after four recrystallizations from ethanol. A mixture with authentic *trans*-1,4-cycloöctanediol bis-*p*-nitrobenzoate[9] was depressed to 133–148°.

Anal. Calcd. for $C_{22}H_{22}N_2O_8$: C, 59.72; H, 5.01. Found: C, 60.08; H, 5.15.

A portion of fractions 14–15 (69 mg.) was converted in 83% yield to the corresponding bis-*p*-nitrobenzoate as above. After three recrystallizations from ethanol it had m.p. 154.0–155.2° and did not depress the m.p. of the derivative prepared from fractions 11–13.

An aliquot of fractions 16–19 (86 mg.) was treated with a 100% molar excess of *p*-nitrobenzoyl chloride as before to give 233 mg. or 87% of a bis-*p*-nitrobenzoate. After six recrystallizations from ethanol it had m.p. 154.0–155.2° and did not depress the m.p. of the derivative obtained from fractions 11–13.

Glycol B Bis-*p*-nitrobenzoate.—A portion of fractions 20–30 (137 mg.) was converted into a bis-*p*-nitrobenzoate in 78% yield. After seven recrystallizations from ethanol, it had m.p. 175.5–180.4°.

Anal. Calcd. for $C_{22}H_{22}N_2O_8$: C, 59.72; H, 5.01. Found: C, 59.89; H, 5.22.

A comparison of infrared spectra showed that the derivative prepared from fractions 20–30 was different from the bis-*p*-nitrobenzoates of the isomeric cycloöctanediols and of glycol A. A mixture of the bis-*p*-nitrobenzoates of glycol A and glycol B had m.p. 140–170°.

Fractions 31–36 (51 mg.) were treated with 280 mg. of *p*-nitrobenzoyl chloride in pyridine to give a derivative in 71% yield. After five recrystallizations from ethanol, it had m.p. 172–180°. A mixture with the derivative prepared from fractions 20–30 had m.p. 171.0–179.5°.

Periodate Tests and C-Methyl Determinations on Glycols A and B.—Both glycols A and B gave negative reactions with periodic acid (see ref. 16, p. 115). C-methyl determinations[15] gave the following values: glycol A, 9.57; glycol B, 8.98; calcd. for one C-methyl group, 10.55.

***trans*-1,4-Cycloöctanediol Bis-*p*-nitrobenzoate.**—A portion of fractions 43–49 (116 mg.) was treated overnight with a 100% excess of *p*-nitrobenzoyl chloride in a few milliliters of pyridine. There was obtained 284 mg. or 83% of crude *trans*-1,4-cycloöctanediol bis-*p*-nitrobenzoate, which after four recrystallizations from ethanol had m.p. 155.4–156.6°. A mixture with an authentic specimen[9] had m.p. 155.5–157.0°.

An aliquot of fractions 50–59 (169 mg.) was converted in 79% yield into a bis-*p*-nitrobenzoate in the same manner. After four recrystallizations from ethanol, it had m.p. 155.5–157.0°. A mixed m.p. with the derivative prepared from fractions 43–49 showed no depression.

***trans*-1,3-Cycloöctanediol.**—Fractions 65–67 (38 mg.) were sublimed at 70° (1 mm.) to give (after two recrystallizations from ethyl acetate) *trans*-1,3-cycloöctanediol, m.p. 109–111° (hot-stage). A mixture with an authentic specimen[9] showed no depression, and the infrared spectra of the two samples were identical.

Derivatives of 2-Hydroxy-2-methylcyclohexanemethanol.—A solution of methylmagnesium iodide was prepared from 6.9 g. of methyl iodide and 1.2 g. of magnesium in 30 ml. of ether. A solution of 2.4 g. of 2-hydroxymethylcyclohexanone[17] (b.p. 82° at 2.6 mm., n^{25}_{D} 1.4767) in 30 ml. of ether was added dropwise over a period of 20 min., and the mixture was refluxed for 1 hr. Water was added to the cooled mixture, followed by iced dilute hydrochloric acid. The ether layer and chloroform extracts of the aqueous layer were dried over magnesium sulfate and distilled, yielding 1.7 g. of 2-hydroxy-2-methylcyclohexanemethanol, b.p. 79° (0.15 mm.), n^{25}_{D} 1.4814, which was converted to the following derivatives.

