phenylisocyanate, and the conversion of III to a bis-hydrazine derivative, probably 2-nitro-3-hydrazinoacrylyl hydrazide, however, indicated that the assigned structures were probably correct.

EXPERIMENTAL[4]

Materials. Ethoxymethylenemalononitrile, I, is commercially available from Kay-Fries Chemicals, Inc., New York. With aqueous ammonia it gave aminomethylenemalononitrile, II, m.p. 143–145° (lit.[2] 146°). Methyl nitroacetate, b.p. 95–96° (18 mm.) was prepared in 32% over-all yield from nitromethane via dipotassium nitroacetate. The procedure has been described by Feuer, Hass, and Warren.[5]

Methyl 2-nitro-3-ethoxyacrylate, III. Two tenths mole (24.0 g.) methyl nitroacetate, heated overnight on the steam bath with 0.3 mole (44.4 g.) ethyl orthoformate and 0.5 mole (51.0 g.) acetic anhydride and the reaction mixture fractionated *in vacuo,* gave as a high boiling main cut 23.1 g. (66%) of III, a mobile yellow liquid, b.p. 119–121° (1.0 mm.).

Anal. Calcd. for $C_6H_9NO_5$: C, 41.11; H, 5.16; N, 8.00. Found: C, 41.04, 41.30; H, 4.99, 5.26; N, 7.62, 7.94.

Methyl 2-nitro-3-aminoacrylate, IV. Addition of 5.0 g. III to 20 ml. cold, stirred 28% ammonium hydroxide, filtration of the pale green solid which immediately precipitated, and washing the filter cake with cold ethyl acetate gave 3.85 g. (95%) crude IV, m.p. 154–156°. A single recrystallization from 200 ml. ethyl acetate furnished 2.75 g. (66%) of an analytical sample as clusters of cream colored needles, m.p. 163.2–163.6°.

Anal. Calcd. for $C_4H_6N_2O_4$: C, 32.89; H, 4.11; N, 19.16. Found: C, 33.03, 33.09; H, 4.16, 4.29; N, 18.53, 18.23, 18.98.

Methyl 2-nitro-3-(N′-phenylureido)acrylate. One half gram of IV, 1 g. phenylisocyanate, and 2 drops pyridine, heated 90 min. on the steam bath, taken up in hot chloroform, filtered, and cooled to crystallize, and the product recrystallized from ether-chloroform, yielded 250 mg. (28%) of chartreuse crystals, m.p. 180.2–182.2°.

Anal. Calcd. for $C_{11}H_{11}N_3O_5$: C, 49.81; H, 4.15; N, 15.84. Found: C, 49.59, 49.76; H, 4.39, 4.45; N, 15.60, 15.61.

2-Nitro-3-hydrazinoacrylyl hydrazide. Dropwise addition of 4.0 g. III in 4.0 ml. methanol to a cooled, swirled solution of 10 ml. 85% hydrazine hydrate in 10 ml. methanol caused immediate formation of a thick yellow slurry. The mixture, diluted with 25 ml. methanol, cooled, and filtered, and the product washed with methanol, and air dried yielded 3.20 g. (88%) of the hydrazino hydrazide, m.p. 232–234° (dec.). Recrystallization from a large quantity of methanol gave an analytical sample, m.p. 235–236° (dec.).

Anal. Calcd. for $C_3H_7N_5O_3$: C, 22.36; H, 4.35; N, 42.50. Found: C, 22.66, 22.68; H, 4.47, 4.57; N, 42.79, 42.57.

Semicarbazidomethylenemalononitrile, V. A solution of 4.88 g. (0.04 mole) I, 9.0 g. (0.08 mole) semicarbazide hydrochloride, and 8.2 g. (0.06 mole) sodium acetate trihydrate in 100 ml. 50% aqueous ethanol, allowed to stand overnight at room temperature, concentrated to 40 ml., and cooled, deposited 3.35 g. (56%) of a light tan solid, m.p. >360°. An analytical sample was obtained as clusters of fine white needles on recrystallization from ethanol.

