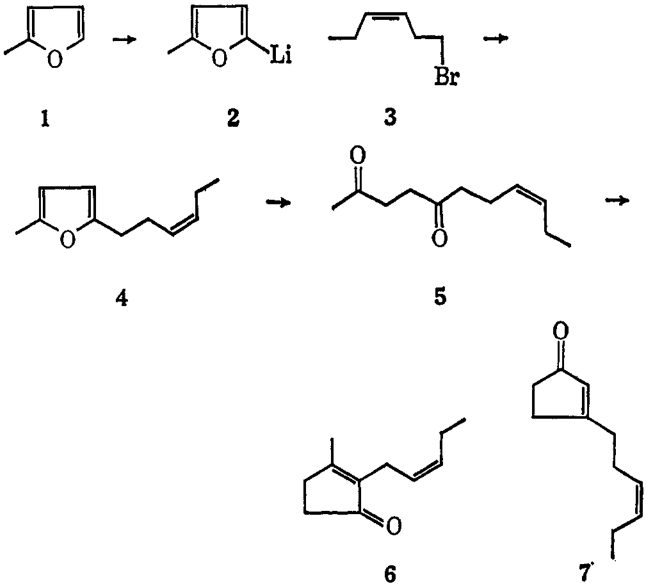
synthesis. In agreement with earlier observations[3,4] the nmr spectrum of crude *cis*-jasmone (**6**) lacks signals attributable to the isomeric cyclopentenone (**7**). The synthesis just described allows the conversion of 2-methylfuran (**1**) to *cis*-jasmone (**6**) in three steps, and in 1-lb runs the over-all yield lies between 40 and 45%.



Experimental Section

cis-**5-Methyl-2-hex-2′-enylfuran** (**4**).—Tetrahydrofuran (30 ml) (distilled over Na) was placed in a 200 ml, three-necked, round-bottom flask fitted with a magnetic stirrer, a dropping funnel, and a condenser. The air was swept out of the flask with dry nitrogen, and a steady flow of the gas was maintained throughout the reaction. Finely cut lithium wire (936 mg, 135 mg-atoms) was introduced, and the suspension was cooled to 0°. A few milliliters of a solution of 5.84 g (63 mmoles) of butyl chloride (freshly distilled) in 25 ml of tetrahydrofuran was added to the stirred suspension to start the reaction. After the reaction had started, as indicated by the appearance of cloudiness (5–10 min), the rest of the butyl chloride solution was added in the course of 1 hr while the cooling bath was maintained at −25 to −30°. Stirring was continued for 1 hr at −25°. 2-Methylfuran (5.18 g, 63 mmoles) (distilled over CaH) was added at −25° over a period of 15 min, and stirring was continued for 4 hr at −15°. *cis*-1-Bromohex-3-ene (**3**) (10.30 g, 63 mmoles) diluted with 10 ml of tetrahydrofuran was then added at −15° in the course of 20 min, and stirring was continued for 1 hr at −15°. The mixture was allowed to stand overnight at room temperature and was subsequently poured on crushed ice, extracted with ether, washed with water and saturated NaCl solution, dried over Na_2SO_4, and evaporated. The remaining oil (9.8 g) was hydrolyzed without purification (distillation of this product was difficult because of foaming). A sample of pure methylhexenylfuran was obtained by collection from vpc (Ucon Polar, 4 ft, 140°). It had $n^{26}\mathrm{D}$ 1.4671; $\nu_{\max}^{\mathrm{CHCl_3}}$ 3100 (w), 3005 (s), 2965 (s), 2925 (s), 2875 (s), 1650 (w), 1615 (m), 1570 (s), 1455 (s), 1385 (m), 1370 (w), 1305 (w), 1215 (m), 1165 (m), 1070 (w), 1025 (s), 1000 (m), 965 (m), 935 (m), and 700 (w) cm^{-1}; nmr ($CDCl_3$), singlet (2 H) at τ 3.95, multiplet (2 H) at τ 4.42, singlet (3 H) at τ 7.68, and triplet (3H) at τ 9.04.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.72; H, 10.26.