2-Hydroxy-2-methylcyclohexanemethanol bis-*p*-nitrobenzoate was prepared by treating the glycol (402 mg.) with *p*-nitrobenzoyl chloride (1.6 g.) in a few milliliters of pyridine at room temperature for 1.5 days. The product was isolated in the usual manner and yielded 467 mg. (36%) of a derivative (calculated as the bis-*p*-nitrobenzoate). An analytical sample obtained after four recrystallizations from ethyl acetate had m.p. 214–215°.

Anal. Calcd. for $C_{22}H_{22}N_2O_8$: C, 59.72; H, 5.01. Found: C, 59.69; H, 5.08.

2-Hydroxy-2-methylcyclohexanemethanol mono-*p*-nitrobenzoate was prepared by treating 204 mg. of the glycol with 1.05 molar equivalent of *p*-nitrobenzoyl chloride in pyridine at 5° overnight. The product amounted to 382 mg. (92%) of a derivative (calculated as the mono-*p*-nitrobenzoate). After four recrystallizations from cyclohexane, it had m.p. 91.5–92.5°.

Anal. Calcd. for $C_{15}H_{19}NO_5$: C, 61.42; H, 6.52. Found: C, 61.09; H, 6.72.

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[17] Prepared from cyclohexanone and formaldehyde by the method of C. Mannich and W. Brose, *Ber.*, **56**, 841 (1923).

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Structures of the Adducts of Cyclopentadiene and Methacrylic Acid and Some of its Derivatives[1]

BY JOHN S. MEEK AND WALTER B. TRAPP[2]

RECEIVED JUNE 4, 1956

The condensation of methacrylic acid and some of its derivatives with cyclopentadiene was studied in an effort to ascertain whether the methyl group or the negative group such as the carboxyl would be in the *endo* position in the major adduct. It was found that the carboxyl and the amide group showed a preference for the *exo* position. The aldehyde group showed an increasing tendency to prefer the *endo* position with longer reaction times and higher temperatures.

Methacrylic acid,[3] methyl methacrylate[3] and methacrolein[4,5] have been reported to give adducts with cyclopentadiene, but their structures were not proven. Recently the condensation of cyclopentadiene and methacrylic acid was reported to give both isomeric adducts I and II and the major product was tentatively assigned structure I[6] in accordance with Alder and Stein's orientation rule of diene syntheses.[7] However, we have found that the major adduct of cyclopentadiene and methacrylic acid is II.

Beckmann, Schaber and Bamberger attempted to prove structures of I and II by treatment with 50 volume per cent. sulfuric acid for 16 hours to see which acid would give a lactone. They re-

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[1] This work was supported in part by the Office of Naval Research.

[2] Taken in part from the Ph.D. Thesis of W. B. Trapp, University of Colorado, 1952.

[3] A. A. Petrov and N. P. Sopov, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **18**, 1781 (1948).

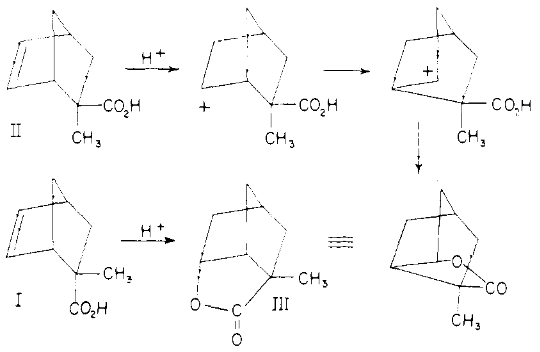
[4] R. Morris, U. S. Patent 2,450,765.

[5] H. Joy and J. Rust, U. S. Patent 2,373,568.

[6] S. Beckmann, R. Schaber and R. Bamberger, *Chem. Ber.*, **87**, 997 (1954).

