9. J.-F. Biellman and H. Liesenfelt. Bull. Soc. Chim. Fr. 4029 (1966).
10. O. Mancera, G. Rosenkranz, and F. Sondheimer. Naturwiss. **43**, 17 (1956).
11. B. Camerino, B. Patelli, and R. Sciaky. Tetrahedron Lett. 554 (1961).
12. J.-F. Biellman and M. Rajic. Bull. Soc. Chim. Fr. 1945 (1961).
13. L. L. Chinn. Selection of oxidants in synthesis. Marcel Dekker Inc., New York, N.Y. 1971. pp. 34–35.
14. D. N. Kirk and M. P. Hartshorn. Steroid reaction mechanisms. Elsevier, New York, N.Y. 1968. p. 178.
15. J. O. Hawthorne, K. A. Schowalter, A. W. Simon, M. H. Wilt, and M. S. Morgan. Oxidation of organic compounds. Vol. 1. *Edited by* R. F. Gould. American Chemical Society Publications, Washington, D.C. 1967. p. 203.
16. D. Amar, V. Permutti, and Y. Mazur. Tetrahedron, **25**, 1717 (1969).
17. C. Djerassi and M. Gorman. J. Am. Chem. Soc. **75**, 3704 (1953).
18. H. Hauptmann. J. Am. Chem. Soc. **69**, 562 (1947).
19. (*a*) J. C. Collins, W. W. Hess and F. J. Frank. Tetrahedron Lett. 3363 (1968); (*b*) *cf.* R. Ratcliffe and R. Rodeborst. J. Org. Chem. **35**, 4000 (1970).
20. C. W. Shoppee, R. E. Lack, and B. C. Newman. J. Chem. Soc. 3388 (1964).
21. J. P. Dusza and W. Bergmann. J. Org. Chem. **25**, 79 (1960).
22. J. F. Eastham and R. Teranishi. Org. Synth. Coll. Vol. IV, 192 (1963).
23. M. Fetizon and M. Golfier. Bull. Soc. Chim. Fr. 167 (1963).
24. C. Djerassi, R. R. Engle, and A. Bowers. J. Org. Chem. **21**, 1547 (1956).
25. H. Werbin, W. Ewald, and I. L. Chaikoff. Biochim. Biophys. Acta, **130**, 556 (1966).
26. J. B. Jones and R. Grayshan. Can. J. Chem. **50**, 1414 (1972).

Synthesis of *cis*-Jasmone and Dihydrojasmone

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cis-Jasmone and dihydrojasmone have been synthesized from levulonitrile by a four-step reaction sequence. Application of ceric ammonium nitrate for dethioketalization is described.

La Jasmone *cis* et la dihydrojasmone ont été synthétisées à partir du levulonitrile selon une séquence réactionnelle en quatre étapes. L'application du nitrate d'ammonium cérique pour la déthiocétalisation est décrite.

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cis-Jasmone (**1***a*) and dihydrojasmone (**1***b*) have commanded undiminished endeavors in their syntheses (1, 2) over the past three decades, owing to their importance in the perfume industry and because they often serve as testing targets pertinent to development of γ-diketone and cyclopentenone syntheses. We wish to report a simple synthesis of both of these natural products which may have certain merits since the starting materials are relatively inexpensive and easily accessible.

It appeared to us that a levulinic acid derivative would be an attractive starting point in view of the presence of differential bifunctionality in the correct positions of the carbon skeleton, amenable to the elaboration of *cis*-jasmone and dihydrojasmone precursors. In this context, levulonitrile was selected because its ketone function can be masked temporarily, while the cyano group is being transformed into another carbonyl by the action of an organometallic reagent.

Thus, levulonitrile (3) was converted to the ethylenethioketal **2** in good yield. Reaction of **2** with appropriate Grignard reagents followed by acid hydrolysis of the resulting imine complexes on work-up furnished **3***a* and *b* respectively.[1] To facilitate isolation of the products in

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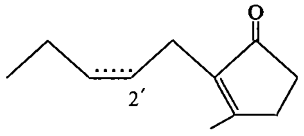
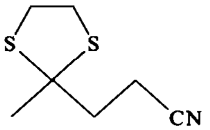
[1] The use of the ethyleneketal protecting group for levulonitrile was found to be unsuitable.

