ether was added 20.0 g. of pure cyanuric chloride in several portions. The solution was stirred for another 15 minutes, excess hydride was decomposed with water, 200 ml. of 10% sulfuric acid was added and the mixture was extracted with ether. The ether extract yielded 1.5 g. of colorless needles which after recrystallization from petroleum ether melted at 124–124.5° (cor.).

Anal. Calcd. for $C_5H_6Cl_2N_4$: C, 31.11; H, 3.13; N, 29.02. Found: C, 31.52; H, 3.10; N, 29.13.

A mixture melting point with an authentic sample of 2-dimethylamino-4,6-dichloro-1,3,5-triazine[8] showed no depression.

Ultraviolet Spectrum.—The ultraviolet absorption spectrum of 2-amino-1,3,5-triazine in a 10^{-5} molar aqueous solution was measured with a Beckman model DU spectrophotometer at 26°. A continuously decreasing absorption was observed from 225 to 240 mμ.

---

[8] W. M. Pearlman and C. K. Banks, THIS JOURNAL, **70**, 3726 (1948).

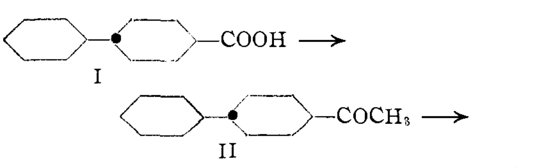
COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VA.

Determination of the Configuration of 4-Cyclohexylcyclohexanols

BY WILLIAM G. DAUBEN, VICTOR M. ALHADEFF AND MASATO TANABE

RECEIVED MAY 11, 1953

In the course of a study of the hydrogenation of 4-hydroxybiphenyl-4′-carboxylic acid,[1] it became of interest to determine, with certainty, the stereochemistry of the 4-phenyl- and the 4-cyclohexylcyclohexanols. In 1948, Ungnade[2] prepared the pure *cis* and *trans*-isomers of this series and assigned the configurations on the basis of method of preparation and on thermodynamic stability. Recently, Dauben and Hoerger[3] showed that by converting a carboxylic acid to a methyl ketone and cleaving the resulting ketone with perbenzoic acid,[4] an acid could be related, stereospecifically with retention, to an alcohol. Since Fieser, *et al.*,[5] have related *trans*-4-cyclohexylcyclohexylcarboxylic acid (I) to *trans*-hexahydroterephthalic acid, a compound whose stereochemistry has been rigorously established by Mills and Keats,[6] application of the methyl ketone–perbenzoic acid sequence above to *trans*-acid I would determine the stereochemistry of the 4-substituted cyclohexanols in an unequivocal manner.



Such a sequence of reactions was performed and it was found that *trans*-acid I was, indeed, related to the *trans*-alcohol III. Thus, the stereochemical configurations of the 4-phenyl- and 4-cyclohexylcyclohexanols assigned by Ungnade[2] are correct. It is of passing interest to note that in this series, the thermodynamically stable isomer is the one which has both of its substituents in equatorial conformations.[7]

Experimental

***trans*-4-Cyclohexylcyclohexylcarboxylic Acid** (I).—The acid was prepared following the procedure of Fieser, *et al.*,[5] m.p. 160.5–161.9° (lit. 161–162°).

***trans*-4-Cyclohexylcyclohexanol** (III).—A solution of 0.9 g. (4.28 millimoles) of *trans*-acid I in 15 ml. of dry ether was added dropwise with stirring to 18 ml. of a 0.6 *M* solution of methyllithium in ether. Following the addition, the mixture was stirred for 12 hours and then poured onto ice. The ethereal layer was removed, washed neutral with water, dried and the solvent removed through a small column. The residue weighs 0.8 g. (89.7%) and was used directly in the oxidation.

Perbenzoic acid (0.638 g.) in 8.8 ml. of chloroform was added to the crude ketone which had been dissolved in 5 ml. of chloroform. The solution was allowed to stand for 8 days at room temperature in the dark. At the end of this time the reaction was diluted with ether and washed thoroughly with dilute sodium hydroxide. The residue remaining after removal of the solvents was heated for 7 hours with 50 ml. of 1 *N* sodium hydroxide in 30 ml. of methanol and the methanol removed under reduced pressure. The aqueous residue was extracted with ether, the ether distilled and the 4-cyclohexylcyclohexanol recrystallized from hexane, yield 0.28 g. (40%), m.p. 99.6–102.4° (lit.[2] 103–104°). The phenylurethan was prepared and melts 154.9–156.6° (lit.[2] 156–156.8°).

---

[1] W. G. Dauben and M. Tanabe, in press.

[2] H. E. Ungnade, *J. Org. Chem.*, **13**, 361 (1948).

