nitrogen occurred and continued for a few minutes. The solution was kept at room temperature overnight. The residue obtained after evaporation of the benzene was purified by crystallization. In case of Vg, VI and VIII (compare Table I), the benzene solution was refluxed for 12 hr. and in case of Vf for 2 hr.

Action of Copper Bronze on Ethylene Sulfides.—A solution of the ethylene sulfide (1 g.) in 10 ml. of dry xylene, containing 0.5 g. of copper bronze was refluxed for 5 hr. and then filtered while hot. Evaporation of the xylene yielded the ethylene.

Ketazine of *o*-Chlorobenzophenone.—A solution of *o*-chlorophenylphenyldiazomethane (prepared from 1.1 g. of *o*-chlorobenzophenone hydrazone) in 20 ml. of dry benzene was refluxed for 4 hr.; the purple color disappeared. The residue obtained after evaporation of the benzene was crystallized from ethyl alcohol as yellow needles, m.p. 176°, yield 0.8 g. The ketazine gives an orange color with concentrated sulfuric acid.

Anal. Calcd. for $C_{26}H_{18}Cl_2N_2$: C, 72.7; H, 4.2; Cl, 16.6. Found: C, 72.7; H, 4.4; Cl, 16.6.

Crystallographic Properties of 2-Styryl-4-thio-α-naphthopyrone.[10]—The 2-styryl-4-thio-α-naphthopyrone crystallizes in the monoclinic system. The somewhat bladed crystals are long prismatic along the crystallographical *b*-axis.

Their optical behavior is very uncommon and characteristic for the substance. In transmitted light the crystals show an intense brownish-orange color without any perceptible pleochroism. In reflected light, the crystals appear bluish-violet with a nearly submetallic luster, while the internal refluxes are always brownish-orange. This strong reflecting power, in combination with the selective absorbtion of green light, explains the following striking phenomenon: aggregates of small crystals appear brownish-violet, while looser accumulations of very fine crystals, like the finely powdered substance, show a bright orange color in consequence of the predominance of internal refluxes.

Between crossed nicols, the crystals show highly abnormal, reddish-orange and emerald green, interference colors which are nearly independent from the thickness of the fine crystals. These abnormal colors are very characteristic for the substance and may be used for its determination. They are due to the great dispersion of the angle of the optical axes which causes also a strong dispersion of the birefringence.

CAIRO, EGYPT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AIN SHAMS UNIVERSITY]

6-Methylbicyclo[5:3:0]dec-7-en-9-one-8-acetic Acid and Related Compounds

BY A. M. ISLAM AND M. T. ZEMAITY

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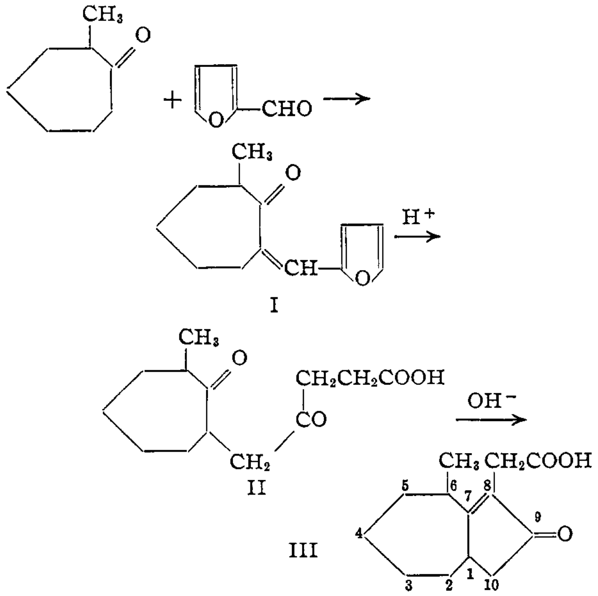
Cyclization of δ-(2-keto-3-methylcycloheptyl)-γ-ketovaleric acid (II), obtained through furan ring opening of 7-furfurylidene-2-methylcycloheptanone (I), leads directly to 6-methylbicyclo[5:3:0]dec-7-en-9-one-8-acetic acid (III). Application of the reaction to other allied bicyclic systems is described.

