tion was mixed with 74.4 g. (0.5 mole) of methyl fumaryl chloride in a 500 ml. three necked flask equipped with stirrer, dropping funnel, and thermometer. The temperature was maintained at 0–5° by cooling with an acetone ice bath while 40 ml. of pyridine was added dropwise with stirring. After 0.5 hr. of additional stirring, 200 ml. of water was added. The mixture was cooled back to 0° and filtered. The brown solid was washed thoroughly with water and air dried; crude yield, 57 g. (71%), m.p. 50–53°. Recrystallization from a mixture of 120 ml. of isopropyl alcohol and 120 ml. of water gave 47 g. of long colorless blades, m.p. 53–54°, unchanged by further recrystallization.

O-Methyl S-isopropyl thiolfumarate was prepared in a similar manner. However, the crude product separated as an oily lower phase. This was extracted into 50 ml. of chloroform, washed with water, and dried over sodium sulfate. The material was then purified by fractional distillation.

O-Methyl S-t-butyl thiolfumarate. The synthesis of this compound describes the method used for the preparation of the remaining thiolfumarates. A solution of 36 g. (0.4 mole) of *t*-butyl mercaptan in 400 ml. of 5% aqueous sodium hydroxide was maintained at 10–15° by cooling while 59.5 g. (0.4 mole) of methyl fumaryl chloride was added dropwise with stirring. An oil separated to the bottom when stirring was stopped. The mixture was stirred for 3 hr. with cooling to −5° in an unsuccessful attempt to induce crystallization. Then the oil was extracted into 50 ml. of chloroform, washed with water, and dried over sodium sulfate. Fractional distillation gave 32 g. (40%) of light yellow product at 69–71° (0.5 mm.), n_D^{25} 1.4948. When this material was chilled at 0° for several hours, it crystallized to colorless blades which melted at 24°.

Acknowledgment. The authors wish to thank Alfred Foulds for the microanalyses, and C. F. Hartman for technical assistance in this work.

PHILLIPSBURG, N. J.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

Chemistry of Dimethylketene Dimer. I. Catalytic Hydrogenation and Ring Cleavage by Alcohols

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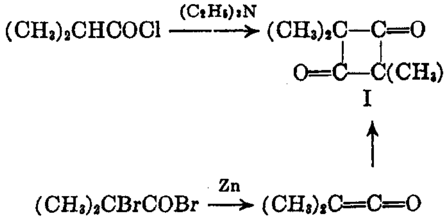
The hydrogenation of dimethylketene dimer (I) was investigated to find the optimum conditions for preparation of the corresponding glycol III. Excellent yields were obtained with a ruthenium catalyst. Hydrogenation over Raney nickel was often accompanied by formation of by-products. In a methanolic medium, some of the dimer was cleaved to form methyl 2,2,4-trimethyl-3-oxovalerate (VI). This reaction, when catalyzed by bases, was generally applicable to other alcohols and to phenols and mercaptans. Another by-product was identified as 1-hydroxy-2,2,4-trimethyl-3-pentanone (V), which presumably was formed by ring opening of the intermediate ketol II and subsequent hydrogenation of the acyclic keto aldehyde IV formed by this cleavage. The glycol III was separated into isomers melting at 148° and 163°, which were characterized by infrared and NMR spectra as the *trans* and *cis* isomers, respectively.

Tetramethyl-1,3-cyclobutanedione (I) was first prepared by Wedekind and Weisswange[1] by the dehydrohalogenation of isobutyryl chloride with triethylamine. At about this same time, Staudinger and Klever[2] succeeded in preparing dimethylketene from bromisobutyryl bromide and zinc, and it was recognized that this compound spontaneously formed a dimer which was identical with I.