[7] K. Alder and G. Stein, *Ann.*, **514**, 1, 197 (1934).

ported the major isomer gave a 9% yield of a lactone melting at 122–123° plus a 66% yield of an hydroxy acid. Their minor isomer gave a different lactone and hydroxy acid in unspecified yield. Prior to the appearance of their work we had tried to lactonize our isomers with 75% sulfuric acid at 25° and found that the major isomer gave a 43% yield of a compound melting at 124–125°. The infrared spectrum showed this compound to have a five-membered lactone ring and structure III was assigned to it. Our minor isomer also gave this same lactone in a yield of only 10% although this isomer appeared to react more rapidly when treated with sulfuric acid. A Wagner–Meerwein rearrangement of the *exo*-acid should give the same lactone as the *endo*-acid as

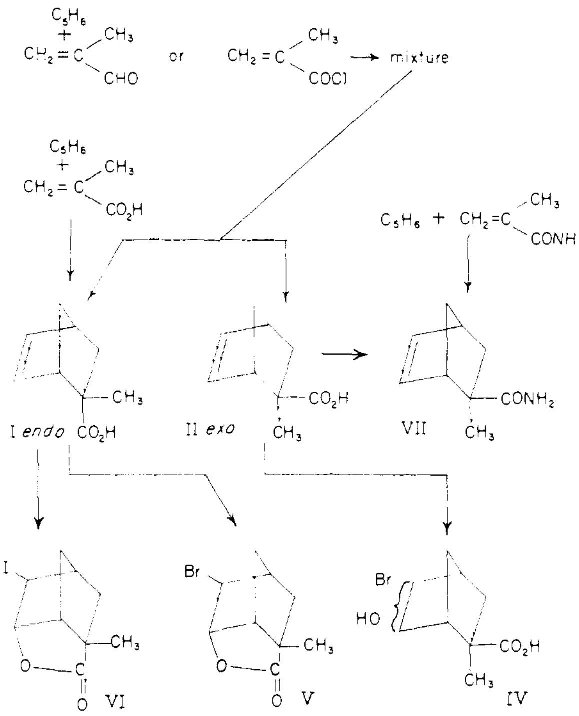


Hence, a structure proof by this method is not satisfactory.

Our assignment is based on the observations that the major isomer formed a bromohydrin IV under the same conditions that led to a bromolactone V from the minor isomer. The major isomer was unreactive toward iodine stock solution[8] while the minor isomer gave an iodolactone VI.

The melting point of our major isomer was 79–80° and that of the minor isomer was 94–95°. Beckmann, Schaber and Bamberger reported melting points of 83 and 109°. Bicyclic compounds frequently have large melting point depressions and our lower melting point for the minor isomer may be explained by this and by the fact that material melting at 92–95° was found by iodine titration to be approximately 94% pure.

Methacrylic acid and cyclopentadiene when heated for 10 minutes at 93° in acetic acid gave a 24% yield of the *endo* isomer I and a 46% yield of isomer II (*exo*). Longer heating at the same temperature or at 150° increased the yield of the *endo* isomer only slightly. When the *exo*-acid was heated at 115° for two hours in a sealed tube no odor of methacrylic acid or cyclopentadiene was noted upon opening the tube. The melting point of the acid was not lowered significantly and recrystallization led only to the recovery of starting material. Therefore, the predominance of II is not due to an equilibrium between the isomers. The *exo*/*endo* ratio was approximately two to one which is not in accordance with Alder's rule of the maximum accumulation of double bonds.[9]



Methacrylamide and cyclopentadiene at 120° gave a 16% yield of crude product which on recrystallization gave only one adduct (VII). This compound was shown to be the *exo* isomer since it could also be prepared from the *exo*-acid II.[6]

Methacrylyl chloride and cyclopentadiene condensed readily at room temperature to give an oil. This was hydrolyzed to a mixture of I and II in which the *endo*-acid predominated.

The cyclopentadiene adduct of methyl methacrylate upon saponification is reported to give almost entirely the *exo*-acid.[6] It is to be noted that there is no α-hydrogen atom in the ester and thus ready epimerization is excluded.