Although many routes have been used for the conversion of cycloheptanone into bicyclo[5:3:0]-decane derivatives,[1] the methods become tedious when applied to the production of substituted derivatives the difficult accessibility of which has hampered the study of their dehydrogenation products, the azulenes.

A new approach to the problem is suggested through the furan ring opening of the furfurylidene derivative of the particular cycloheptanone followed by cyclization of the keto-acid produced to the bicyclic ketone. The resulting bicyclic ketone is of interest as it possesses a carboxymethyl group which is of value in further synthetic work.



I

II

III

Furan ring opening of some furfurylidene derivatives of ketones has been reported in the literature,[2-4] the most general procedure involving treatment of an alcoholic solution of the furfurylidene derivative with concentrated hydrochloric acid.

Condensation of 2-methylcycloheptanone with furfuraldehyde in the presence of sodium methoxide gave the corresponding furfurylidene compound I. Heating this compound with concentrated hydrochloric acid in ethyl alcohol solution gave the ketovaleric acid II. Aldolization of II in the presence of potassium hydroxide solution furnished the bicyclic ketone III. Although the conversion of the cycloheptanone into the bicyclic ketone is small (17% over-all), the method is simple and leads to the production of substituted bicyclo-[5:3:0]decanes which are difficult to obtain otherwise.

Application of the same procedure to furfurylidene derivatives of 2-methylcyclohexanone and 2,2-diphenylcyclohexanone yielded 5-methylbicyclo[4:3:0]non-6-en-8-one-7-acetic acid (IVa) and 5,5-diphenylbicyclo[4:3:0]non-6-en-8-one-7-acetic acid (IVb), respectively.

However, extension of the synthesis to 7-furfurylidene-2,2-diphenylcycloheptanone was un-

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[1] M. Gordon, *Chem. Revs.*, **50**, 127 (1952).

[2] R. Robinson, *J. Chem. Soc.*, 1390 (1938).

[3] H. Dannenberg, *Ann.*, **585**, 16 (1954).

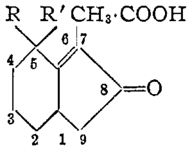
[4] H. Midorikawa, *Bull. Chem. Soc. Japan*, **26**, 302 (1953).

TABLE I

Compound	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
7-Furfurylidene-2-methylcycloheptanone[a]	75	118[d]				
7-Furfurylidene-2,2-diphenylcycloheptanone[b]	50	114	84.17	84.16	6.47	6.55
6-Furfurylidene-2-methylcyclohexanone[b,5]	84	51	75.78	75.56	7.36	7.18
6-Furfurylidene-2,2-diphenylcyclohexanone[b]	66	102	84.12	84.12	6.14	6.39
2,6-Difurfurylidene-4-methylcyclohexanone[c]	70	130	76.10	76.24	6.01	5.68
2,7-Difurfurylidenecycloheptanone[c]	80	100	76.10	76.12	6.01	6.25

[a] In spite of the sharp boiling point, no satisfactory analytical figures were obtained. [b] From petroleum ether (b.p. 60–80°). [c] From ethyl alcohol. [d] Boiling point (0.6 mm.).

successful. Difficulty was encountered in the furan ring opening step and most of the substance was recovered unchanged. This compound, in contrast with other furfurylidene compounds, was colorless and gave a yellow color with concentrated sulfuric acid. Its existence in the cycloheptenone form is possible and is still under investigation.



IVa, R = CH_3, R′ = H
IVb, R = R′ = C_6H_5

Attempted furan ring opening of difurfurylidene derivatives of cyclohexanone, 4-methylcyclohexanone and cycloheptanone gave rise to amorphous or tarry products.

Hiroshi Midorikawa[4] reported the failure to hydrolyze 2,6-difurfurylidenecyclohexanone, 2-furfurylidene-3-pentanone and 1,3-difurfurylidene-2-butanone and stated that branched chains hinder the ring-opening. However, all the compounds dealt with by the authors in the present investigation possessed a branched chain, which forms, in this case, a part of the alicyclic ring, and still most of them were hydrolyzed smoothly under the normal reaction conditions.

