nally, substituted 2,3-dihydropyrazine 1,4-dioxides offer intriguing possibilities for biologic investigation, since it is know that different *N*-oxides such as nicotinamide *N*-oxide, various purine *N*-oxides, 4-nitroquinoline *N*-oxide, and chlordiazepoxide function variously as biological oxidants, antimetabolites, oncogenic agents, and tranquilizers.[19]

Experimental Section[20]

2,5-Dihydroxy-3,6-diphenyl-5,6-dihydropyrazine 1,4-Dioxide (4).—To a solution of 4.57 g (23.4 mmol) of phenylglyoxal dimethyl acetal oxime[4] (**4**) in 22.5 ml of glyme was added 22.5 ml of a pH 3.5 buffer (1 *N* acetic acid, 0.1 *N* sodium acetate; the oxime was insoluble in this buffer alone or in aqueous methanol). This homogeneous solution was stirred and refluxed. Tlc (Eastman alumina sheets no. 6063, acetone as eluent) indicated a slow reaction rate and 24 hr was required for 1 (R_f 0.49) to disappear and to be replaced by a new compound (R_f 0.22). The solution was then cooled to room temperature, and the solvents were partially removed under reduced pressure (water aspirator). The resulting orange oil and pale yellow liquid was treated with 10 ml of water and extracted with ethyl acetate (three 50-ml portions). These extracts were combined and dried over sodium sulfate; the solvent was then removed to give 3.5 g of an orange oil that crystallized into colorless prisms (perhaps the dimerization occurs at this stage). Recrystallization of this material from ethyl acetate–benzene gave 1.98 g (13.3 mmol, 57%) of colorless prisms. A second crop of 0.50 g (3.4 mmol, 14%) was obtained by concentrating the mother liquor. Infrared spectra run on these two crops of crystals were identical with one another and with that of the analytical sample. This latter sample was prepared by recrystallizing the material twice from ethyl acetate–benzene to give colorless prisms: mp 114.5–117.5°; uv max (MeOH) 221.0 nm (log ϵ 4.31) and 249.0 (4.00, shoulder); ir (KBr) 3225, 3050, 2935, 2875, 2815, and 1595 cm^{-1}; 100-MHz nmr (DMSO-d_6) τ −1.82 (singlet, 0.83 H),* 1.60–1.85 (multiplet, 1.84 H), 2.21(doublet, 1.01 H, J = 9.0 Hz),* 2.42–2.64 (multiplet), 2.73 (singlet, 8.66 H together with previous multiplet), 3.68 (doublet of doublets, 0.84 H, J = 9.0 and 3.0† Hz), and 3.84 (doublet, 0.78 H, J = 3.0 Hz).

Anal. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73. Found: C, 64.49; H, 4.85.

Phenylglyoxal 2-Oxime (2).—After 745 mg (2.50 mmol) of of 2,5-dihydroxy-3,6-diphenyl-5,6-dihydropyrazine 1,4-dioxide (**4**) was dissolved in 1.5 ml of dimethyl sulfoxide (which previously sat over 5 A molecular sieves for 12 hr), dry nitrogen was blown over the clear solution before it was capped. The stirred reaction solution was then heated to 44–46° for 25 hr. The solvent was then removed by freeze-drying. The resultant oil had ir (KBr) 3125 and 1698 cm^{-1}. As ample of **4** decomposed in a similar manner in DMSO-d_6 had 100-MHz nmr τ −3.20 (singlet, 0.98 H),* 0.35 (singlet, 1.01 H), and 2.58 (singlet, 5.02 H). The material obtained was at least 95% pure by nmr and was not purified further but used immediately in the preparation of **3**.

Peaks indicated by an asterisk disappear on addition of D_2O; that indicated by dagger collapses to a doublet (J = 3.0 Hz).

Registry No.—**2**, 32538-02-6; **4**, 32538-03-7.

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(19) The role of *N*-oxides in metabolism and the biologic properties of various types of *N*-oxides have been reviewed: M. H. Bickel, *Pharm. Rev.*, **21** (4), 325 (1969).

