Isolation of the Disulfide from a Kinetic Run.—The thiol (20.6 mg.) was dissolved in 200 ml. of distilled water; 150 ml. of this solution was used for three kinetic runs. The reaction mixtures remaining after the completion of the runs were combined, and the unused thiol solution was added; the combined solutions corresponded to 175 ml. of the original thiol solution. The solution was allowed to stand 1 hr. to allow time for the oxidation of the newly added thiol. The solution was made 1 *M* in sulfuric acid, was extracted several times with chloroform, the chloroform was evaporated to dryness *in vacuo* and the residue was taken up in 2–3 ml. of chloroform. The solution was treated with charcoal, was filtered and petroleum ether was added until the solution was faintly cloudy. The solution after cooling yielded 8.6 mg. (48%) of the disulfide, m.p. 143–145°; the mixed m.p. with an authentic sample was 146–147°. This isolation of the disulfide, coupled with the spectral data on the oxidation solutions at the end of the reaction, indicates that the thiol is oxidized quantitatively to the disulfide and that the reaction stops at the disulfide stage.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, CAIRO UNIVERSITY AND AIN SHAMS UNIVERSITY]

Organic Sulfur Compounds. XXXIV. Synthesis of Ethylenes and Ethylene Sulfides by Action of Diazoalkanes on Thioketones

BY ALEXANDER SCHÖNBERG, ABD EL KADER FATEEN AND ABD EL MAGED AMINE SAMMOUR

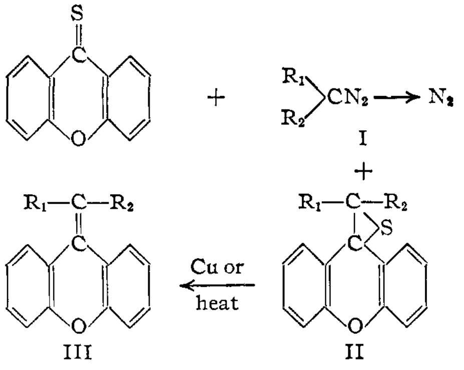
RECEIVED JUNE 10, 1957

Various ethylene sulfides have been prepared by the interaction of diazoalkanes with xanthione and Michler thioketone. Some of these ethylene sulfides were allowed to react with copper bronze in boiling xylene, yielding the corresponding ethylene compounds. The ethylene derivatives IIIa, c and f show thermochromic properties, IIIc has piezochromic properties. Treatment of 2-(4′-methoxystyryl)-4-thio-α-naphthopyrone (VIIa) with diphenyldiazomethane in boiling benzene gave the ethylene derivative VIII. 2-Styryl-4-thio-α-naphthopyrone (VIIb) crystallizes from benzene as violet or yellow crystals. By crystallographic investigations, this phenomenon was elucidated.

Experiments with Xanthione and Michler Thioketone.—Schönberg and Nickel[1] found that xanthone with diphenyldiazomethane yielded the ethylene sulfide derivative II (R_1, R_2 = C_6H_5), which on treatment with copper bronze produced 9-(diphenylmethylene)-xanthene (III, R_1, R_2 = C_6H_5).

This reaction has now been extended with *p,p′*-dichlorodiphenyldiazomethane (Ia), *o*-chlorophenylphenyldiazomethane (Ib), *p*-nitrophenylphenyldiazomethane (Ic), *p*-xenylphenyldiazomethane (Id), methylphenyldiazomethane (Ie), di-*p*-tolyldiazomethane (If) and *p*-tolylphenyldiazomethane (Ig) (scheme A). The reactions led to the formation of ethylene sulfides, except with *p*-tolylphenyldiazomethane where the ethylene derivative IIIg was obtained, presumably by thermal decomposition of IIg. Similar pyrolytic decompositions have been observed by Schönberg and Vargha.[2] IId was not obtained analytically pure. The ethylene sulfides IIa, b, c and f as well as the impure IId were transformed to the corresponding ethylenes IIIa, b, c and f by refluxing in xylene with copper bronze.