cis-**1-Bromohex-3-ene** (**3**).[8]—A mixture of *cis*-hex-3-en-1-ol[6] (5.36 kg, 53.6 moles), dry pyridine (1.19 kg, 15.1 moles), and petroleum ether (bp 30–50°, 2 l.) are placed in a 20-l. three-necked flask fitted with a reflux condenser, drying tube, stirrer, thermometer, and dropping funnel. After the solution had been cooled to −10°, phosphorus tribromide (5.8 kg, 21.5 moles) was added slowly at −10 to 0°. After addition was completed, the reaction mixture was stirred for 2 hr within the same temperature range. Evaporation of the petroleum ether at atmospheric pressure was followed by distillation of the residue at 10 mm. The fraction with bp 45–52° was shaken consecutively with water (1 l.), aqueous sodium carbonate solution (500 ml), and water. After drying over sodium sulfate, the liquid was distilled through a Vigreux column, giving *cis*-1-bromohex-3-ene (**3**) (5.76 kg, 66% yield), bp 40–48° (7 mm), $n^{20}\mathrm{D}$ 1.4726. The *cis*-hex-3-en-1-ol used in this synthesis showed three peaks in a ratio of 1:1:8 on vapor phase chromatography using a Ucon Nonpolar 4-ft column at 110°. The retention times were 14, 24, and 29.5 min, respectively. The major product was *cis*-hex-3-en-1-ol, while the minor product with a retention time of 24 min was probably the corresponding *trans* isomer.

cis-**Undec-8-ene-2,5-dione** (**5**).—Crude methylhexenylfuran (**4**) (9.8 g) was dissolved in 10 ml of glacial acetic acid. Water (5 ml) and aqueous sulfuric acid (0.4 ml, 20%) were added and the mixture was stirred for 3 hr at 120° (bath temperature). The solution was cooled, poured in water, extracted with pentane, washed with saturated $NaHCO_3$ solution and water, dried over Na_2SO_4, and evaporated. The dark brown oil (8.4 g) obtained was distilled through a Claisen head, and the following fractions were collected: (1) bp 34–41° (0.1 mm), 1.247 g; (2) bp 55–70° (0.08 mm), 0.126 g; (3) bp 79–82° (0.05 mm), 4.627 g; and residue, 0.545 g. Fraction 1 consisted mainly of recovered furan (**4**). Fraction 3 was the desired diketone (**5**) containing 7% of an unidentified by-product (*trans* isomer?) revealed by vpc examination on a Ucon Nonpolar 4-ft column at 170°. Redistillation of fraction 3 gave pure diketone **5**: bp 64–66° (0.02 mm); 4.3 g; $n^{26}\mathrm{D}$ 1.4521; $\nu_{\max}^{\mathrm{CHCl_3}}$ 3010 (s), 2970 (s), 2930 (m), 2875 (m), 1712 (s), 1455 (m), 1410 (m), 1365 (s), 1305 (w), 1220 (m), 1175 (m), 1090 (m), and 970 (m) cm^{-1}; nmr ($CDCl_3$) peaks at τ 4.46 (2 H, multiplet), 7.21 (4 H, singlet), 7.74 (3 H, singlet), and 9.01 (3 H, triplet).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.58; H, 10.13.

cis-**Jasmone** (**6**).—A mixture of undecenedione **5** (2.799 g), 7 ml of ethanol, and 25 ml of 0.5 *N* NaOH was allowed to reflux under nitrogen for 5 hr. The mixture was cooled, extracted with pentane, washed with water, dried over Na_2SO_4, and evaporated. The remaining oil (2.522 g) was distilled through a microspinning-band column at 80–100° (bath temperature) and 0.05-mm pressure, giving *cis*-jasmone (**6**) (2.087 g): $\nu_{\max}^{\mathrm{CHCl_3}}$ 2930, 1685, 1645, and 1385 cm^{-1}; nmr ($CDCl_3$), multiplet (2 H) at τ 4.53, doublet (2 H) at τ 6.97, singlet (3 H) at τ 7.86, and triplet (3 H) at τ 8.98; $\lambda_{\max}^{\mathrm{EtOH}}$ 234 mμ (ϵ 13,930). Thin layer chromatography (SiO_2, hexane + 20% ethyl acetate developed with phosphomolybdic acid) indicated two minor impurities with R_f 0.17 and 0.30 (*cis*-jasmone, R_f 0.25). Vapor phase chromatography using a Ucon Nonpolar 4-ft column at 165° revealed two components in a ratio of 8:92 with retention times of 26 and 31.5 min, respectively. The 2,4-dinitrophenylhydrazone was formed in 81% yield, mp 112–115°, and its melting point remained constant at 115–117° after one crystallization from ethanol.

Acknowledgment.—We are indebted to Firmenich and Cie, Geneva, for generous financial support of this investigation.

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[8] We are indebted to Dr. J. A. Jenni, Firmenich and Cie, Geneva, for this procedure.