(20) The infrared spectra were taken on a Perkin-Elmer Model 337 spectrophotometer. Ultraviolet spectra were recorded using a Cary Model 14 spectrophotometer using matched 1-cm quartz cells. Nmr spectra were run by Mr. Joseph Ahnell using a Varian HA-100 spectrometer. Melting points were taken using a Kofler hot-stage microscope and are uncorrected.

A New Synthesis of *cis*-Jasmone

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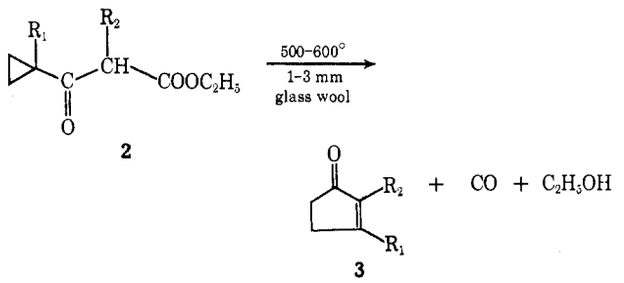
The synthesis of *cis*-jasmone (**1**) has received considerable attention in recent years.[1-10] This contribution stems from our recent discovery of the thermal rearrangement of 3-cyclopropyl-3-oxopropanoates (**2**) to 2-cyclopentenones (**3**).[11] *cis*-Jasmone (29–32% overall) and the acetylenic analog **6** (39% overall) were prepared as shown in Scheme I.[12]



Experimental Section

Melting points were determined on a Mel-Temp apparatus, and neither melting points nor boiling points were corrected. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. Preparative gas–liquid chromatography (glpc) was done on a Varian-Aerograph Model A90-P3 thermal conductivity machine, and retention times were compared on a Varian Aerograph Model 1200 flame ionization machine; individual conditions are noted below. Infrared data were obtained with a Perkin-Elmer Model 237B grating spectrophotometer, and nmr spectra were recorded on a Varian Model A-60 A nmr spectrometer. Mass spectra were done on a Varian-Atlas Model CH-7 (modified) mass spectrometer by Professor R. R. Engel (Queens). Pyrolyses were done with a Hevi-Duty Electric Company Type 77-T (600 W, "Multi-Unit") tube oven.

Ethyl 2-(1′-Methylcyclopropanecarbonyl)-4-heptynoate (5).—Keto ester **5** was prepared by a standard alkylation sequence[11] using 5.02 g (0.105 mol) of 50% sodium hydride dispersion in mineral oil, 17.02 g (0.100 mol) of **2**,[13] and 10.25 g (0.100 mol)

(1) G. Büchi and B. Egger, *J. Org. Chem.*, **36**, 2021 (1971).

(2) G. Stork, G. L. Nelson, F. Rouessac, and O. Gringore, *J. Amer. Chem. Soc.*, **93**, 3091 (1971).

(3) J. Ficini, J. D. Angelo, J. P. Genêt, and J. Noiré, *Tetrahedron Lett.*, 1569 (1971).

(4) L. Crombie, P. Hemesley, and G. Pattenden, *J. Chem. Soc. C*, 1024 (1969).

(5) M. Fetizon and J. Schablar, *Fr. Ses Parfums*, **12**, 330 (1969).

(6) T. Akiyama, *Yugagaku*, **17**, 217 (1968); *Chem. Abstr.*, **69**, 45980k (1968).

(7) K. Sisido, Y. Kawasima, and T. Isida, *Perfum. Essent. Oil Rec.*, **57**, 364 (1966).

(8) T. Yoshida, A. Yamaguchi, and A. Komatsu, *Agr. Biol. Chem.*, **30**, 370 (1966).

(9) J. Schablar (Synarome), German Patent 1,959,513 (1970); *Chem. Abstr.*, **73**, 44996r (1970).