Anal. Calcd. for $C_5H_5N_5O$: C, 39.72; H, 3.31; N, 46.34. Found: C, 39.61, 39.86; H, 3.46, 3.56; N, 46.97, 46.69.

Ultraviolet spectra. Solvent methanol. λ_{max} (log ϵ): *I,* 248 (4.11); *II,* 267 (4.17), 344 (3.11); *III,* 252^{s} (3.18); *IV,* 235 (3.20), 312 (3.11); *V,* 249 (3.87); *VI,* 214^{s} (4.03), 240^{s} (3.81). Superscript s = shoulder or inflection.

U. S. Naval Ordnance Laboratory
White Oak, Silver Spring, Md.

---

[4] All melting points are corrected. Microanalyses by Professor Katherine Gerdeman, Department of Chemistry, University of Maryland. Ultraviolet spectra were determined with a Cary Model 14 spectrophotometer using 1-cm. silica cells.

[5] H. Feuer, H. B. Hass, and K. S. Warren, *J. Am. Chem. Soc.,* **71,** 3078 (1949).

Studies of Configuration. V. The Preparation and Configuration of *cis*-3-Methoxycyclopentanecarboxylic Acid

Donald S. Noyce and Joan S. Fessenden

Received November 13, 1958

In continuing the investigation of the ether-acid chloride rearrangement[1] we have undertaken the preparation of 3-methoxycyclopentanecarboxylic acid and have characterized the *cis* isomer.

The preparation of 3-oxocyclopentanecarboxylic acid has been previously described by Hope,[2] by Ingold, Shoppee, and Thorpe,[3] by Vaughn,[4] and more recently by Shemyakin and co-workers.[5] The addition of diethyl malonate to diethyl itaconate using a molar excess of diethyl malonate afforded tetraethyl 1,1,3,4-butanetetracarboxylate (I) in 93% yield. Sodium ethoxide in toluene converted I to triethyl 3-oxo-1,2,4-cyclopentanecarboxylate (II) in 66% yield. Hydrolysis and decarboxylation afforded 3-oxocyclopentanecarboxylic acid (III) in nearly quantitative yield. The procedure of Vaughn[4] in which the intermediates I and II are not isolated afforded 3-oxocyclopentanecarboxylic acid in 54% yield from diethyl itaconate.

Of several methods of reduction investigated, hydrogenation over Raney nickel of either the sodium salt of III or the methyl ester afforded the most tractable mixtures of *cis*- and *trans*-3-hydroxycyclopentanecarboxylic acid (IV). Crystallization from ether-pentane at low temperatures afforded 60% of a crystalline isomer, m.p. 50.4–51.8°. Evidence is presented below to show that this is the *cis*-isomer.

Conversion of 3-hydroxycyclopentanecarboxylic acid to its lactone was attended with some difficulty. Direct heating of crude IV resulted in polymerization and no lactone was obtained. Heating a dilute solution of the mixed isomers of IV in

---

[1] D. S. Noyce and H. I. Weingarten, *J. Am. Chem. Soc.,* **79,** 3093, 3098 (1957).

[2] E. Hope, *J. Chem. Soc.,* **101,** 892 (1912).

[3] C. K. Ingold, C. W. Shoppee, and J. F. Thorpe, *J. Chem. Soc.,* 1477 (1926).

[4] H. A. Vaughn, Jr., Dissertation, Columbia University; *Chem. Abstr.,* **51,** 16314 (1957).

[5] M. M. Shemyakin, L. A. Shchukina, E. I. Vinogradova, M. N. Kolosov, R. G. Vdovina, M. G. Karapetyan, V. Ya. Rodionox, G. A. Ravdel, Yu. B. Shvetsov, E. M. Bamdan, E. S. Shaman, K. M. Ermolaev, and E. P. Semkin, *Zhur. Obshcheĭ Khim.,* **27,** 742 (1957); *Chem. Abstr.,* **51,** 16313 (1957).

dibutyl ether gave a very small yield of lactone (3%). Using dibutyl phthalate as the solvent, the crystalline isomer was converted to the lactone of *cis*-3-hydroxycyclopentanecarboxylic acid (V) in 24% yield. Purification by sublimation gave material of m.p. 53.7–54.5°. The infrared spectrum of V showed a carbonyl peak at 5.62μ (1779 cm.$^{-1}$). A shift of about 0.02μ towards shorter wave lengths appears to be general in changing from a five-membered ring to the more constrained [2.2.1] bicyclic system, as exemplified by cyclopentanone (5.77μ) and camphor (5.75μ).