Methacrolein and cyclopentadiene gave evidence of forming increasing amounts of the *endo* isomer with increasing severity of conditions. Beckmann, Schaber and Bamberger found that heating for two to three hours on a water-bath at reflux temperature gave an oil which after several distillations melted at 56–58° and upon purification through the semicarbazone melted at 67–68°. Oxidation by silver oxide gave only the *exo*-acid.[6] Reaction temperatures of 150° for 11 hours gave us material which after distillation was separated into a fraction, m.p. 55–60°, an intermediate fraction and a third fraction, m.p. −5 to +13°. The first fraction on oxidation with silver oxide gave the *exo*-acid. The third and largest fraction gave the *endo*-acid.

Heating the aldehyde adduct at 195° gave cyclopentadiene and methacrolein. It seems likely that at low temperatures the product composition is largely *exo* due to kinetic control while at higher

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[8] This reagent was used after C. S. Rondestvedt, Jr., and C. D. Ver Nooy (THIS JOURNAL, **77**, 4878 (1955)) showed that quantitative yields of iodolactones were obtained with adducts of cyclopentadiene and various *trans*-cinnamic acids where the carboxyl group was *endo* while the isomers with *exo*-carboxyl groups were inert.

[9] For a statement of the Alder rules and a discussion of them, see M. C. Kloetzel, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., p. 10.

temperatures the reaction is reversible and the product composition is under thermodynamic control. Generally *exo* isomers predominate under severe conditions and are thermodynamically more stable.[10] In these cases the isomers differ in the positions of a carbon-containing moiety and a hydrogen atom. In the present case the isomers differ in the location of a methyl and a formyl group which are comparable sterically.

Experimental

2-Methylbicyclo[2.2.1]-5-heptene-2-carboxylic Acid (I and II).—Glacial methacrylic acid (17.2 g., 0.2 mole) and freshly distilled cyclopentadiene (13.2 g., 0.2 mole), 0.1 g. of *p-t*-butylcatechol and 25 ml. of toluene were heated in a sealed glass tube for 2 hours at 150–157°. Distillation gave 3 g. of methacrylic acid and 20.8 g. (68%) of product, b.p. 113° (4.5 mm.), m.p. 41–57°. Upon recrystallization from 50% acetic acid, 80% of the material was separated manually into needles of I, m.p. 94–95°, and granules of II, m.p. 79–81.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found for isomer **I**: C, 70.94; H, 7.94. Isomer II: C, 70.97; H, 8.16.

Lactonization of I and II.—Equal quantities (0.89 g.) of I and II were placed in glass-stoppered flasks along with 10 ml. of 75% sulfuric acid and shaken at 25°. After ten minutes all of I had dissolved, but 40 minutes was required for II. At that time both samples were diluted with 500 vol. per cent. of water. Unchanged II (0.02 g.) precipitated and the remaining solution was ether extracted to obtain the product. With sample I no unchanged acid appeared. The ether extracts were shaken with sodium bicarbonate and the product from I after removal of the ether and recrystallization from ethanol gave 90 mg. (10%) of III, m.p. 121–122°. The product from II after sublimation weighed 0.37 g. (42%) and melted at 124–125° and its melting point was not depressed when mixed with the product from I. The analytical sample melting point was not depressed when mixed with the product from I. The analytical sample melted at 125–126° after recrystallization from aqueous ethanol; reported[6] 122–123°.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95; sapn. equiv., 152. Found: C, 71.30; H, 7.92; sapn. equiv., 152.

Bromolactone V.—To a solution of 0.400 g. (2.62 mmoles) of I in 10 ml. of 5% sodium carbonate was added bromine water containing a trace of potassium bromide. The temperature was maintained below 10° and the addition was stopped when the color persisted. On standing, 0.40 g. (66.5%) of V precipitated, m.p. 74–75°. The material was insoluble in 10% sodium bicarbonate, and had a peak at 5.58 μ in its infrared spectrum which indicated a five-membered lactone ring.

Anal. Calcd. for $C_9H_{11}BrO_2$: C, 46.77; H, 4.80. Found: C, 46.64; H, 4.84.

Bromohydrin of II.—Compound II when treated similarly gave no precipitate on standing. However, acidification resulted in a 73% yield of IV, m.p. 141–147°; recrystallization from acetone–petroleum ether, raised the melting point to 150–151.5°.

Anal. Calcd. for $C_9H_{13}BrO_3$: C, 43.43; H, 5.22. Found: C, 43.32; H, 5.42.