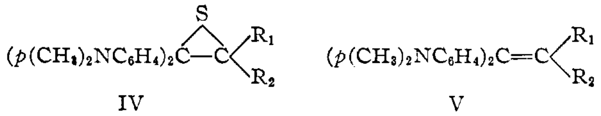
SCHEME A



I, II and III
a, R_1, R_2 = $C_6H_4Cl(p)$
b, R_1 = $C_6H_4Cl(o)$, R_2 = C_6H_5
c, R_1 = $C_6H_4NO_2(p)$, R_2 = C_6H_5
d, R_1 = $C_6H_4{\cdot}C_6H_5(p)$, R_2 = C_6H_5
e, R_1 = CH_3, R_2 = C_6H_5
f, R_1, R_2 = $C_6H_4CH_3(p)$
g, R_1 = $C_6H_4CH_3(p)$, R_2 = C_6H_5

The action of various diazoalkanes on Michler thioketone led to the formation of the ethylene sulfides (IVa-d,h) or the ethylene derivatives (Ve-g) (Scheme B). The ethylene sulfide (IVa) was transformed to the corresponding ethylene (Va) on treatment with copper bronze in boiling xylene. When a benzene solution of Michler thioketone and diphenyldiazomethane was refluxed, Vg was obtained, while Staudinger[3] on working at room temperature obtained IVg. Vg previously has been prepared by a different method.[4]

SCHEME B



IV and V
a, R_1 = CH_3, R_2 = C_6H_5
b, R_1 = CH_3, R_2 = $C_6H_4CH_3(p)$
c, R_1, R_2 = $C_6H_4Cl(p)$
d, R_1 = $C_6H_3(CH_3)_2(2,5)$, R_2 = C_6H_5
e, R_1 = $C_6H_4Cl(o)$, R_2 = C_6H_5
f, R_1 = $C_6H_4{\cdot}C_6H_5(p)$, R_2 = C_6H_5
g, R_1, R_2 = C_6H_5
h, R_1, R_2 = $C_6H_4CH_3(p)$

The action of 9-diazofluorene on Michler thioketone led to the formation of bis-(*p*-dimethylaminophenyl)-dibenzofulvene (VI), which has previously been synthesized by a different method by Bergmann[5] and Hervey.

Attention is drawn to the very good yields obtained in the experiments given and to the fact

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(1) A. Schönberg and S. Nickel, *Ber.*, **64**, 2323 (1931).

(2) A. Schönberg and L. v. Vargha, *Ann.*, **483**, 176 (1930).

(3) H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 833 (1920).

(4) H. Staudinger, *ibid.*, **3**, 862 (1920).

(5) E. Bergmann and J. Hervey, *Ber.*, **62**, 893 (1929).