The structure of dimethyketene dimer as a cyclic 1,3-diketone has been well established by the formation of typical carbonyl derivatives,[1,3] the Beckmann rearrangement of oximes,[4] the Wolff-Kishner reduction of the disemicarbazone,[3] and electron diffraction studies.[5] An unsuccessful attempt was made to obtain the corresponding glycol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol (III), by reduction of I with sodium amalgam.[6] Catalytic hydrogenation under relatively mild conditions produced the intermediate ketol, 3-hydroxy-2,2,4,4-tetramethylcyclobutanone (II). Gross[7] first carried out this reduction over platinum oxide catalyst[8] in equipment similar to the Adams-Voorhees apparatus,[9] but Miller[4] obtained better results (80% yield) with Raney nickel under 5–6 atm. pressure of hydrogen. More drastic conditions, up to 150° and 100 atm. over Raney nickel, were used by Miller to force the hydrogenation to the glycol III.

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[1] E. Wedekind and W. Weisswange, *Ber.*, **39**, 1631 (1906).

[2] H. Staudinger and H. W. Klever, *Ber.*, **39**, 968 (1906).

[3] H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

[4] L. L. Miller, *Structure of Some Derivatives of Dimethylketene*, Ph.D. thesis, Cornell University, 1937.

[5] W. N. Lipscomb and V. Schomaker, *J. Chem. Phys.*, **14**, 475 (1946).

[6] E. Wedekind and M. Miller, *Ber.*, **44**, 3285 (1911).

[7] P. F. Gross, *The Structure of Ketene Dimer*, Ph.D. thesis, Cornell University, 1936.

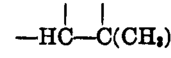
[8] R. Adams, V. Voorhees, and R. L. Shriner, *Org. Syntheses*, Coll. Vol. I, 463 (1941).

[9] R. Adams and V. Voorhees, *Org. Syntheses*, Coll. Vol. I, 61 (1941).

TABLE I

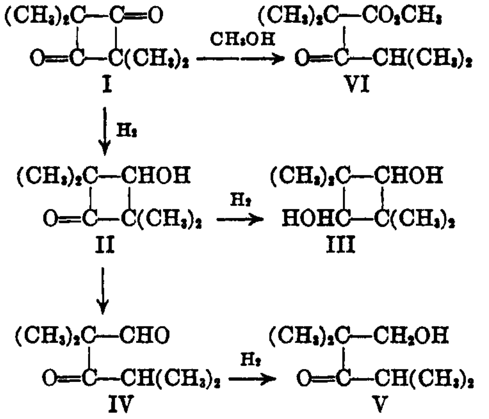
ESTERS OF 2,2,4-TRIMETHYL-3-OXOVALERIC ACID,

$(CH_3)_2CH\overset{O}{\overset{\|}{C}}C(CH_3)_2\overset{O}{\overset{\|}{C}}OR$

R	Method[b]	Yield, %	B.P.	Press., mm.	n_D^{20}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sapon. Equiv. Calcd.	Sapon. Equiv. Found
CH_3—	A	32[e]	88–91	22	1.4244	62.8	63.3	9.30	9.56	172	177
	B	89	74.5–75	10	1.4236						
C_2H_5—	B	87	81.5–82	9.5	1.4230	64.5	64.8	9.67	9.78	186	184
$(CH_3)_2CH$—	B	54	113–116	36	1.4209					200	204
$CH_2{=}CHCH_2$—	B	73	95–96	10	1.4369	66.6	66.7	9.15	9.18		
n-C_4H_9—	D[c]	18[e]	113–114	14	1.4288	67.3	67.3	10.3	10.4	214	219
$(CH_3)_3C$—	C	73	100–104	16	1.4212	67.3	66.9	10.3	10.3		
C_6H_5—	F	86	95–96	0.5	1.4859					234	229
—CH_2CH_2—	D	77	185–187	5.5	1.4484	63.1	63.4	8.76	8.79	171	168
$HOCH_2C(CH_3)_2CH_2$—	D	56[f]	130–139	2.5–3.5	1.4488	63.9	63.9	9.84	9.89	244	247
—$CH_2C(CH_3)_2CH_2$—	D	5[f]	184	3.5	1.4488	65.6	66.0	9.36	9.47	192	194
$S(CH_2CH_2—)_2$[a]	G	93.5	110	4 μ[j]	1.4720	59.8	60.1	8.46	8.53	201	208
$CH_3CH_2C(CH_2—)_3$	G	52	140	1 μ[j]	1.4587	65.0	65.0	9.03	9.02	185	185
$C(CH_2—)_4$	G	57	91–92[g]			63.8	63.7	8.63	8.65	174	169
	E	57	113–114[h]			67.9	68.2	9.44	9.38		
	E[d]	11	106–107[i]			67.7	67.5	7.69	7.80		