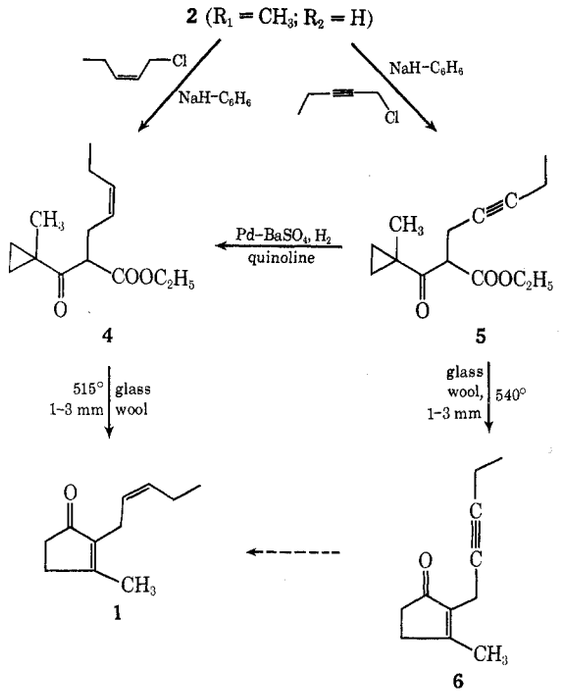
(10) P. Bedoukian, *Perfum. Essent. Oil Rec.*, **57**, 495 (1966); this is a review article with 20 references.

(11) W. F. Berkowitz and A. A. Ozorio, *J. Org. Chem.*, **36**, 3787 (1971).

(12) The Alkyne **6** has previously been partially hydrogenated to **1** in 72.6% yield.[7]

(13) Ketone **2** was prepared by carbethoxylation of methyl methylcyclopropyl ketone in 80% yield.[11] The starting ketone was obtained either from Aldrich Chemical Co., Cedar Knolls, N. J., or by the procedure of N. L. Goldman, *Chem. Ind. (London)*, 1024 (1963), which starts with α-acetyl-α-methyl-γ-butyrolactone.

SCHEME I



of 1-chloro-2-pentyne[14] (freshly distilled, bp 122.5°) in 400 ml of dry benzene. Work-up gave 25.75 g of amber oil which was fractionated on an 18-in. Teflon annular spinning band column and gave 3.67 g of **2** and 12.68 g of keto ester **5** (68.5% based on unrecovered **2**).

A portion of the product was redistilled for analysis: bp 86.5° (0.005 mm); ir (CCl_4) 5.71 (ester CO) and 5.89 μ (ketone CO) (no peak was observed in the region 4.5–5.0 μ); nmr ($CDCl_3$) δ 4.18 (q, 2, J = 7.2 Hz, $-COOCH_2CH_3$), 3.82 (t, 1, J = 7.5 Hz, $-COCHRCOO-$), 2.65 (d, t, 2, J = 7.5, 2.2 Hz, $-CHCH_2C{\equiv}C-$), 1.85–2.4 (m, 2, $-C{\equiv}CCH_2CH_3$), 1.40 (s, 3, $>CCH_3$), 1.25 (t, 3, J = 7.2 Hz, $-COOCH_2CH_3$), 1.07 (t, 3, J = 7.5 Hz, $C{\equiv}CCH_2CH_3$), 0.6–1.1 (m, 4, cyclopropyl CH_2); mass spectrum (70 eV) m/e 236 (molecular ion).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.02; H, 8.59.

Ethyl 2-(1′-Methylcyclopropanecarbonyl)-*cis*-4-heptenoate (4). Method A.—Keto ester **4** was prepared by a standard alkylation sequence[11] using 0.80 g (0.0165 mol) of a 50% dispersion of sodium hydride in mineral oil, 2.549 g (0.0150 mol) of **2**,[13] and 2.406 g (0.023 mol) of *cis*-1-chloro-2-pentene[15] in 55 ml of dry benzene. Work-up gave 3.5 g of pale yellow oil which was fractionated on an 8-in. stainless steel spinning band column and gave 1.796 g (50%) of **4**, bp 68.5–72° (0.005 mm), which was substantially pure by thin layer chromatography (benzene, silica gel G).

Method B.—Keto ester **4** was also prepared by partial hydrogenation of 7.09 g (0.030 mol) of **5** in a mixture of 75 ml of absolute ethanol, 150 mg of synthetic quinoline, and 150 mg of 5% palladium on barium sulfate (Engelhard Industries) at 765 mm and room temperature.[16] Hydrogen uptake (745 ml, 101%) ceased abruptly after 33 min. The reaction mixture was filtered through Celite which was washed thoroughly with ethanol. The filtrate and ethanol washes were combined and concentrated under reduced pressure to give 7.19 g of green oil. The oil was dissolved in 75 ml of benzene, washed twice with cold dilute hydrochloric acid and once with saturated aqueous sodium bicarbonate, then dried over magnesium sulfate and concentrated under reduced pressure to give 6.74 g of green oil. This was fractionated as before, giving 5.811 g (83%) of **4**, bp 67–75° (0.005 mm), also pure by thin layer chromatography.