TABLE I

ACTION OF DIAZOALKANES ON THIOKETONES

Diazoalkane	Color of product	Yield, g., color react. with H_2SO_4	M.p., °C., and color of melt	Solvent of crystaln.	Formula		Analyses, %
(A) Experiments with xanthione							
p,p'-Dichlorodiphenyldiazomethane (from 1.2 g. of *p,p'*-dichlorobenzophenone hydrazone[11])	Light-yellow	1.8	170	Benzine	$C_{26}H_{16}Cl_2OS$	Calcd.	Cl, 15.9
		Violet	Deep-orange	(80–100°)	IIa	Found	Cl, 16.4
o-Chlorophenylphenyldiazomethane (from 1.1 g. of *o*-chlorobenzophenone hydrazone[12])	Colorless	1.6	195	Benzine	$C_{26}H_{17}ClOS$	Calcd.	Cl, 8.6; S, 7.7
		Purple	Deep-yellow	(100–120°)	IIb	Found	Cl, 8.3; S, 7.4
p-Nitrophenylphenyldiazomethane (from 1 g. of *p*-nitrobenzophenone hydrazone[13])	Yellow	1.9	182	Benzine	$C_{26}H_{17}NO_3S$	Calcd.	C, 73.8; H, 4.1; N, 3.3; S, 7.6
		Brown	Purple	(100–120°)	IIc	Found	C, 74.3; H, 4.1; N, 3.4; S, 7 7
Methylphenyldiazomethane (from 0.6 g. of acetophenone hydrazone)	Light-yellow	1.3	105	Methyl	$C_{21}H_{16}OS$	Calcd.	C, 79.7; H, 5.1; S, 10.1
		Red		alcohol	IIe	Found	C, 79.9; H, 5.4; S, 10.0
Di-*p*-tolyldiazomethane (from 1 g. of 4,4'-dimethylbenzophenone hydrazone)	Colorless	1.6	176	Benzine	$C_{28}H_{22}OS$	Calcd.	C, 82.7; H, 5.5; S, 7.9
		Purple	Orange	(60–80°)	IIf	Found	C, 82.9; H, 5.9; S, 7.9
p-Tolylphenyldiazomethane (from 1 g. of *p*-methylbenzophenone hydrazone)	Light-yellow almost colorless	1.6	185	Benzine	$C_{27}H_{20}O$	Calcd.	C, 90.0; H, 5.6
		Yellow after short time	Deep orange	(60–80°)	IIg	Found	C, 90.4; H, 5.9
(B) Experiments with Michler thioketone							
Methylphenyldiazomethane (from 0.4 g. of acetophenone hydrazone)	Almost colorless	1.1	134	Methyl	$C_{25}H_{28}N_2S$	Calcd.	N, 7.2
		No color	Not sharp	alcohol	IVa	Found	N, 7.5
Methyl-*p*-tolydiazomethane (from 0.5 g. of *p*-methylacetophenone hydrazone)[14]	Colorless	1.3	124	Methyl	$C_{26}H_{30}N_2S$	Calcd.	C, 77.6; H, 7.5; N, 7.0; S, 8.0
		Yellow turning red		alcohol	IVb	Found	C, 77.7; H, 7.7; N, 7.0; S, 7.8
p,p'-Dichlorodiphenyldiazomethane (from 1 g. of *p,p'*-dichlorobenzophenone hydrazone)	Colorless	1.7	180	Benzine	$C_{30}H_{28}Cl_2N_2S$	Calcd.	C, 69.4; H, 5.4; Cl, 13.5; N, 5.4; S, 6.2
		Violet esp. when heated to 50°	Red-brown	(100–120°)	IVc	Found	C, 69.3; H, 5.5; Cl, 13.6; N, 5.2; S, 6.3
2,5-Dimethylphenylphenyldiazomethane (from 0.8 g. of 2,5-dimethylbenzophenone hydrazone)	Almost colorless, light-yellow	1.7	189	Benzine	$C_{32}H_{34}N_2S$	Calcd.	C, 80.3; H, 7.2; N, 5.9; S, 6.7
		Colorless	Orange-brown	(100–120°)	IVd	Found	C, 80.4; H, 7.2; N, 5.7; S, 6.5
o-Chlorophenylphenyldiazomethane (from 0.8 g. of *o*-chlorobenzophenone hydrazone)	Yellow	1.5	182	Methyl	$C_{30}H_{29}ClN_2$	Calcd.	C, 79.6; H, 6.4; Cl, 7.7; N, 6.2
		No color	Orange	alcohol	Ve	Found	C, 79.3; H, 6.5; Cl, 7.6; N, 6.1
p-Xenylphenyldiazomethane (from 1g. of *p*-phenylbenzophenone hydrazone)[15]	Deep-yellow	1.6	263	Benzene-benzine	$C_{36}H_{34}N_2$	Calcd.	C, 87.4; H, 6.9; N, 5.7
		Violet			Vf	Found	C, 87.4; H, 7.1; N, 5.5
Diphenyldiazomethane (from 0.7 g. of benzophenone hydrazone)	Yellow	0.9	190	Benzine	$C_{30}H_{30}N_2$	Calcd.	N, 6.7
		No color		(100–120°)	Vg	Found	N, 6.9
9-Diazofluorene (0.7 g.)	Deep orange	0.9	235	Benzine	$C_{30}H_{28}N_2$	Calcd.	N, 6.7
		No color		(100–120°)	VI	Found	N, 6.8
Di-*p*-tolyldiazomethane (from 0.8 g. of di-*p*-tolylketone hydrazone)	Yellow	1.6	164	Benzine	$C_{32}H_{34}N_2S$	Calcd.	C, 80.3; H, 7.2; N, 5.9; S, 6.7
		Orange		(100–120°)	IVh	Found	C, 80.6; H, 7.3; N, 5.8; S, 6.7
(C) Experiment with VIIa							
Diphenyldiazomethane (from 0.6 g. of benzophenone hydrazone)	Orange	1.1	190–191	Ethyl	$C_{35}H_{26}O_2$	Calcd.	C, 87.8; H, 5.5
		Violet		alcohol	VIII	Found	C, 87.6; H, 5.4