[a] Analysis for sulfur: calcd., 7.97; found, 7.99. [b] Refers to type of catalyst and general procedure as described in Experimental; minor modifications in reaction conditions were used. [c] Heated at 150° for 6 hr. [d] Reaction mixture was heated to 250°. [e] Conversion. [f] Monoester and diester were obtained from same experiment. [g] M.p. (from acetone-hexane). [h] M.p. (from acetone). [i] M.p. (from ethyl alcohol). [j] Falling film molecular still.

By-products of the reduction, which was carried out in methanol, included 2,4-dimethyl-3-pentanone and a high-boiling oil of undetermined composition.



We have examined this catalytic hydrogenation in greater detail, and have determined the nature of the products obtained under various reaction conditions. The hydrogenation was first studied over a number of common hydrogenation catalysts. Results with palladium, platinum, and rhodium catalysts were very poor. Moderate yields of III, contaminated with low-melting by-products, were obtained with copper–chromium-oxide and supported nickel catalysts. Outstanding results were obtained with a ruthenium catalyst. The hydrogenation proceeded rapidly with no detectable formation of by-products; pure III (a mixture of *cis* and *trans* isomers) was recovered by removal of the catalyst and evaporation of the solvent.

We found, as did Miller,[4] that a high-boiling liquid by-product was produced when the hydrogenation over Raney nickel was carried out in a methanolic medium. This by-product consisted of two compounds: 1-hydroxy-2,2,4-trimethyl-3-pentanone (V) and methyl 2,2,4-trimethyl-3-oxovalerate (VI). V was apparently produced by reduction of I to the cyclic ketol II, followed by cleavage to an acyclic keto aldehyde IV and subsequent hydrogenation to V. Miller noted that the cyclic ketol II dissociated exothermically in dilute alkali to give 2,4-dimethyl-3-pentanone and a formate, evidently through the formation and cleavage of IV. The formation of V in a catalytic hydrogenation system is, therefore, not unexpected, although one might anticipate that this acyclic ketol would then undergo reductive cleavage to 2,4-dimethyl-3-pentanone and methanol.[10] This, indeed, may have been the source of the dimethylpentanone found by Miller in his hydrogenation product.

The other by-product, VI, arose from cleavage of I by methanol. This reaction was relatively slow even at elevated temperatures, but when catalyzed by basic reagents, such as sodium alkoxides or quaternary ammonium bases, the alcoholysis of I was rapid and exothermic. The base-catalyzed alcoholysis was found to be a general reaction and was used to prepare a number of

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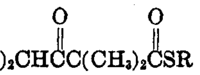
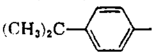
[10] H. Adkins, *Reactions of Hydrogen with Organic Compounds Over Copper–Chromium-Oxide and Nickel Catalysts*, University of Wisconsin Press, Madison, Wis., 1937, pp. 130, 142.

