and the residual pale yellow liquid was taken up in 25 ml. of anhydrous ether. The ice-cooled ethereal solution was saturated with anhydrous gaseous ammonia and the solvent was allowed to evaporate. Two crystallizations of the residue from boiling water gave 0.90 g. (48%) of large colorless, glistening plates, m.p. 198.5–199.5°, unchanged upon further recrystallization.

Anal. Calcd. for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.05. Found: C, 68.91; H, 9.21; N, 10.00.

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(7) Melting points are uncorrected. Analyses and infrared spectra by Mr. E. R. Hoffman and staff of these laboratories.

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The Conversion of *o*-Alkoxycinnamic Acids to Coumarins[1,2]

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In connection with other work in progress in this laboratory it was necessary to to prepare *o*-

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