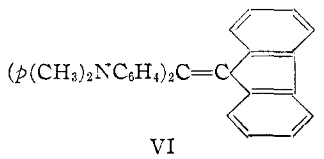
TABLE II

ACTION OF COPPER BRONZE ON ETHYLENE SULFIDES

Ethylene sulfide	Color of the ethylene (color in u.v.-light)	Yield, g.	Color react. with H_2SO_4	M.p., °C., Color of melt	Solvent for crystaln.	Formula		Analyses, %
IIa	Light-yellow[a]	0.7	Crystals turn yellow after short time	205 Red-orange	Benzine (80–100°)	$C_{26}H_{16}Cl_2O$ IIIa	Calcd. Found	C, 75.2; H, 3.9; Cl, 17.1 C, 75.4; H, 4.0; Cl, 16.8
IIb	Colorless (intense blue)	.8	Crystals turn yellow	183 Yellow-red	Benzine (100–120°)	$C_{26}H_{17}ClO$ IIIb	Calcd. Found	C, 82.0; H, 4.5; Cl, 9.3 C, 82.2; H, 4.6; Cl, 9.4
IIc	Yellow[b] (intense yellow-green)	.9	Brown	175 Deep-purple	Benzine (100–120°)	$C_{26}H_{17}NO_3$ IIIc	Calcd. Found	N, 3.6 N, 3.9
IId	Yellow (intense yellow-green)	.7	Olive	186 Red	Ethyl alcohol	$C_{32}H_{22}O$ IIId	Calcd. Found	C, 91.0; H, 5.3 C, 90.7; H, 5.5
IIf	Light yellow green[c] (intense green)	.75	Orange	187 Deep-orange	Benzine (60–80°)	$C_{28}H_{22}O$ IIIf	Calcd. Found	C, 89.8; H, 5.9 C, 89.8; H, 6.0
IVa	Colorless	.6	Yellow	104 Light-yellow	Methyl alcohol	$C_{25}H_{28}N_2$ Va	Calcd. Found	C, 84.3; H, 7.8; N, 7.8 C, 84.3; H, 7.9; N, 8.1

[a] Its solution in methyl phthalate is light yellow on cold and orange on hot.* [b] By crushing the yellow crystals in an agate mortar, they turn orange red, which turn yellow on exposure to ether vapors or after a few days; its solution in methyl phthalate is yellow on cold and orange on hot.* [c] Its solution in methyl phthalate is light yellow on cold and orange on hot.* * Color changes in methyl phthalate are reversible.

that it is possible to work with the crude diazoalkane benzene solutions obtained by the oxidation of the corresponding hydrazones with mercuric oxide or manganese dioxide. These hydrazones are known with the exception of the hydrazones of *o*-chlorobenzophenone, *p*-nitrobenzophenone and



VI

p-phenylbenzophenone. The ketazine of *o*-chlorobenzophenone has been obtained from *o*-chlorophenyl-phenyldiazomethane.

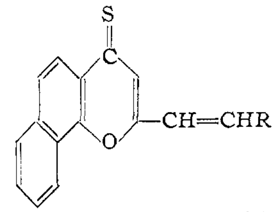
The following diazomethane derivatives have been prepared for the first time: Ia, b, c, d: I (R_1 = $C_6H_3(CH_3)_2(2,5)$, R_2 = C_6H_5) and I (R_1 = CH_3, R_2 = $C_6H_4CH_3(p)$).

Thermochromic and Piezochromic Properties.—Similar to 9-(diphenylmethylene)-xanthene[1] (III, R_1, R_2 = C_6H_5), the ethylene derivatives IIIa, c and f, show thermochromic properties, thus the light yellow crystals of IIIa give an orange-red melt (at 205°), which on cooling yields quantitatively the original crystals. Thermochromic properties are also shown by IIIa in dimethyl phthalate.[6]

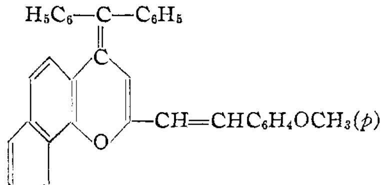
Attention is also drawn to the piezochromic behavior of the yellow crystals of 9-(*p*-nitrophenyl-phenylmethylene)-xanthene (IIIc). They turn orange-red when crushed in an agate mortar, and the yellow color is restored either when left aside for a few days or when the crushed crystals are exposed to diethyl ether vapors. A similar observation is known in the case of diflavylene,[7] and this was reaffirmed by Theilacker.[8]

The nature of these color changes is still obscure. It may not be the pressure that causes this change, but the elevation of temperature for an extremely short time during the crushing that plays that role. In consequence of the rapid cooling the form obtained by heat, whatever the nature may be, is frozen in.