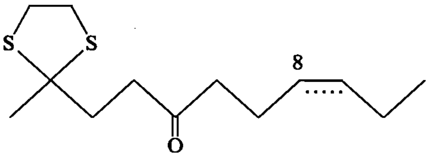


1

a $\Delta^{2'}$
b saturated

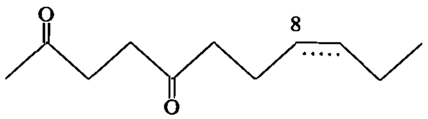


2



3

a Δ^{8}
b saturated



4

a Δ^{8}
b saturated

the scale we used, Girard T derivatives were prepared; however, this technique would not be required in larger preparations where fractional distillation would be expedient and sufficient.

The next task called for removal of the dithioketal group, and this was performed either by utilizing the elegant procedure recently disclosed by Wynberg and his collaborators (4), or by ceric ammonium nitrate oxidation (5) in aqueous acetonitrile, a novel and efficacious method which could be of wide applicability to regenerate carbonyl compounds from the corresponding 2-substituted 1,3-dithiolanes and 1,3-dithianes under very mild conditions. In our hands, this latter convenient process was found to be superior to Wynberg's method for dithioketal cleavage involved in the synthesis reported herein. Cyclization of **4***a*, *b* to *cis*-jasmone and dihydrojasmone was effected by alkali according to the literature (1*k*). These synthetic compounds were shown to be identical with authentic specimens of the natural products by spectroscopy (i.r., n.m.r.) and chromatography (t.l.c.).

The approach described in this paper defines a potentially useful general fabrication of the γ-diketone synthon, since homologues of levulonitrile can be prepared readily by the cyanoethylation of nitroalkanes followed by the Nef reaction (3).

Experimental

I.r. spectra were recorded on a Perkin-Elmer 710 Spectrophotometer using methylene chloride as solvent. N.m.r. spectra were taken on a Varian A56/60A spectrometer in the solvent indicated and with tetramethylsilane as internal standard. Mass spectra were obtained from a Finnigan 1015 mass spectrometer and high resolution mass spectra were measured with an AEI MS9 Spectrometer (University of Alberta) operating at 70 eV. Solutions were dried over anhydrous magnesium sulfate.

Levulonitrile Ethylenethioketal

A mixture of levulonitrile (4.20 g), ethanedithiol (4.0 ml), and boron trifluoride etherate (1.0 ml) and anhydrous magnesium sulfate (5 g) in benzene (40 ml) was allowed to stand at ambient temperature for 2 days. It was then diluted with benzene (100 ml), washed with 2% potassium hydroxide, dried, and evaporated *in vacuo*. Levulonitrile ethylenethioketal (6.53 g, 88.2%) was obtained as a clear oil, b.p. 78–80° (0.6 Torr). I.r. ν 2240 cm^{-1}; n.m.r. (CCl_4) τ 6.68 (4H, s), 7.56 (4H, sym. m), 8.22 (3H, s); mass (M^+): calcd. for $C_7H_{11}N^{32}S$, 173.0334; found, 173.0330.

Anal. Calcd. for $C_7H_{11}NS$: C, 48.5; H, 6.4; N, 8.1; S, 37.0. Found: C, 48.7; H, 6.2; N, 8.2; S, 36.8.

cis-Undec-8-ene-2,5-dione Monoethylenethioketal (*3a*)

To a Grignard reagent prepared from *cis*-1-bromohex-3-ene (1.62 g) and magnesium turnings (240 mg) in dry ether (20 ml) was introduced a solution of levulonitrile ethylenethioketal (173 mg) in ether (5 ml). After stirring at room temperature for 18 h, the reaction mixture was run into dilute hydrochloric acid and extracted with ether. The crude product was treated directly with Girard T reagent (200 mg) in methanol (10 ml) containing glacial acetic acid (0.2 ml) for 3 h under reflux. T.l.c. homogeneous *cis*-undec-8-ene-2,5-dione monoethylenethioketal (**3***a*) (156 mg, 60.5%) was obtained from the Girard derivative. An analytical sample was prepared by evaporative distillation in high vacuum (bath temperature 100–110°). I.r. ν 1710 cm^{-1}; n.m.r. (CDCl$_3$)τ4.65 (2H, m), 6.79 (4H, s), 8.25 (3H, s), 9.05 (3H, t, $J = 7.5$ Hz); mass (M$^+$): calcd. for $C_{13}H_{22}O^{32}S_2$, 258.1113; found, 258.1107.