TABLE II

S-ESTERS OF 2,2,4-TRIMETHYL-3-OXOTHIOVALERIC ACID,  $(CH_3)_2CH\overset{O}{\overset{\|}{C}}C(CH_3)_2\overset{O}{\overset{\|}{C}}SR$

R	Method	Yield, %	B.P.	Press., μ	n_D^{20}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
n-$C_{12}H_{25}$—	G	72	78–88	20	1.4705	70.2	70.2	11.1	11.4	9.4	9.4
—$(CH_2)_6$—	G	76	108–133	1	1.4951	61.4	61.4	8.8	9.0	14.9	14.6
 $(CH_3)_2C$—	G	60	58–59[a]			70.6	70.7	8.5	8.5	10.5	10.5

[a] M.p. (from ethyl alcohol).

esters of 2,2,4-trimethyl-3-oxovaleric acid (Table I). Further study showed that phenols (Table I) and mercaptans (Table II) were esterified under the same general conditions, although at a somewhat slower rate.

On the basis of the boiling range, 90–93° (34 mm.), reported by Miller, we concluded that his high-boiling liquid by-product was primarily VI, b.p. 88–91° (22 mm.), and that most of the acyclic ketol V underwent cleavage to 2,4-dimethyl-3-pentanone. We found that VI is very resistant to further hydrogenation or hydrogenolysis, which explains its survival in Miller's hydrogenation experiment.

Miller separated a sample of III, m.p. 124–135°, into fractions by vacuum sublimation, and concluded that the two geometric isomers melted at 127–128° and 147–148°. The relative amounts of the sublimates indicated that the original mixture contained about 70% of the lower melting isomer. By repeated crystallization of III, we isolated the modification melting at 147–148°; but a similar separation of the diacetate of III, followed by regeneration of the glycol by methanolysis, produced an isomer melting at 162.5–163°. A better method of segregating the isomers was developed through the diformate esters of III, which separated easily into solid and liquid components. The glycol isomers were regenerated by methanolysis and purified by recrystallization from toluene. With these pure geometric isomers as standards, an analytical method based on infrared spectra was devised. It indicated that the product obtained by catalytic hydrogenation of I contained about 50% of each isomer.

The configuration of the glycol isomers was assigned on the basis of NMR spectra, which exhibited one peak corresponding to the methyl groups of the lower melting isomer, but two peaks for the higher melting isomer. *Cis*-III contains two types of methyl groups: those on the same side of the ring as the hydroxy groups, and those on the opposite side. This situation is not found in *trans*-III, where all methyl groups are equivalent (each methyl group is *cis* to one hydroxy group and *trans* to the other). These spectra again associate the higher and lower melting isomers with the *cis* and *trans* structures, respectively. This interpretation was substantiated by the NMR spectrum of the cyclic ketol II, which exhibited two methyl group peaks. The structure of II is similar to *cis*-III in that two methyl groups are *cis* to the hydroxy group, and the other two are *trans*.

The dipole moments of the *cis* and *trans* isomers in dioxane solution were determined from changes in dielectric constant and specific volume, which were linear with respect to corresponding changes in weight fraction. The extrapolations of these plots coincided within 0.1% of the dielectric constant and specific volume of peroxide-free dioxane. The moments, 2.39 D. and 2.10 D. for the *cis* and *trans* isomers, respectively, were consistent with the structural assignments previously described.[11]

EXPERIMENTAL

Hydrogenation of tetramethyl-1,3-cyclobutanedione (I). Four hundred grams of tetramethyl-1,3-cyclobutanedione, 600 ml. of methanol, and 20 g. of 5% ruthenium-on-carbon powder[12] were placed in a 1780-ml. stainless steel rocking autoclave and hydrogenated at 125° under 1000–1500 p.s.i. of hydrogen for 1 hr. The hydrogenation product was filtered and evaporated to dryness. The yield of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (III, mixed isomers, m.p. 129–150°) was 403 g. (98%). The infrared spectrum indicated that the product contained no carbonyl compounds.

Formation of methyl 2,2,4-trimethyl-3-oxovalerate (VI) *and 1-hydroxy-2,2,4-trimethyl-3-pentanone* (V). Hydrogenation of tetramethyl-1,3-cyclobutanedione over Raney nickel in methanol as the reaction medium gave erratic results. Good yields of crystalline tetramethylcyclobutanediol were obtained in some experiments, but, frequently, the glycol was contaminated with liquid by-products. The following experiment was an example of excessive by-product formation.