Experimental[6]

Condensation of Furfuraldehyde with Ketones.—To the calculated amounts of furfuraldehyde and ketone (1:1 moles) in absolute methyl alcohol was added a 10% methyl alcoholic solution of sodium methoxide (approximately 1 mole), and the reaction mixture was left overnight. Most of the alcohol was removed under reduced pressure and the reaction mixture was thrown into water and extracted with ether. All the furfurylidene derivatives prepared in this investigation are given in Table I and gave wine-red color with concentrated sulfuric acid except 7-furfurylidene-2,2-diphenylcycloheptanone which gave yellow coloration.

General Furan Ring Opening Procedure.—A mixture of 15 g. of the furfurylidene derivative, 50 ml. of concentrated hydrochloric acid and 200 ml. of ethyl alcohol was heated under reflux for 18 hr. The reaction mixture was concentrated to half its volume under reduced pressure, and a mixture of 100 ml. of glacial acetic acid, 100 ml. of concentrated hydrochloric acid and 200 ml. of water was added. Heating under reflux was continued for a further 2 hr. The reaction mixture was concentrated under reduced pressure, cooled and extracted several times with ether. The ether layer was washed with saturated sodium chloride solution, dried and evaporated.

Applied to 7-furfurylidene-2-methylcycloheptanone this process gave δ-(2-keto-3-methylcycloheptyl)-γ-ketovaleric acid (II) (28%), which crystallized from petroleum ether (b.p. 40–60°) in colorless plates, m.p. 118–120°.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.50; H, 8.39.

6-Furfurylidene-2-methylcyclohexanone gave δ-(2-keto-3-methylcyclohexyl)-γ-ketovaleric acid (22%), which crystallized from petroleum ether (b.p. 60–80°) in colorless needles, m.p. 108–110°.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.71; H, 8.30.

Similarly, 6-furfurylidene-2,2-diphenylcyclohexanone gave δ-(2-keto-3,3-diphenylcyclohexyl)-γ-ketovaleric acid (29%), which crystallized from petroleum ether (b.p. 60–80°) in colorless needles, m.p. 128°.

Anal. Calcd. for $C_{23}H_{24}O_4$: C, 75.82; H, 6.59. Found: C, 75.57; H, 6.53.

Under the hydrolysis conditions described above, 7-furfurylidene-2,2-diphenylcycloheptanone was recovered unchanged (m.p. and mixed m.p.). Also, difurfurylidene derivatives of cyclohexanone, cycloheptanone and 4-methylcyclohexanone gave much tar from which no pure material was obtained.

General Aldolization Procedure.—A mixture of 2 g. of the γ-ketovaleric acid and 100 ml. of aqueous 5% potassium hydroxide solution was heated under reflux for 3 hr. After being cooled, the reaction mixture was acidified with ice-cold dilute sulfuric acid and extracted with ether. The ether layer was washed, dried and evaporated.

6-Methylbicyclo[5:3:0]dec-7-en-9-one-8-acetic acid (III) (80%) crystallized from petroleum ether (b.p. 40–60°) in colorless plates, m.p. 110°. Light absorption in ethyl alcohol exhibited maxima at 230 (ε 11,100) and 285 mμ (ε 499). Islam and Raphael[7] record for bicyclo[5:3:0]dec-7-en-9-one, λ_{max} 233 (ε 12,600) and 289 mμ (ε 190).

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.12; H, 8.16.

5-Methylbicyclo[4:3:0]non-6-en-8-one-7-acetic acid (IVa) (75%) crystallized from petroleum ether (b.p. 40–60°) in colorless needles, m.p. 95°. Light absorption in ethyl alcohol exhibited maxima at 230 (ε 6800) and 295 mμ (ε 108). Islam and Raphael[8] record for bicyclo[4:3:0]non-6-en-8-one λ_{max} 228 (ε 16,500) and 286 mμ (ε 140).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.69; H, 7.85.

5,5-Diphenylbicyclo[4:3:0]non-6-en-8-one-7-acetic acid (IVb) (72%) crystallized from ethyl alcohol in colorless needles, m.p. 178–180°. Light absorption in ethyl alcohol exhibited an inflection at 235 (ε 9600) and a maximum at 327 mμ (ε 4957).

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.45; H, 6.53.

ABBASSIA, CAIRO, EGYPT

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(5) N. Wolff, *Compt. rend.*, **174**, 1469 (1922), recorded m.p. 51°.

(6) Melting points are not corrected.

(7) A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 3151 (1955).

(8) A. M. Islam and R. A. Raphael, *ibid.*, 4086 (1952).