Experiment with 2-(4′-Methoxystyryl)-4-thio-α-naphthopyrone VIIa.—The action of diazoalkanes on 4-thiochromones in analogy to scheme A has not yet been described. The formation of VIII, obtained by the action of diphenyldiazomethane on 2-(4′-methoxystyryl)-4-thio-α-naphthopyrone (VIIa)[9] is the first example of this type. VIIa and b furnish yellow or violet crystals, at first believed in each case to be a mixture of two substances. This however was found to be erroneous as shown by a crystallographic investigation[10] of VIIb.[9]



VII, a, R = $C_6H_4OCH_3(p)$
b, R = C_6H_5



VIII

Experimental

Hydrazones.—The hydrazones were obtained by refluxing the ketone (1 mole) and hydrazine hydrate (1 mole) in the least amount of *n*-butyl alcohol, for 2 hr. The hydrazone which usually separated out on cooling was filtered off and can be used directly for the preparation of the diazoalkane.

Action of Diazoalkanes on Thioketones.—The experiment was done by the following general method: The thioketone (1 g.) in 10 ml. of dry benzene was treated with 20 ml. of a benzene solution of the diazoalkane. A mild evolution of

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[6] For an explanation of the thermochromic properties of xanthene derivatives compare A. Schönberg, A. Mustafa and W. Asker, THIS JOURNAL, **73**, 2876 (1951).

[7] A. Schönberg and W. Asker, *J. Chem. Soc.*, 272 (1942).

[8] W. Theilacker, G. Kortüm and G. Friedheim, *Chem. Ber.*, **83** 519 (1950).

[9] A. Schönberg, A. Fateen and A. Sammour, THIS JOURNAL, **78** 4689 (1956).

[10] Report by A. Rittmann and E. E. Hennawi, National Research Centre, Cairo, Egypt.

[11] J. Boëseken and W. D. Cohen, *Chem. Zentr.*, **86**, I, 1376 (1915).

[12] Prepared from *o*-chlorobenzophenone, yellow crystals from ethyl alcohol, m.p. 120°.

[13] Prepared from *p*-nitrobenzophenone, intense yellow crystals from ethyl alcohol, m.p. 97°.

[14] R. Sorge, *Ber.*, **35**, 1070 (1902).

[15] Prepared from *p*-phenylbenzophenone, colorless crystals from ethyl alcohol, m.p. 123°.

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

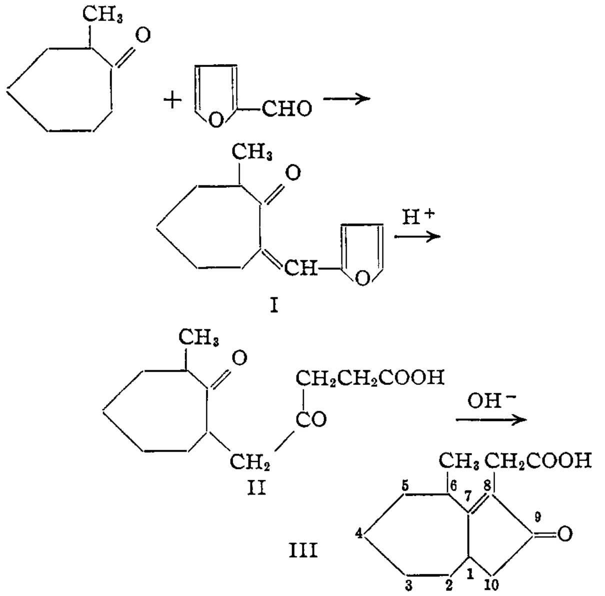
BY A. M. ISLAM AND M. T. ZEMAITY

RECEIVED JUNE 18, 1957

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.



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).