5,5-Dioxopyrido[2,1-*b*]benzo[*f*]pyridinium Salts[1]

C. K. BRADSHER AND D. F. LOHR, JR.

Department of Chemistry, Duke University,
Durham, North Carolina

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If pyrido[2,1-*b*]benzo[*f*]-1,3-thiazepinium perchlorates (I) are treated with hydrogen peroxide and acetic acid under essentially the conditions that

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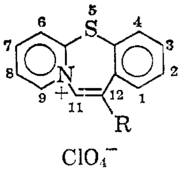
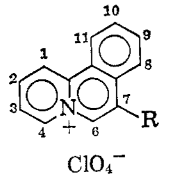
were reported[2] to bring about oxidation of diaryl sulfides to sulfones, dethionylation occurs affording phenanthridizinium (benzo[*a*]quinolizinium) salts (II).[3]



I



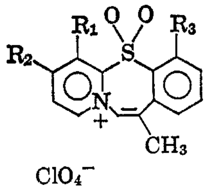
II

The possibility that the intermediates in this transformation may have been sulfones, 5,5-dioxopyrido[2,1-*b*]benzo[*f*]pyridinium salts (III), was rejected[3] on the basis of analogy to known[4] sulfur extrusion reactions as well as on the measurement of the actual consumption of hydrogen peroxide during the oxidation phase of the reaction.[3]

The first 5,5-dioxopyrido[2,1-*b*]benzo[*f*]pyridinium salts (III) have been prepared by the oxidation of the corresponding thiazepinium salt I in a mixture of trifluoroacetic acid and hydrogen peroxide at 64°. The results have been summarized in Table I. An interesting observation was made in connection with the oxidation of 6,12-dimethylpyrido[2,1-*b*]benzo[*f*]-1,3-thiazepinium perchlorate. If a large excess of hydrogen peroxide was used the product was the expected sulfone IIIb, but if the hydrogen peroxide was reduced to only 1.5 moles/mole of sulfide the product (45% yield) was the dethionylation product, 1,7-dimethylphenanthridizinium perchlorate. This is all the more remarkable since earlier efforts to effect dethionylation of the thiazepinium salt by use of hydrogen peroxide–acetic acid had resulted in failure.[5]

TABLE I

5,5-DIOXO[2,1-*b*]BENZO[*f*]-1,3-THIAZEPINIUM PERCHLORATES



III

Compd	R1	R2	R3	H_2O_2,[a] ml	CF_3COOH,[a] ml	64°, hr	Yield, %
a	H	H	H	14.0	3.5	24	80
b	CH_3	H	H	1.0	5.0	8[b,c]	85
c	CH_3	H	CH_3	2.7	6.5	48[b,d]	23[e]
d	H	CH_3	H	0.5	5.0	18	46
e	H	CH_3	CH_3	1.0	5.0	18	40
f	H	H	CH_3	3.0	8.0	24	40

[a] Volumes are per gram of sulfide (II). [b] At 56°. [c] Refluxed an additional 15 hr. [d] Refluxed an additional 6 hr. [e] Some product may have been destroyed during vacuum evaporation of the reaction mixture.

It was found that when 5,5-dioxo-12-methylpyrido[2,1-*b*]benzo[*f*]1,3-thiazepinium perchlorate (IIIa) was heated with acetic acid and hydrogen peroxide under the usual conditions no dethionylation occurred. The possibility that a sulfone is the intermediate in the oxidative dethionylation of benzo[*f*]-1,3-thiazepinium salts (I) is definitely excluded.

One further observation was that the dethionylation is in no way dependent upon the presence of a methyl group at position 12. The parent pyrido[2,1-*b*]benzo[*f*]thiazepinium perchlorate (I, R = H) will undergo dethionylation under the usual conditions to afford phenanthridizinium perchlorate (II, R = H) in 63% yield.

Experimental Section

The elemental analyses were carried out by Ilse Beetz, Mikroanalytisches Laboratorium, Kronach, Germany, or Dr. C. Janssen, Research Laboratorium, Beerse, Belgium. Melting points were taken in capillaries in a Laboratory Devices Mel-Temp block and are corrected. The ultraviolet absorption spectrum was measured in 95% ethanol with a Cary Model 14 spectrophotometer using 1-cm silica cells.

5,5-Dioxo-12-methylpyrido[2,1-*b*]-1,3-thiazepinium Perchlorates (III).—A solution of the thiazepinium salt I in a mixture of trifluoroacetic acid and 30% hydrogen peroxide was heated at 56° (refluxing acetone bath) or 64° (refluxing methanol bath) and the solution cooled. Addition of ether caused the salt to separate. Except as noted (Table II) the product was colorless and was crystallized from methanol and melted with decomposition.

