

TABLE I
 RATE DATA FOR $K[RCONOCOC_6H_5]$ AND PHYSICAL CONSTANTS FOR $RCONHOCOC_6H_5$

R	10 ⁴ k, ^a min ⁻¹	Relative rates ^{b,c}	Mp, °C	
			Obsd ^d	Lit. ^e
Phenyl	7.06	5.12	163.5–164.5	161–162, 163–164
<i>p</i> -Methylphenyl	11.8	3.29	159–160	161–162, 163–164
<i>m</i> -Methylphenyl	9.47	4.38	121–123	123–125
<i>o</i> -Methylphenyl	7.05	0.198	106–107	108–109

^a First-order rate constant at $30 \pm 0.02^\circ$ in DMSO; average of four or five runs, average deviation from mean less than 3.4% (except R = *o*-methylphenyl, two runs, 4.5%). ^b At 30° ; rate in DMSO/rate in 0.1 N NH_3 . ^c Rates in ammonia solution are from ref 2 and 3. ^d Corrected. ^e References 2 and 3.

 TABLE II
 EQUIVALENT CONDUCTANCE OF $K[p-CH_3C_6H_4CONOCOC_6H_5]$
 IN DMSO

Concn, <i>M</i>	Equip conductance, ^a cm ² equiv ⁻¹ ohm ⁻¹
0.0250	15.1
0.0125	16.6
0.00833	17.9
0.00500	21.2
0.000536	24.8

^a At $25.0 \pm 0.1^\circ$.

Experimental Section

The benzoyl acylhydroxamates were prepared by adaptation of previous methods^{2,3,6} as were the potassium salts^{7,8} used in the rate measurements. Melting points are listed in Table I. The colorimetric method previously developed⁸ for following the rate of disappearance of the alkali hydroxamates was adapted for the present system. Kinetic runs were made to approximately 75% complete reaction, first-order kinetics being observed in all cases. Initial concentrations of salts were 0.0248 to 0.0258 *M* (one run for R = phenyl, 0.0168 *M*). Rate constants were calculated as before,⁸ except that the slopes of the graphs were evaluated by the least-squares method. The dimethyl sulfoxide was dried over barium oxide and distilled at reduced pressures.

The conductance measurements were made with a Serfass conductivity bridge using a dip cell with platinum black coated electrodes calibrated against 0.100 *N* potassium chloride. A potassium benzoyl *p*-methylbenzhydroxamate solution in dimethyl sulfoxide (0.0250 *M*) was prepared. Conductance measurements were then made as rapidly as possible on this solution and on diluted solutions. A second set of conductance measurements were made beginning with a 0.00500 *M* solution.

***N*-*n*-Butyl-*N'*-phenylurea.**—Potassium benzoyl benzhydroxamate (0.73 g, 0.0026 mole) and *n*-butylamine (3.00 g, 0.0411 mole) were added to dimethyl sulfoxide (30 ml), and the resulting solution was maintained at 30° for sufficient time to ensure complete rearrangement of the hydroxamate. The solution was evaporated to dryness *via* an air current and the resulting residue was extracted with hot benzene. *N*-*n*-Butyl-*N'*-phenyl urea was crystallized from the benzene: mp 125 – 128° , lit.⁹ mp 129 – 130° , 83% crude yield. The melting point and infrared spectrum of the urea were the same as those of a sample prepared independently from phenyl isocyanate and *n*-butylamine.

Acknowledgment.—We wish to express our thanks to the National Science Foundation for financial support of this work and to Dr. R. H. Anderson for use of his least-squares computer program.

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An Efficient Synthesis of *cis*-Jasmone

G. BÜCHI AND H. WÜEST

Department of Chemistry, Massachusetts Institute of Technology,
 Cambridge, Massachusetts