A mixture of 285 g. of tetramethyl-1,3-cyclobutanedione, 400 ml. of methanol, and 20 g. of Raney nickel (ethanolic slurry) was hydrogenated in a 1-l. stainless steel rocking autoclave at 150° and 1500 p.s.i. of hydrogen. Absorption of hydrogen was rapid at first, but soon became very slow. After 18 hr., the reaction mixture was removed and filtered; 50 g. of Raney nickel was added to the filtrate, and the mixture was hydrogenated under the same conditions for 5 hr. The product was filtered and distilled at atmospheric pressure until excessive decomposition of the distilland was evident. The distillation was completed under reduced pressure, and 91 g. of liquid product was collected at 50–80° (2 mm.). This material was combined with 140 g. of liquid product, b.p. 62–72° (3 mm.), collected from a similar

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[11] G. F Wright, University of Toronto, private communication.

[12] Baker and Company, Newark, N. J.

experiment, and the mixture was fractionated through an 8-foot spinning band column at 10:1 reflux ratio.

The infrared spectrum of a 26-ml. fraction [b.p. 51.8–51.0° (3.4–3.1 mm.)] indicated that the material was methyl 2,2,4-trimethyl-3-oxovalerate (VI) contaminated with a small amount of 1-hydroxy-2,2,4-trimethyl-3-pentanone (V). Comparison with an authentic sample of VI confirmed the identification. Identity of a 25-ml. fraction, b.p. 62.6° (3.5–3.6 mm.), n_D^{20} 1.4382, as V was suggested by bands in the infrared spectrum at 2.9 μ and 5.9 μ and by a doublet at 7.3–7.4 μ, characteristic of hydroxy, carbonyl, and *gem*-dimethyl groups. This spectrum was identical with that of a sample, b.p. 103–107° (26 mm.), n_D^{20} 1.4384, obtained from hydrogenation of tetramethylcyclobutanedione in continuous-process equipment. The *p*-nitrobenzoate of the latter sample melted at 83–84°, in agreement with the reported value[13] of 82–83° for this derivative of 1-hydroxy-2,2,4-trimethyl-3-pentanone.

Anal. Calcd. for $C_{15}H_{19}NO_5$: N, 4.78. Found: N, 4.80.

3-Hydroxy-2,2,4,4-tetramethylcyclobutanone (II). Twenty-eight grams (0.2 mole) of tetramethyl-1,3-cyclobutanedione, 300 ml. of methanol, and 4 g. of an ethanolic slurry of Raney nickel were placed in a stirred vessel and hydrogenated at 40° under 45 p.s.i. of hydrogen until 0.2 mole was absorbed. The reaction mixture was filtered and evaporated on a steam bath. The residual solid was recrystallized from a benzene-hexane mixture to give 19.6 g. (70%) of 3-hydroxy-2,2,4,4-tetramethylcyclobutanone (II), m.p. 114°. (Miller[4] reported a melting point of 113–114°.) The melting point of a mixture of I and II was sharply depressed. The 2,4-dinitrophenylhydrazone of II melted at 154.5–156° (corr.); Miller reported 152.5–153.5°.

Reaction of tetramethyl-1,3-cyclobutanedione (I) *with alcohols, phenols, and mercaptans. A. Methanol.* A mixture of 100 g. of tetramethyl-1,3-cyclobutanedione (I) and 100 g. of methanol was heated under nitrogen in an autoclave for 12 hr. at 160°. Unchanged I was filtered from the reaction mixture, and the liquid product was distilled to give, after removal of more I, 39.5 g. (32% conversion) of methyl 2,2,4-trimethyl-3-oxovalerate[14] (VI).