1,7-Dimethylphenanthridizinium Perchlorate.—One gram of 6,12-dimethylpyrido[2,1-*b*]benzo[*f*]-1,3-thiazepinium perchlorate was heated at 56° (refluxing acetone bath) for 8 hr with a mixture containing 5 ml of trifluoroacetic acid and 0.14 ml of 30% hydrogen peroxide, and then refluxed on the steam bath for 8 hr. Addition of ether to the cooled solution precipitated 0.41 g (45%) of 1,7-dimethylphenanthridizinium perchlorate. The analytical sample crystallized from methanol as fine buff-colored needles: mp 175–176.5°; λ_{max}, mμ (log ϵ), 238 (4.48), 274 (sh) (4.37), 279 (4.42), 332 (sh) (3.71), 348 (4.05), and 364 (4.18).

Anal. Calcd for $C_{15}H_{14}ClNO_4$: C, 58.54; H, 4.59; N, 4.55. Found: C, 58.54; H, 4.56; N, 4.38.

Attempt to Effect Dethionylation of 5,5-Dioxo-12-methylpyrido[2,1-*b*]benzo[*f*]-1,3-thiazepinium Perchlorate (IIIa).—A 0.10-g sample of IIIa and 0.20 ml of 30% hydrogen peroxide were dissolved in acetic acid with a minimum amount of warming and the volume was made up to 10 ml by addition of acetic acid. Aliquots were withdrawn before heating and at intervals while the solution was heated at 100°. Observation of the ultraviolet absorption at 355 mμ[3] indicated that no phenanthridizinium salt had been formed.

1-(2-Isonitrosoethyl)-2-phenylthiopyridinium Chloride.—A solution containing 3.0 g of 2-phenylthiopyridine and 1.5 g of chloroacetaldoxime[6] in 5 ml of tetramethylene sulfone was allowed to stand in the refrigerator for 3 weeks. The addition of ethyl acetate precipitated a solid which was washed with ethyl acetate and then crystallized from methanol–ether as buff-colored flakes, mp 179–180°, yield 1.74 g (39%).

Anal. Calcd for $C_{13}H_{13}ClN_2O_2S$: C, 55.61; H, 4.67; N, 9.98. Found: C, 55.71; H, 4.67; N, 10.17.

Pyrido[2,1-*b*]benzo[*f*]-1,3-thiazepinium Perchlorate (I, R = H).—A solution of 0.80 g of 1-(2-isonitrosoethyl)-2-phenylthiopyridinium chloride and 15 ml of 48% hydrobromic acid was refluxed for 12 hr. The acid was removed under vacuum in a rotary evaporator. The residue was dissolved in methanol-water and precipitated by addition of 35% perchloric acid. The precipitate was recrystallized from methanol as pale yellow irregular crystals, mp 189–191°.

Anal. Calcd for $C_{13}H_{10}ClNO_4S$: C, 50.08; H, 3.23; N, 4.49. Found: C, 50.39; H, 3.26; N, 4.87.

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[4] H. H. Szmant, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p 163.

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[6] R. W. L. Kimber and J. C. Parham, *ibid.*, **28**, 3205 (1963).

TABLE II

OXIDATION PRODUCTS

III	Mp, °C	Form	Formula	C, %		H, %		N, %	
				Calcd	Found	Calcd	Found	Calcd	Found
a	252–254	*a*	$C_{14}H_{12}ClNO_6S$	47.00	47.07	3.38	3.46	3.92	3.99
b	226–227[b]	*a*	$C_{15}H_{14}ClNO_6S$	48.45	48.41	3.80	3.78	3.77	3.71
c	239–241[c]	*d*	$C_{16}H_{16}ClNO_6S$	49.81	49.97	4.18	4.12	3.63	3.80
d	181–183[c]	*d*	$C_{15}H_{14}ClNO_6S$	48.45	48.52	3.80	3.70	3.77	3.90
e	228–230	*d*	$C_{16}H_{16}ClNO_6S$	49.81	49.89	4.18	4.25	3.63	3.71
f	268–270[c]	*a*	$C_{15}H_{14}ClNO_6S$	48.45	48.63	3.80	3.94	3.77	4.08

[a] Needles. [b] Crystallized from acetonitrile–methanol. [c] Evacuated capillary. [d] Irregular.

Phenanthridizinium Perchlorate (II, R = H).—A solution of 0.8 g of pyrido[2,1-*b*]benzo[*f*]-1,3-thiazepinium perchlorate (I), 1.0 ml of 30% hydrogen peroxide, and 10 ml of glacial acetic acid was heated at 56° for 18 hr, then at 100° for 12 hr. From the cooled solution a buff-colored solid was precipitated by addition of ether. Recrystallization of the solid afforded 0.43 g (63%) of colorless needles, mp 193–195°. A recrystallized sample melted at 197–198° (lit.[6] mp 197°), had the expected composition, and did not depress the melting point of an authentic sample[6] of phenanthridizinium perchlorate.