Hydrolysis of V afforded a pure sample of *cis*-3-hydroxycyclopentanecarboxylic acid (*cis*-IV), m.p. 52.2–52.9°, which showed no depression in melting point when admixed with the crystalline isomer of IV isolated above.

Conversion of the hydroxyl group of *cis*-IV to the methyl ether by a stereospecific method would give *cis*-3-methoxycyclopentanecarboxylic acid (*cis*-VI) of established configuration. Methyl iodide and silver oxide is the method of choice. Mislow[6] has shown that the use of an alcoholate and alkyl halide is frequently accompanied by some racemization, whereas methyl iodide and silver oxide gives material of high optical purity. He concludes that the silver oxide procedure gives optically pure material.

Methylation of *cis*-IV was carried out essentially by the method of Bonner[7] using a larger excess of methyl iodide and silver oxide, to give methyl *cis*-3-methoxycyclopentanecarboxylate which was not isolated but directly subjected to mild alkaline hydrolysis to afford *cis*-VI in 93% yield, which was characterized by analysis, neutralization equivalent, infrared spectrum, and preparation of the *p*-toluidide and the *p*-phenylphenacyl ester.

EXPERIMENTAL[8]

3-Oxocyclopentanecarboxylic acid (III). Diethyl malonate (2 moles), sodium (1 mole) in ether, and diethyl itaconate (1 mole) afforded *tetraethyl 1,1,3,4-butanetetracarboxylate* (I) in 93% yield, b.p. 153–156° (0.5 mm.), n_D^{21} 1.4420 (lit.[3] 198–199°/10 mm.). Hydrolysis of I afforded *1,2,4-butanetricarboxylic acid*, m.p. 121.2–121.8° (lit.[2] 122°). Treatment of I with sodium ethoxide in toluene afforded *ethyl 3-oxo-1,2,4-cyclopentanecarboxylate* (II) in 66% yield, b.p. 160–161° (1 mm.), n_D^{24} 1.4602 (lit.[3] 205–210°/15 mm.). Hydrolysis of II with refluxing 8% sulfuric acid afforded III in nearly quantitative yield, b.p. 140–145° (3.5 mm.) m.p. 57.9–59.3°, (lit.[2] b.p. 172–174°/10 mm., m.p. 62–64°). Crystallization from ether-hexane gave material of m.p. 62.7–63.3°. The procedure of Vaughn,[4] in which sodium hydride is used and no intermediates are isolated, afforded III in 54% yield from diethyl itaconate.

Also characterized were *ethyl 3-oxocyclopentanecarboxylate*, b.p. 95° (5.5 mm.) n_D^{22} 1.4518 (lit.[3] b.p. 109–111°/10 mm.), and *methyl 3-oxocyclopentanecarboxylate*, b.p. 94–98° (14 mm.) n_D^{23} 1.4565.

Methyl 3-hydroxycyclopentanecarboxylate. Methyl 3-oxocyclopentanecarboxylate, 25 g., in 40 ml. of absolute ethanol was reduced at 1700 p.s.i. and 100° with Raney nickel catalyst. Hydrogenation was complete in about 1 hr. The catalyst was removed by filtration, and the filtrate fractionally distilled to afford 25 g. (98.5%) of methyl 3-hydroxycyclopentanecarboxylate, b.p. 106° (15 mm.), n_D^{26} 1.4602–1.4612. A portion was redistilled and a center cut taken for analysis, n_D^{26} 1.4608.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.30; H, 8.41. Found: C, 58.51; H, 8.55.