A sample of methyl 2,2,4-trimethyl-3-oxovalerate prepared from tetramethyl-1,3-cyclobutanedione was compared with a sample prepared from methyl 2-bromo-2-methylpropionate by Zeltner's method.[15] Identity was confirmed by comparison of infrared spectra. Both samples reacted with hydrazine to form 4,4-dimethyl-3-isopropyl-2-pyrazolin-5-one, m.p. 81.5–82.5° (corr.).

B. Ethyl alcohol. A solution of 0.1 g. of sodium in 100 ml. of absolute ethyl alcohol was placed in a 50-ml. flask equipped with a thermometer and a reflux condenser. The solution was cooled to 10°, and 50 g. of tetramethyl-1,3-cyclobutanedione (I) was added in small portions through a condenser. The tetramethyl-1,3-cyclobutanedione dissolved instantly in a strongly exothermic reaction, and the flask was cooled to keep the temperature below 50°. When addition was complete, the reaction mixture was acidified with 2 ml. of acetic acid and was distilled. The yield of ethyl 2,2,4-trimethyl-3-oxovalerate was 58 g. (87%).

C. t-Butyl alcohol. Four grams of a 50% dispersion of sodium hydride in mineral oil was dissolved in 250 ml. of *t*-butyl alcohol and 140 g. of tetramethyl-1,3-cyclobutanedione (I) was added. The mixture was stirred and heated slowly. At 60°, an exothermic reaction started, the temperature rose rapidly, and the mixture began to reflux. The solution was stirred for 1 hr. with no further heating, then acidified with 10 ml. of acetic acid, and distilled. The yield of *t*-butyl 2,2,4-trimethyl-3-oxovalerate was 156 g. (73%).

D. Ethylene glycol. A mixture of 70 g. of tetramethyl-1,3-cyclobutanedione (I), 15 g. of ethylene glycol, and 15 ml. of pyridine was heated in an autoclave at 200° for 12 hr. The homogeneous product was distilled to give, after removal of 20 g. of forerun, 63 g. (77%) of ethylene glycol bis(2,2,4-trimethyl-3-oxovalerate).

E. 2,2,4,4-Tetramethyl-1,3-cyclobutanediol (III). A mixture of 110 g. of tetramethyl-1,3-cyclobutanedione (I), 50 g. of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (III), and 0.5 g. of sodium was heated to 100°, and 2 ml. of absolute ethyl alcohol was added to the slurry. An immediate reaction occurred; the temperature rose to 140–145°, where it was maintained for 45 min. The reaction mixture solidified when cooled, and was broken up and dissolved in hot acetone. The crystalline product obtained on cooling was recrystallized five times from acetone to give 87 g. (57%) of 2,2,4,4-tetramethyl-1,3-cyclobutanediol bis(2,2,4-trimethyl-3-oxovalerate), m.p. 113–114°. Mixed melting points with I or III were depressed 15° or more.

F. Phenol. A mixture of 80 g. of tetramethyl-1,3-cyclobutanedione (I), 53 g. of phenol, and 0.1 g. of sodium was heated to 90°; 2 ml. of ethyl alcohol was added, and heating was continued to 190–195°. The mixture was held at this temperature for 30 min. and then allowed to cool. Distillation gave 114 g. (86%) of phenyl 2,2,4-trimethyl-3-oxovalerate.

G. 1-Dodecanethiol. A mixture of 101 g. of 1-dodecanethiol, 70 g. of tetramethyl-1,3-cyclobutanedione (I), 0.5 g. of sodium, and 300 ml. of xylene was stirred and refluxed for 3 hr. The solution was distilled to remove low-boiling components up to a base temperature of 215° at 3 mm. The residue was distilled in a cyclic falling film molecular still at 78–88° (20 μ) to give 123 g. (72%) of *S*-dodecyl 2,2,4-trimethyl-3-oxothiovalerate.