Synthesis of Menthenone and Dihydro Rose Oxide

KENT C. BRANNOCK AND HERMAN E. DAVIS

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee

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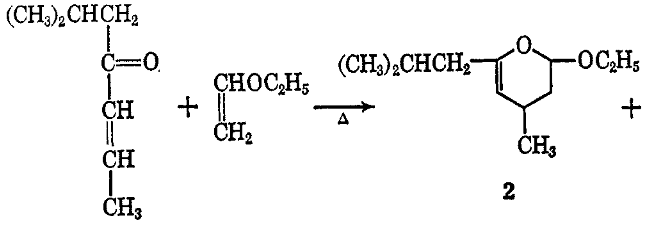
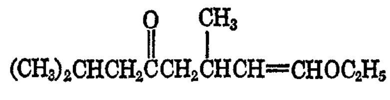
We wish to report a new and convenient synthetic route to menthenone (2-isopropyl-5-methyl-2-cyclohexene-1-one) (7) and dihydro rose oxide (tetrahydro-2-isobutyl-4-methylpyran) (5).[1–4] The condensation of acetaldehyde with methyl isobutyl ketone[5] gave a mixture of the *cis* and *trans* isomers of 6-methyl-2-hepten-4-one (1). The Diels–Alder reaction of 1 with ethyl vinyl ether at elevated temperatures gave a mixture of the *cis* and *trans* isomers of 2-ethoxy-3,4-dihydro-6-isobutyl-4-methyl-2H-pyran (2) along with the lesser amounts of the *cis* and *trans* isomers of 8-ethoxy-2,6-dimethyl-7-octen-4-one (3). The *cis* and *trans* assignments were based on the magnitude of the -HC=CH- coupling constants in the nmr spectra.[6]



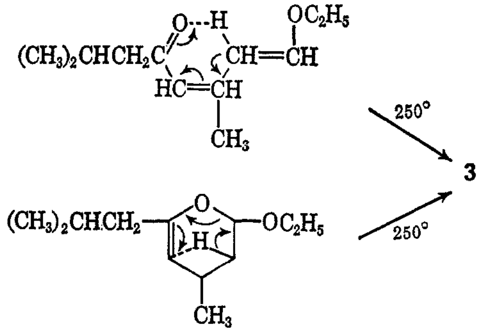
1



$$(CH_3)_2CHCH_2\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{CH_3}{|}}{C}HCH{=}CHOC_2H_5$$

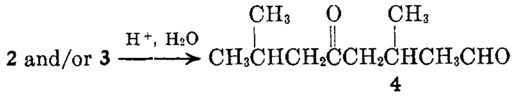
3

As the temperature at which the Diels–Alder reaction was carried out was increased, the relative amount of 3 increased. It is not clear whether 3 was formed directly from the reactants or whether it was derived from 2 by rearrangement. It is possible to explain the formation of 3 by either route as shown. We did show, however, that 2 on heating at 250° was largely converted to 3.



2

Acid-catalyzed hydrolysis of both 2 and 3 gave 3,7-dimethyl-5-oxooctanal (4), which on treatment with base gave methenone (7).



$$2 \text{ and/or } 3 \xrightarrow{H^+,\ H_2O} CH_3\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{CH_3}{|}}{C}HCH_3CHO$$

4

The hydrogenation of 4 over a supported nickel catalyst gave a mixture of the *cis* and *trans* isomers of dihydro rose oxide (5) as the major product and 3,7-dimethyl-1,5-octanediol (6) as the minor product. The use of a copper chromite catalyst gave the diol as the major product and 5 as the minor product. The diol was readily converted to a mixture of the *cis* and *trans* isomers of 5 by refluxing it in a solvent in the presence of a catalytic amount of an acid.

Experimental Section

6-Methyl-2-hepten-4-one (1).—A mixture of acetaldehyde (132 g, 3 moles) and 4-methyl-2-pentanone (400 g, 4 moles) was cooled in an ice bath and added over a 2-hr period to a solution of potassium hydroxide (11 g) in isopropyl alcohol (300 ml) and 4-methyl-2-pentanone (1200 g, 12 moles). The reaction mixture was stirred and kept at 10–15° during and for 15 min after the addition. Ethyl ether (300 ml) was added, and the solution was washed with water to remove potassium hydroxide.

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