3-Hydroxycyclopentanecarboxylic acid (IV). Ten grams of the acid III was neutralized with a slight excess of alcoholic sodium hydroxide, and hydrogenated at 2000 p.s.i. and 100° with Raney nickel catalyst. Reduction was complete in 1 hr. The catalyst was removed by filtration; most of the ethanol was removed by distillation, and the residue was acidified with dilute hydrochloric acid. The resulting solution was extracted with 4 portions of ether, the ether extracts dried with anhydrous sodium sulfate, and the ether removed by distillation. There was obtained 7.0 g. of residue. From an ether-pentane mixture, crystals (2.0 g., 20%) of crude IV were slowly deposited m.p. 39–43°.

cis 3-Hydroxycyclopentanecarboxylic acid (*cis*-IV). Methyl 3-hydroxycyclopentanecarboxylate, 10.0 g., was heated with dilute sodium hydroxide on a steam bath for 20 hr. The solution was acidified and continuously extracted with ether. The ether extracts, after drying, were concentrated to a small volume and pentane was added dropwise to turbidity. After cooling for 4 days at Dry Ice temperature, 2.4 g. (27%) of crystals, m.p. 37–44°, were deposited. After recrystallization from ether–pentane, the melting point is 50.4–51.8°. Systematic fractional crystallization afforded a total of 5.4 grams of *cis*-3-hydroxycyclopentanecarboxylic acid (*cis*-IV). The *p-bromophenacyl ester*[9] crystallized from hexane as white needles, m.p. 92.2–92.4°.

Anal. Calcd. for $C_{14}H_{15}O_4Br$: C, 51.41; H, 4.59; Br, 24.44. Found: C, 51.56; H, 4.63; Br, 24.42.

The *p-toluidide* of *cis*-IV was prepared by the method of Cheronis and Entriken[10] from the acid and *p*-toluidine. It was crystallized from aqueous methanol, m.p. 138.2–139.0°.

Anal. Calcd. for $C_{13}H_{17}O_2N$: N, 6.39. Found: N, 6.56.

3-Oxo-2-oxabicyclo[2.2.1]heptane (V). A solution of 3.0 g. of *cis*-IV in 15 ml. of butyl phthalate was heated at 150° for 2 hr. The mixture was fractionally distilled to afford 0.72 g. of V, b.p. 92–93° (10 mm.), m.p. 50.5–52.2°. Attempts to recrystallize the waxy white solid failed. Sublimation at 10 mm. yielded waxy white crystals, m.p. 51.2–52.6°. The center fraction of a second sublimation was taken for analysis, m.p. 53.7–54.5°.

Anal. Calcd. for $C_6H_8O_2$: C, 64.29; H, 7.19. Found: C, 64.33; H, 7.29.

Hydrolysis of the lactone to cis-IV. Sublimed V (20 mg.) was treated with warm 0.5*N* sodium hydroxide. The solution was acidified immediately with hydrochloric acid, and extracted with 3 portions of methylene chloride. The combined extracts were dried with sodium sulfate, filtered, and the methylene chloride removed by evaporation. The residue was crystallized from ether-pentane, affording about 15 mg. of *cis*-IV, m.p. 52.2–52.9°, which showed no depression

---

(6) K. Mislow, *J. Am. Chem. Soc.*, **73**, 4043 (1951).

(7) W. A. Bonner, *J. Am. Chem. Soc.*, **73**, 3126 (1951); D. S. Noyce and D. B. Denney, *J. Am. Chem. Soc.*, **76**, 768 (1954).

(8) All melting points are corrected; boiling points are uncorrected. Distillations were carried out through a two-foot modified Podbielniak column. Infrared spectra were recorded with a Baird recording infrared spectrometer. Analyses were performed by the Microanalytical Laboratory of the University of California.

(9) R. L. Shriner and R. C. Fuson, "*Systematic Identification of Organic Compounds*," John Wiley and Sons, New York, N. Y., 1948, p. 157.

(10) N. D. Cheronis and J. B. Entriken, "*Semimicro Qualitative Organic Analysis*," T. Y. Crowell Co., New York, N. Y., 1947, p. 208.

of m.p. when admixed with *cis*-IV isolated from the mixture of isomers.