Separation of cis and trans isomers of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (III). *A. Preparation of formate ester.* A solution of 321 g. of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (III, a mixture of approximately equal amounts of *cis* and *trans* isomers), 276 g. of formic acid, and 200 ml. of benzene was refluxed for 5 hr. The solution was cooled, another 276-g. quantity of formic acid was added, and refluxing was continued for 4 hr. After being cooled, the solution was diluted with benzene, washed with water, dilute bicarbonate solution, and again with water, and finally dried over sodium sulfate. Distillation through a 48-in. packed column gave, after removal of the solvent, 315 g. (70%) of 2,2,4,4-tetramethyl-1,3-cyclobutanediol diformate, b.p. 132–133° (53 mm.). The purity of this material, as determined by gas chromatography, was 98%.

B. trans Isomer. On standing at room temperature, the 2,2,4,4-tetramethyl-1,3-cyclobutanediol diformate (315 g.) deposited a large portion of crystalline material. Filtration of this mixture gave 167 g. of solid, m.p. 58–65°, which was recrystallized from petroleum ether (b.p. 30–60°) to give 144 g. of *trans*-III diformate, m.p. 67–68°. A 132-g. portion of this material was dissolved in a solution of 2 g. of sodium in 900 ml. of methanol and allowed to stand at room temperature for 24 hr. After addition of 9 ml. of acetic acid, the solution was evaporated to dryness on a steam bath and the solid residue was dissolved in 900 ml. of boiling toluene. The hot toluene solution was filtered to remove sodium acetate, concentrated to a volume of 450 ml., and allowed to cool. The crystalline glycol (*trans*-III) was filtered off and dried at 100° oven; it weighed 78 g. and melted sharply at 148°.

C. cis Isomer. The liquid portion of the 2,2,4,4-tetramethyl-1,3-cyclobutanediol diformate (143 g., recovered from the separation described above) was converted to the free glycol by the same methanolysis procedure that was applied to the solid diformate. After the crystallization from toluene, the mixture of glycol isomers (79 g.) melted at 130–154°. A 57-g. sample was dissolved in 400 ml. of refluxing toluene, the solution was cooled to 80°, and the liquid was decanted from the glycol which had crystallized. The crystallized glycol was dissolved in another 400-ml. portion of

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(13) J. Decombe, *Compt. rend.*, **203**, 1077 (1936).

(14) E. Baumgarten, R. Levine, and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 864 (1944).

(15) J. Zeltner, *Ber.*, **41**, 592 (1908).

boiling toluene; the solution was cooled to 100° and decanted from the crystallized product. At this point, the recrystallized glycol weighed 24 g. and melted at 160–163°. A final recrystallization from 350 ml. of toluene gave 22 g. of pure *cis*-2,2,4,4-tetramethyl-1,3-cyclobutanediol, m.p. 162.5–163.5°.

Acknowledgment. We are indebted to J. H. Chaudet, of these laboratories, for the determination and interpretation of the nuclear magnetic resonance spectra.

KINGSPORT, TENN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Ring Enlargement Produced by the Alkaline Fusion of ω-Bromocamphene

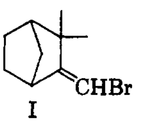
JOSEPH WOLINSKY

Received June 9, 1960

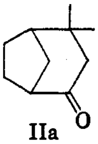
It is shown that "dicamphenyl ether," the major product produced by potassium hydroxide fusion of ω-bromocamphene (I), is a mixture composed largely of the ring expanded vinyl ethers (VIIIa) and (VIIIb). The "Schmelzketon," a minor product from the alkaline fusion of I, which was considered to be a single compound by earlier investigators is shown to be a mixture of 4,4-dimethylbicyclo[3,2,1]octan-2-one (IIa), 4,4-dimethylbicyclo[3,2,1]octan-3-one (IIb), and camphenilanaldehyde, whereas the "Oxidationketon" is a mixture of IIa, IIb, and carbocamphenilone (VI). The structures of IIa and IIb are suggested by a study of the NMR spectra of these ketones and their α-bromoderivatives. The reaction of I with potassium *t*-butoxide affords a mixture of the ring expanded enol ethers (XIX) and (XX). The formation of 2-butyne from 1,2-dibromo-2-methylpropane under similar conditions suggests that the cyclic acetylene (XXI) is an intermediate in the base induced ring enlargements of I.