Dibromide of II.—Five grams (0.033 mole) of II was dissolved in 70 ml. of 5% sodium bicarbonate and agitated at 5–10°. Bromine dissolved in petroleum ether (30–60°) was added dropwise until color persisted. A white dibromide precipitated, weighing 1.58 g. (21%), m.p. 198–199°. The dibromide was soluble in 5% sodium bicarbonate and the infrared spectrum showed a carboxylic carbonyl peak at 5.87 μ.

Anal. Calcd. for $C_9H_{12}Br_2O_2$: C, 34.64; H, 3.88. Found: C, 34.52; H, 4.00.

Iodolactone VI.—One gram of I gave 1.30 g. of iodolactone, m.p. 83–86°, when treated with iodine in basic solution.[8]

Anal. Calcd. for $C_9H_{11}IO_2$: C, 38.87; H, 3.99. Found: C, 39.13; H, 3.83.

A 0.2263-g. sample of I, m.p. 92–95° absorbed 94% of the calculated amount of iodine stock solution. When II was similarly treated with a small amount of iodine no discharge of color occurred and acidification precipitated 88% of unchanged II.

Formation of I under Various Conditions.—A series of samples of 43 g. gross weight containing 0.2 mole each of methacrylic acid and cyclopentadiene in acetic acid (12 ml.) with *p-t*-butylcatechol were exposed to varying conditions of time and temperature. Aliquots were then assayed for I with iodine stock solution.

Time	Temp., °C.	Mole % endo
0 min.	25	0
10 min.	93	24
45 min.	93	27
8 hr.	93	27
2.5 hr.	150	29

Hydrolysis of V and VI.—One-half gram (2.16 mmoles) of V was added to a solution of 1.0 g. of potassium hydroxide in 15 ml. of water and 15 ml. of 95% ethanol and the mixture was heated on a steam-bath for 30 minutes. The solution was cooled, filtered and extracted with ether. Acidification of the aqueous solution followed by a fourfold ether extraction, drying over sodium sulfate and evaporation of the solvent gave 260 mg. (71.7%) of hydroxy lactone, m.p. 124–128°. Recrystallization from water raised the melting point to 129–130°.

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.21; H, 7.07.

The compound gave a positive periodate test, indicating a vicinal diol was formed by hydrolysis in the reagent. The infrared spectrum showed the following in hexachlorobutadiene and Nujol mulls: carbonyl at 5.78 μ, hydroxyl at 3.02 μ (sharp, indicates either intramolecular bonding or intermolecular bonding where the bonding plays a prominent part in the crystal structure), carboxyl type stretch absent; in CCl_4 solution: 2.79 μ free OH, 2.94 μ bonded OH, 5.60 μ unbonded lactone carbonyl, 5.70 μ bonded lactone carbonyl. Upon dilution the ratio of the intensities of the unbonded peaks to the bonded peaks increased, showing intermolecular bonding. From chemical and spectral evidence the assignment of **2-methylbicyclo[2.2.1.]-5,6-di-endohydroxyheptane-2-endocarboxylic acid 2,6-lactone** was made.

A 396-mg. sample of VI was similarly treated with base, and 175 mg. (73%) of product was obtained, m.p. 124–129°. There was no melting point depression when mixed with the hydroxy lactone prepared from V.

2-Methylbicyclo[2.2.1.]-5-heptene-2-carboxamide (VII).—One-tenth of a mole (8.5 g.) of methacrylamide, 13.2 g. (0.2 mole) of cyclopentadiene, 0.1 g. of *p-t*-butylcatechol and 12 ml. of methanol were heated together at 120° for 4.5 hours in a sealed glass tube. The methanol was evaporated and the residue was extracted with water to remove methacrylamide. Extraction with ethanol left 5 g. of polymeric material which was removed by filtration. Upon standing three weeks the alcoholic solution afforded 2.5 g. (16.5%) of crystals, m.p. 110–120°. Sublimation at 92° gave 1.9 g. (12.6%) of VII, m.p. 154–155°; reported[3] 152–153°.