[3] W. G. Dauben and E. Hoerger, THIS JOURNAL, **73**, 1504 (1951).

[4] R. B. Turner, *ibid.*, **72**, 878 (1950); T. F. Gallagher and T. H. Kritchevsky, *ibid.*, **72**, 882 (1950).

[5] L. F. Fieser, *et al.*, *ibid.*, **70**, 3186 (1948).

[6] W. H. Mills and G. H. Keats, *J. Chem. Soc.*, 1373 (1935).

[7] D. H. R. Barton, *Experientia*, **6**, 316 (1950).

CHEMICAL LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA

The Structure of the Solid Product from the Condensation of Methyl γ-Bromocrotonate with Sodium Methoxide[1]

BY ANDRE S. DREIDING AND RICHARD J. PRATT

RECEIVED MAY 6, 1953

Owen and Sultanbawa[2] reported the isolation of a small amount of a solid from the reaction of methyl γ-bromocrotonate with dry sodium methoxide in benzene. The product was characterized by its analysis (empirical formula of $C_5H_6O_2$), melting point (168–169°) and ultraviolet absorption spectrum ($\lambda_{\max}^{\text{alc}}$ 303 mμ, $E_{1\text{cm}}^{1\%}$ 2600). The authors considered that it was possibly methyl cyclopropenecarboxylate.

A re-examination of the reaction confirmed the observations of Owen and Sultanbawa, the solid product being formed in 1.3% yield. However, its high melting point and its spectrum, which appeared uncharacteristic of either of the double bond isomers of methyl cyclopropenecarboxylate, suggested a reconsideration of its structure.

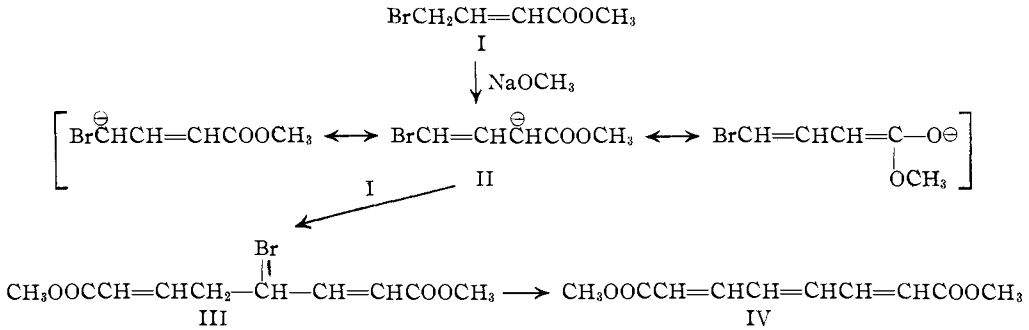
α-Haloesters are known to be attacked by bases with the formation of enolates.[3] The vinylogous reaction with methyl γ-bromocrotonate (I) is the abstraction of a proton from the γ-position with the

---

[1] Supported in part by grants to the Detroit Institute of Cancer Research from the American Cancer Society, Inc., the Michigan Cancer Foundation and The Kresge Foundation.

[2] L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3098 (1949).

[3] M. S. Newman and B. J. Magerlein, "The Glycidic Ester Condensation" in R. Adams, "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., p. 413.



formation of the anion II. The cyclopropene ring would have to be formed by an intramolecular nucleophilic displacement of a vinyl type bromine atom. An alternative (and perhaps more likely) reaction is the displacement by II of an allyl type bromine atom in another molecule of methyl γ-bromocrotonate with the formation of III. Further elimination of the elements of hydrobromic acid gives dimethyl 2,4,6-octatrienedioate (IV) with an empirical formula of $C_5H_6O_2$. This type of reaction with a base has been described for 9-fluorenyl bromide,[4] for diethyl bromo- and chloromalonate,[5] and for allyl chloride.[6]

The properties of Owen and Sultanbawa's product coincided closely with those reported for dimethyl 2,4,6-octatrienedioate (IV, m.p. 172°,[7a] $\lambda_{\max}^{\text{methanol}}$ 303 mμ[7b]). That this is indeed its structure has now been shown by hydrogenation and saponification which afforded an 83% yield of suberic acid.

Several attempts to improve the yield of IV in the self-condensation of I by the use of inverse addition, different bases and different solvents were without success. The consistently low yield may be due to the large number of structural and geometrical isomers which could conceivably be formed in this reaction.