More than thirty years ago Lipp[1] observed that potassium hydroxide fusion of ω-bromocamphene (I) afforded, *in low yield*, a steam-volatile "Schmelzketon" which was assigned structure IIa, and named R-homocamphenilone, on the basis that it was converted by oxidation to camphenic acid (III) and was not affected by sodium amide.[2] The major product of the alkaline fusion of I, a nonvolatile oil, was represented as "dicamphenyl ether" (IV) since acid hydrolysis was alleged to give camphenilanaldehyde (V)[3] in quantitative yield. It was further claimed[1] that the oxidation of "dicamphenyl ether" with chromium trioxide produced an "Oxidationketon" which was identical with the "Schmelzketon."

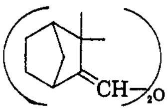
Later, Hückel[4,5] described the conversion, by successive treatment with lead tetraacetate and alkali, of camphene (Ia) to a ketone which by reason of its conversion to camphenic acid (III) and carbocamphenilone (VI) was arbitrarily assigned structure IIb[5] and also given the name R-homocamphenilone. Hückel[5] made no reference to Lipp's work[1] and apparently overlooked a report[6] which recorded the identity of Hückel's ketone[4] with Lipp's "Schmelzketon."



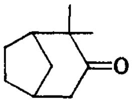
I



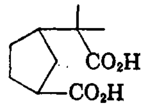
IIa



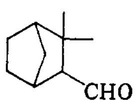
IV



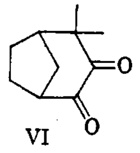
IIb



III



V



VI

Matsubara[7] on the other hand, has recently stated that the "Schmelzketon" and "Oxidationketon" are different and only the latter substance is identical with Hückel's ketone. Moreover, Matsubara reversed the original structural assignments,[1,5] the "Schmelzketon" was shown to be 4,4-dimethylbicyclo[3,2,1]octan-3-one (IIb), while Hückel's ketone and the "Oxidation keton" were characterized as 4,4-dimethylbicyclo[3,2,1]octan-2-one (IIa).

In view of the conflicting statements in the literature and the interesting mechanistic consequences of these reactions we were led to reinvestigate this matter. It soon became apparent that the

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[1] P. Lipp, *J. Prakt. Chem.*, **105**, 50 (1922); P. Lipp, A. Gotzen, and F. Reinartz, *Ann.*, **453**, 1 (1927).

[2] A decision between structures IIa and IIb for the ketone on the basis of its stability toward sodium amide is invalid since both ketones possess active methylene groups adjacent to the carbonyl group and would be expected to form stable salts with sodium amide.

[3] Camphenilanaldehyde was identified by a positive Tollens test and by the melting point of a semicarbazone derivative. It is not clear whether the homogeneity of this derivative was established.

[4] W. Hückel and K. Hartmann, *Ber.*, **70**, 959 (1937).

[5] W. Hückel, *Ber.*, **80**, 41 (1947).

[6] M. Ishidate, N. Inoue, and H. Fukushima, *Bull. soc. chem. Japan*, **17**, 491 (1942).

[7] Y. Matsubara, *Nippon Kagaku Zasshi*, **76**, 1088 (1955); *Chem. Abstr.*, **51**, 17827 (1957). Y. Matsubara and M. Morita, *Nippon Kagaku Zasshi*, **76**, 1101 (1955); *Chem. Abstr.*, **51**, 17831 (1957). Y. Matsubara, *Nippon Kagaku Zasshi*, **78**, 719, 723 (1957); *Chem. Abstr.*, **53**, 21716 (1959).