The materials prepared by methods A and B were shown to be identical by comparison of thin layer chromatography R_f values and infrared spectra. Keto ester **4** exhibited ir (CCl_4) 5.71 (ester CO) and 5.89 μ (ketone CO) (no peak was observed in the region 4.5–5.0 μ); nmr (CCl_4) δ 5.21 (symmetrical m, 2, consistent with $CH_{2a}CH_x{=}CH_yCH_{2b}$ with $\Delta\nu$ = 10.5 Hz, J_{xy} = 10 Hz, $J_{ax,by}$ = 6.5 Hz, $J_{ay,bx}$ = 1 Hz), 4.07 (q, 2, J = 7 Hz, $COOCH_2CH_3$), 3.50 (t, 1, J = 7.5 Hz, $-COCHRCOO-$), 2.46 (broadened triplet, 2, J = 6.5 Hz, $-CHCH_2C{=}$), 2.05 (broadened pentuplet, 2, J = 7 Hz, $={CCH_2CH_3}$), 1.35 (s, 3, $>CCH_3$), 1.23 (t, 3, J = 7 Hz, $COOCH_2CH_3$), 0.95 (t, 3, J = 7.5 Hz, $={CCH_2CH_3}$), 0.5–1.0 (m, 4, cyclopropyl CH_2); mass spectrum (70 eV) m/e 238 (molecular ion).

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.73; H, 9.44.

***cis*-Jasmone (1).**—Pyrolysis[11] of 1.297 g (0.00545 mol) of **4** at 515° and 1–5 mm (glass wool packing) gave 1.067 g of mobile yellow oil which was fractionated on an 8-in. stainless steel spinning band column and gave 0.512 g (57%) of **1**, bp 52.5° (0.05 mm). A repeat with 4.863 g (0.0204 mol) of **4** at 535° and 1–5 mm (glass wool packing) gave 3.416 g of crude **1** which, after distillation as before, gave 1.785 g (53%) of **1**. Further purification by preparative glpc[17] gave material which was identical by glpc,[18] ir, nmr, and mass spectrum analyses with authentic material (kindly provided by Professor Stork).

3-Methyl-2-(2′-pentynyl)-2-cyclopentenone (6).—Pyrolysis[11] of 3.516 g (0.0149 mol) of **5** at 540° and 0.5–2 mm (glass wool packing) gave 2.725 g of crude **6** which was distilled on an 8-in. stainless steel spinning band column and gave 1.260 g (53%) of **6**, bp 79° (1.5 mm). A portion of this material was further purified by preparative glpc,[17] giving pure **6**: ir (CCl_4) 5.86 (conjugated CO) and 6.04 μ (C=C) (no peak was observed in the region 4.5–5.0 μ); nmr (CCl_4) δ 2.99 (br s, 2, $={CCH_2C{\equiv}}$), 2.83–1.83 (m, 9), 2.21 (br s, 3, ring CH_3), 1.12 (t, t, 3, J = 7, 0.5 Hz, $={CCH_2CH_3}$); mass spectrum (70 eV) m/e 162 (molecular ion). The 2,4-dinitrophenylhydrazone derivative had mp 164–165° (lit.[7] mp 166°).

Registry No.—**1**, 4907-07-7; **4**, 32979-72-9; **5**, 32969-89-4; **6**, 7051-37-8.

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(14) Kindly provided by Dr. W. I. Taylor of International Flavors and Fragrances, Union Beach, N. J.

(15) The alkenyl halide was the gracious gift of Professor G. Stork, Chemistry Department, Columbia University, New York, N. Y.

(16) The procedure of D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, **78**, 2518 (1956).

(17) A 20 ft × 3/8 in. column packed with 30% SE-30 silicone gum rubber on Chromosorb P at 175° was used.

(18) A 5 ft × 1/8 in. column packed with 20% SE-30 silicone gum rubber on Chromosorb P at 180° was used.