The *p*-bromophenacyl ester was crystallized from hexane, m.p. 90.2–90.5°. It showed no depression in m.p. with the *p*-bromophenacyl ester prepared above.

cis-3-Methoxycyclopentanecarboxylic acid (*cis*-VI). In a 300-ml. flask, equipped with stirrer, reflux condenser, and drying tube, were placed 10 g. of glass beads, 20 g. of Drierite, 50 g. of freshly precipitated anhydrous silver oxide, 150 ml. of methyl iodide, and 4.0 g. of *cis*-IV. The mixture was heated under reflux with stirring for 3 days with the addition of methyl iodide when necessary to keep the volume constant. The crude isolated material still showed a slight hydroxyl band in the infrared spectrum, so the methylation was continued for an additional 2 days with fresh silver oxide and additional methyl iodide.

The crude product, isolated by filtration, washing, and evaporation of the low boiling fraction, was treated with 100 ml. of standardized 0.8*N* sodium hydroxide and heated on the steam bath. After 45 min. the theoretical amount of base had been used, as determined by titration of an aliquot. The solution was cooled, acidified, and extracted with five 100-ml. portions of ether. The dried ether solution was distilled to afford 4.1 g. (93%) of *cis*-3-methoxycyclopentanecarboxylic acid, b.p. 136–139° (10 mm.), n_D^{26} 1.4587.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.34; H, 8.34; OCH_3, 21.52; neut. equiv., 144. Found: C, 58.16; H, 8.32; OCH_3, 21.58; neut. equiv., 145.

The *p-toluidide* was prepared by the method of Cheronis and Entriken[10] and crystallized from aqueous methanol, m.p. 81.9°.

Anal. Calcd. for $C_{14}H_{19}O_2N$: C, 72.05; H, 8.22; N, 6.00. Found: C, 72.36; H, 8.04; N, 6.58.

The *p-phenylphenacyl ester* was crystallized from aqueous ethanol, m.p. 79.5–79.7°.

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.53; H, 6.57. Found: C, 74.36; H, 6.63.

Acknowledgments. This work was aided in part by a grant from the National Science Foundation (G-2387) and by a National Science Foundation Fellowship (to Joan S. Fessenden). We wish to thank Professor W. E. Doering for making the procedure of Vaughn available to us.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIF.

Perchlorates of Conjugate Acids of Azobenzene and Substituted Azobenzenes[1]

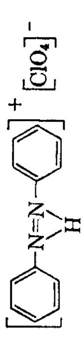
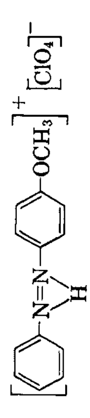
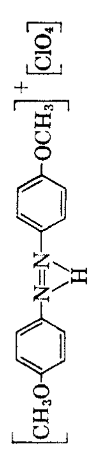
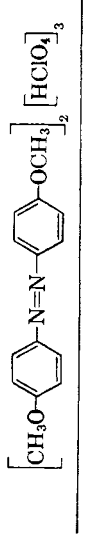
SI-JUNG YEH AND H. H. JAFFÉ

Received November 14, 1958

In an attempt to establish the structure of the conjugate acids of substituted azobenzenes, we have prepared the perchlorates of the conjugate acids of azobenzene, and of its 4-methoxy and 4,4′-dimethoxy derivatives.

TABLE I

ANALYSES AND PHYSICAL PROPERTIES OF THE PERCHLORATES

Substances	Decomposition Point, °C.[b]	Neutralization Equivalent		Analysis[a]					
				C		H		N	
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
	198	284	283	50.80	50.98	4.00	3.92	9.66	9.91
	200	311	311	50.01	50.00	4.16	4.17	8.88	8.98
	205	337	343	49.22	49.20	4.52	4.42	8.06	8.19
	152	296	293	82.84	83.58	4.31	3.98	7.04	7.13

[a] Elemental analysis were performed by A. Bernhardt, Mülheim (Ruhr), Germany. [b] Uncorrected.

---

[1] This work has been supported by a Bonita Geho Memorial Grant for Cancer Research from the American Cancer Society. This support is gratefully acknowledged.