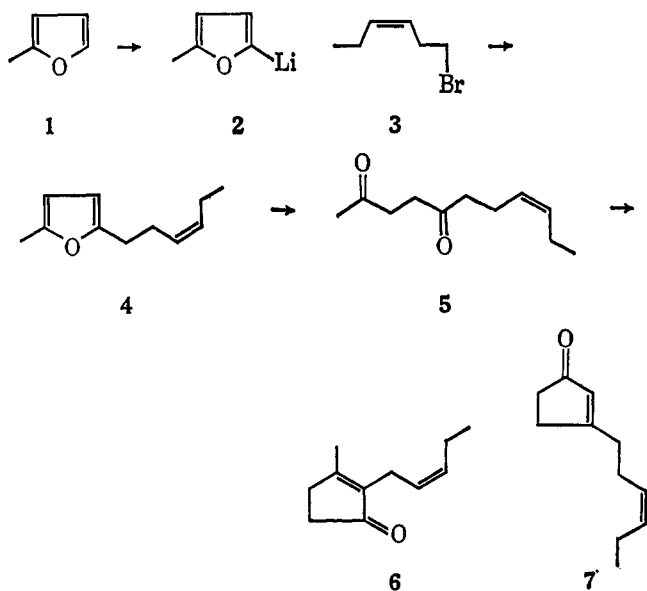
Received October 18, 1965

The flower oils of several varieties of *Jasminum* contain the ketone *cis*-jasmone (6). Although *cis*-jasmone constitutes less than 5% of these essential oils, it is indispensable in the reproduction of jasmine fragrance from substances of synthetic origin. An early synthesis¹ yielded mainly *trans*-jasmone with less desirable olfactory properties. Total syntheses of authentic *cis*-jasmone (6) have been described,^{2–4} but the routes employed are somewhat lengthy and the substance remained relatively inaccessible. We have now developed a synthesis which allows the production of *cis*-jasmone (6) on a large scale and in good over-all yield.

Metalation of 2-methylfuran (1) with butyllithium in tetrahydrofuran solution yielded 2-lithio-5-methylfuran (2)⁵ which on condensation with *cis*-1-bromohex-3-ene (3), prepared from *cis*-hex-3-en-1-ol⁶ gave *cis*-5-methyl-2-hex-2'-enylfuran (4) whose nmr spectrum ($CDCl_3$) had resonances at τ 3.95 (2 H, singlet), 4.42 (2 H, multiplet), 7.68 (3 H, singlet), and 9.04 (3 H, triplet, $J = 7$ cps). Purification of this intermediate was not necessary and hydrolysis of the crude product in aqueous acetic acid containing some sulfuric acid furnished the known diketone⁴ 5 with nmr absorptions (in $CDCl_3$) at τ 4.46 (2 H, multiplet), 7.21 (4 H, singlet), 7.74 (3 H, singlet), and 9.01 (3 H, triplet, $J = 7$ cps). Finally, base-catalyzed cyclization of the diketone 5, using Hunsdiecker's conditions, gave *cis*-jasmone (6), $\nu_{max}^{CHCl_3}$ 1685 and 1645 cm^{-1} ; λ_{max}^{EtOH} 234 $m\mu$ (ϵ 13,930), further characterized by a 2,4-dinitrophenylhydrazone, mp 115 – 117° .⁷ An infrared spectrum of synthetic *cis*-jasmone (6) was identical with that of an authentic sample.³ Careful gas chromatographic analysis of the final product showed that the *cis/trans* ratio in synthetic jasmone is not lower than that in the 1-bromohex-3-ene (3) used demonstrating that *cis-trans* isomerization does not accompany the final stages of the

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synthesis. In agreement with earlier observations^{3,4} the nmr spectrum of crude *cis*-jasmonone (6) lacks signals attributable to the isomeric cyclopentenone (7). The synthesis just described allows the conversion of 2-methylfuran (1) to *cis*-jasmonone (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 Na₂SO₄, 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_D^{20} 1.4671; $\nu_{\max}^{\text{CHCl}_3}$ 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 (CDCl₃), 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 C₁₁H₁₈O: C, 80.44; H, 9.83. Found: C, 80.72; H, 10.26.

***cis*-1-Bromohex-3-ene (3).**²—A mixture of *cis*-hex-3-en-1-ol² (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 reac-

tion 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_D^{20} 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 NaHCO₃ solution and water, dried over Na₂SO₄, 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 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_D^{20} 1.4521; $\nu_{\max}^{\text{CHCl}_3}$ 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 (CDCl₃) 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 C₁₁H₁₈O₂: C, 72.49; H, 9.96. Found: C, 72.58; H, 10.13.

***cis*-Jasmonone (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 Na₂SO₄, 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*-jasmonone (6) (2.087 g): $\nu_{\max}^{\text{CHCl}_3}$ 2930, 1685, 1645, and 1385 cm⁻¹; nmr (CDCl₃), 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; $\lambda_{\max}^{\text{EtOH}}$ 234 m μ (ϵ 13,930). Thin layer chromatography (SiO₂, hexane + 20% ethyl acetate developed with phosphomolybdic acid) indicated two minor impurities with R_f 0.17 and 0.30 (*cis*-jasmonone, 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.

5,5-Dioxypyrido[2,1-*b*]benzo[*f*]pyridinium Salts¹

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

Department of Chemistry, Duke University,
Durham, North Carolina

Received November 1, 1965

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

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

(1) This research was made possible by a research grant, NSF-G 109901, of the National Science Foundation.