Experimental[8]

Dimethyl 2,4,6-Octatrienedioate (IV).—To a stirred and cooled suspension of dry sodium methoxide (prepared from 1.4 g. (0.06 mole) of sodium and 20 cc. of dry methanol followed by distillation of the methanol) in 80 cc. of dry benzene was added slowly 10 g. (0.056 mole) of methyl γ-bromocrotonate. The ice-bath was allowed to warm to room temperature and the dark mixture was stirred for a total of 45 hours. After the addition of 80 cc. of water, the benzene layer was separated and the aqueous layer was extracted with ether. The organic solution was washed with 10% hydrochloric acid and water, dried (magnesium sulfate) and concentrated. A solution of the dark residue in 10 cc. of carbon tetrachloride deposited on chilling 0.072 g. (1.3%) of dimethyl 2,4,6-octatrienedioate (IV), m.p. 164–167°. Recrystallization from methanol afforded colorless needles, m.p. 169.5–170° (reported[7a] 172°); $\lambda_{\max}^{\text{alc}}$ 301 mμ (ε 51,000), $\lambda_{\text{inflection}}^{\text{alc}}$ 290 and 314 mμ (ε 37,400 and 43,100), $\lambda_{\min}^{\text{alc}}$ 238 mμ (ε 1,170) (reported[7b] $\lambda_{\max}^{\text{methanol}}$ 303 mμ).

The mother liquor was concentrated to a dark brown heavy oil, which weighed 3.1 g., $\lambda_{\max}^{\text{alc}}$ 248 and 303 mμ (ε 2,290 and 1,270). While no further crystalline material was obtained from this oil, the spectrum suggests the possible presence of IV or a compound with a similar chromophore (possibly a geometrical isomer of IV) to an approximate extent of 2.5%.

The yield in this reaction was not improved when the sodium methoxide was added to a benzene solution of methyl γ-bromocrotonate, when sodium hydride, sodamide or potassium *t*-butoxide was used instead of sodium methoxide or when the benzene was replaced with ether or with collidine.

Suberic Acid.—A solution of 30 mg. (0.153 mmole) of dimethyl 2,4,6-octatrienedioate (IV, prepared as described in the preceding experiment) in 5 cc. of ethanol was shaken under an atmosphere of hydrogen with 5 mg. of prereduced Adams catalyst. Ten and five-tenths milliliters (0.470 mmole) of hydrogen was absorbed. The residue after filtration and concentration was heated with 3 cc. of 35% aqueous potassium hydroxide to give, after acidification and crystallization from ether–petroleum ether, 22 mg. (83%) of suberic acid, m.p. 139–141°. There was no depression in m.p. when mixed with an authentic sample.

ROLLIN H. STEVENS MEMORIAL LABORATORY
DETROIT INSTITUTE OF CANCER RESEARCH, AND
DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY
DETROIT, MICHIGAN

The Preparation of 4-Bromo- and 4-Iodo-ω-nitrostyrene

BY XORGE ALEJANDRO DOMINGUEZ, JORGE SLIM S. AND ARTURO ELIZONDO

RECEIVED MARCH 30, 1953

In the course of our research work it was necessary to prepare 4-bromo- and 4-iodo-ω-nitrostyrene. It has recently been reported by Schales and Graefe[1] that several substituted ω-nitrostyrenes showed antibacterial activity and it seemed of interest to test 4-bromo-ω-nitrostyrene and 4-iodo-ω-nitrostyrene against *Staphylococcus aureus* and report their syntheses. The former was prepared but not characterized by Worrall.[2] Their antibacterial activity was determined according to the procedure of Schales and Graefe.[1] The concentrations of the test compounds needed to inhibit bacterial growth by 50% after an incubation time of 18 hours were: 0.73 mg./100 ml. for the 4-bromo-ω-nitrostyrene and 1.06 mg./100 ml. for the 4-iodo-ω-nitrostyrene.

The necessary 4-bromo- and 4-iodobenzaldehydes were prepared from the corresponding nitriles employing Stephen's reaction[3] as modified by Sah[4] in yields of 65 and 68%, respectively. The 4-halo-arylnitroalkenes were easily obtained by condensation of the corresponding 4-halobenzaldehydes with nitromethane using ammonium

---

(4) J. Thiele and A. Wanschedt, *Ann.*, **376**, 278 (1910).

(5) For reference see A. H. Blatt, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 275.

(6) M. S. Kharasch and E. Sternfeld, THIS JOURNAL, **61**, 2318 (1939).

(7) (a) R. Kuhn and Ch. Grundmann, *Ber.*, **69**, 1757 (1936); (b) *ibid.*, **69**, 1979 (1936).

(8) The melting points are uncorrected. We are indebted to Dr. J. M. Vandenbelt of Parke, Davis and Co. for the ultraviolet absorption spectrum of IV.

(1) O. Schales and H. A. Graefe, THIS JOURNAL, **74**, 4486 (1952).

(2) D. E. Worrall, *ibid.*, **56**, 1556 (1934).

(3) H. Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).

(4) P. P. T. Sah, THIS JOURNAL, **64**, 1487 (1942).