A 4.6-g. sample of II was treated with thionyl chloride in ether and gave 4.5 g. (76%) of acid chloride, b.p. 57° (4.5 mm.), $n^{20}\mathrm{D}$ 1.4950, $n^{25}\mathrm{D}$ 1.4929, d^{25}_4 1.1266.

Anal. Calcd. for $C_9H_{11}ClO$: C, 63.34; H, 6.50; *MR*, 43.78. Found: C, 63.05; H, 6.76, *MR*, 43.85.

Ten ml. of cold concentrated ammonium hydroxide was added dropwise to 150 mg. of the acid chloride of II. The mixture was diluted with 20 ml. of water and filtered, yielding 120 mg. (93%) of solid amide, m.p. 157–157.5°. Purification by sublimation raised the m.p. to 157.5–158°. When this material was mixed with VII it melted at 154–155°.

A 460-mg. sample of I gave 80 mg. of acid chloride, $n^{20}\mathrm{D}$ 1.4910.

Anal. Calcd. for $C_9H_{11}ClO$: C, 63.34; H, 6.50. Found: C, 63.23; H, 6.53.

Since the acid chlorides from I and II differed significantly in their refractive index, attempts to thermally isomerize the acid chloride of II were made. However, no change in the refractive index was noted after 51 days at room temperature in the dark, 60 hours at 80°, 2 hours at 150° or one hour at

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[10] R. B. Woodward and H. Baer, THIS JOURNAL, **66**, 645 (1944).

175° although slight discoloration occurred in the latter two cases.

Condensation of Methacrylyl Chloride and Cyclopentadiene.—A mixture of 5.0 g. (0.048 mole) of methacrylyl chloride, prepared from glacial methacrylic acid and thionyl chloride, 6.6 g. (0.1 mole) of cyclopentadiene and 0.1 g. *p-t*-butylcatechol was kept in a sealed glass tube for a week at room temperature. Distillation of the black oil gave a 61% yield of heart fraction, b.p. 126° (95 mm.), $n^{22}\text{D}$ 1.4930, d^{29}_4 1.1227; lit.[3] for the chloride prepared from mixed acid adducts $n^{20}\text{D}$ 1.4950.

A mixture of 10 ml. of 10% aqueous potassium hydroxide and 1.12 g. (6.6 mmoles) of the acid chloride adduct was heated at 55–60° for 10 minutes. A small amount of tar was removed by filtration, and acidification gave 1.07 g. of acid, m.p. 60–63°. Recrystallization gave 0.85 g. of mixed crystals which were separated manually; 60% (0.51 g.) melted at 93–94° and this melting point was not depressed with samples of I previously obtained. The remaining 40% (0.34 g.) melted at 78–79° and showed no melting point depression when mixed with II.

2-Methylbicyclo[2.2.1]-5-heptene-2-carboxaldehyde.—A mixture of 285 g. (4.06 moles) of methacrolein, 225 g. (3.4 moles) of cyclopentadiene and 1 g. of *p-t*-butylcatechol was heated in a 2-l. steel bomb at 150–155° for 11 hours. An exothermic reaction occurred at about 95° when the reactants were heated. Distillation through an 18" Vigreux column gave 388.8 g. (84%) of adduct, b.p. 80–85° (31 mm.). Cooling and decantation gave three fractions: 22%, m.p. 55–60°; 28%, m.p. 20–45°, and 50%, m.p. −5 to +13°.

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88. Found for the first fraction: C, 79.42; H, 8.80. For the last fraction: C, 79.41; H, 8.66.

Other preparations conducted at slightly higher temperatures gave products containing less of the higher melting (*exo*) isomer while runs conducted under less severe conditions gave increased amounts of this isomer.

When the crude product was heated at atmospheric pressure to a temperature of 180–195°, a distillate consisting of both methacrolein and cyclopentadiene came over at a head temperature of 58°.

A 2.72-g. (0.02 mole) sample of the third fraction above was oxidized with silver oxide, and 1.95 g. (65%) of crude I was obtained, m.p. 88–91°. Recrystallization from 50% acetic acid gave 1.4 g. (46%), m.p. 95–96°, which gave no melting point depression with I obtained previously.

Oxidation of the first fraction gave 2.3 g. of crude II, m.p. 70–76°. Recrystallization raised the melting point to 79–80°, yield 1.8 g. (60%). A mixed melting point with II was not depressed.

When 21 g. of methacrolein, 24 g. of cyclopentadiene and a tenth gram of inhibitor were heated in a sealed tube at 170° for 10 hours, more than the usual amount of methacrolein was recovered and a relatively small amount of adduct was obtained. In addition 3 g. of product was obtained, b.p. 170–178° (50 mm.), $n^{20}\text{D}$ 1.5242, d^{20}_4 1.0718. This was believed to be **2-methyl-1,2,3,4,5,8,9,10-octahydro-1,4,5,8-dimethanonaphthalene-2-carboxaldehyde.**

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97; *MR*, 57.62. Found: C, 83.93; H, 8.71, *MR*, 57.75.

A 2,4-dinitrophenylhydrazone formed in 86% yield, m.p. 208–210°. After two recrystallizations from ethanol the m.p. was raised to 218–219°, yield 75%.

Anal. Calcd. for $C_{20}H_{22}N_4O_4$; N, 14.65. Found: N, 14.49.

Acknowledgment.—The analyses were performed by Galbraith Laboratories. The methacrylamide and methracylic acid were gifts of the Rohm and Haas Co. The authors wish to thank Dr. W. J. Potts of the Dow Chemical Co. for running and interpreting the spectrum of the hydroxy lactone.

Boulder, Colorado

[Contribution from Abbott Laboratories]

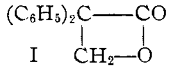
Reactions of α,α-Diphenyl-β-propiolactone with Amines and Thiols

By H. E. Zaugg, H. J. Glenn, R. J. Michaels, R. U. Schock and L. R. Swett

Received February 11, 1957

The reactions of α,α-diphenyl-β-propiolactone with four heterocyclic secondary amines, two primary amines, with the sodium salts of ethyl mercaptan and of thiophenol and with thiourea are described and compared with analogous reactions of β-propiolactone itself. The conversion of products of these reactions to compounds of potential pharmacological interest is reported.

The seemingly capricious nature of the aminolysis reaction of β-propiolactone has been demonstrated by Gresham and co-workers.[1] Three principal factors, namely, solvent, mode of combination of the reactants and nature of the amine used, were found to be operative in determining whether hydroxy amides (carbonyl–oxygen bond fission) or β-amino acids (alkyl–oxygen bond fission) are formed. Hurd and Hayao[2] later showed that aromatic amines tend to react with β-propiolactone to give almost exclusively the corresponding amino acids. In contrast, a more recent study[3] with β-(*p*-nitrophenyl)-β-propiolactone showed that this β-hindered lactone reacts with most amines, regardless of conditions, to give β-hydroxy amides. Only benzylamine and cyclohexylamine give appreciable yields of the corresponding amino acids, and then only under carefully controlled conditions. The present work extends the study of these reactions to the α-hindered lactone, α,α-diphenyl-β-propiolactone (I).[4] Reaction of I with excess N-(γ-aminopropyl)-morpholine at room temperature without solvent gave the amino acid IIa in 60% yield and the hydroxy amide IIIa in 12% yield. From the reaction with *n*-butylamine, only the hydroxy amide IIIb could be isolated albeit in only 45% yield. The four heterocyclic amines piperidine, morpholine, pyrrolidine and N-methylpiperazine gave the corresponding amino acids, IIb, c, d and e, as the only isolable products, the first three in high yields (80–90%) but the last in only 46% yield. Employment of acetonitrile as solvent seemed to have little influence on the course of these amine reactions. However, non-polar media. such



I

$$\begin{array}{ll}(C_6H_5)_2C & \!\!-\!\!-\!\!CO \\ | & \;\;| \\ CH_2 & \!\!-\!\!-\!\!O\end{array}$$

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(1) T. Gresham, J. Jansen, F. Shaver, R. Bankert and F. Fiedorek, This Journal, **73**, 3168 (1951).

(2) C. Hurd and S. Hayao, *ibid.*, **74**, 5889 (1952).

(3) A. Dornow and E. Schumacher, *Arch. Pharm.*, **286**, 205 (1953).

(4) H. Zaugg, This Journal, **72**, 2998 (1950).