Anal. Calcd. for $C_{13}H_{22}OS_2$: C, 60.5; H, 8.5; S, 24.8. Found: C, 60.8; H, 8.6; S, 24.2.

cis-Undec-8-ene-2,5-dione (4a)

(*a*) Following the procedure of Wynberg and coworkers (4), a solution of chloramine T (570 mg) in 80% methanol (2.5 ml) was added to **3***a* (150 mg) in methanol (2 ml) and ethanol (1 ml). After stirring at room temperature for 2 min, water was added and it was extracted with ether (80 ml). The ether solution was washed with 10% sodium hydroxide, water, and dried. The crude diketone **4***a* (102 mg) secured by evaporation of solvent was purified by preparative t.l.c. on silica gel (benzene; R_f 0.2); yield 80 mg (70%). I.r. ν 1710 cm^{-1}; n.m.r. (CDCl$_3$) τ 4.65 (2H, m), 7.32 (4H, s), 7.83 (3H, s), 9.05 (3H, t, $J = 7$ Hz); mass spectrum *m*/*e* 182 (M$^+$).

(*b*) Ceric ammonium nitrate (550 mg) was added to a stirred solution of **3***a* (62 mg) in 75% aqueous acetonitrile (4 ml) at ambient temperature. At the end of 5 min the reaction was quenched with water and extracted with ether (50 ml). The ether extract was then washed with water to remove coloring material, dried, evaporated, and the resulting product was subjected to preparative t.l.c. to give **4***a* (34 mg, 77.8%).

cis-Jasmone

A mixture of *cis*-undec-8-ene-2,5-dione (80 mg), 0.5 *N* sodium hydroxide (1.0 ml), and ethanol (2.0 ml) was refluxed under nitrogen for 5 h. On cooling, the mixture was acidified with dilute hydrochloric acid and extracted with ether. The crude product was purified by preparative t.l.c. on silica gel (benzene:ether, 85:15; R_f 0.6) to give *cis*-jasmone (55 mg, 76.4%). I.r. ν 1690, 1640 cm^{-1}; n.m.r. (CDCl$_3$) τ 4.64 (2H, m), 7.02 (2H, d, $J = 5$ Hz), 7.92 (3H, s), 9.00 (3H, t, $J = 7$ Hz); mass spectrum *m*/*e* 164 (M$^+$). 2,4-DNP, m.p. 115–116° (lit. (1*b*) m.p. 116°).

Undecan-2,5-dione Monoethylenethioketal (3b)

A solution of levulonitrile ethylenethioketal (1.00 g) in dry ether (10 ml) was added to a stirred Grignard reagent prepared from 1-bromohexane (10.00 g) and magnesium turnings (1.44 g) in ether (80 ml). The reaction mixture was stirred at room temperature for 20 h and added dropwise to a stirred mixture of dilute hydrochloric acid and chloroform. After separation into layers, the aqueous phase was extracted with chloroform (2 × 60 ml). The combined extracts were dried and evaporated to given an oil. The diketone monoethylenethioketal **3***b* (1.035 g, 65.5%) was isolated by treatment of the crude oil with Girard T reagent (1.20 g) in refluxing methanol (40 ml, containing 1.0 ml glacial acetic acid) for 3 h. I.r. ν 1710 cm^{-1}; n.m.r. (CDCl$_3$) τ 6.68 (4H, s), 7.1–8.0 (6H, m), 8.25 (3H, s), 8.5–8.9 (8H, m), 9.11 (3H, t, $J = 5$ Hz); mass (M$^+$): calcd. for $C_{13}H_{24}O^{32}S_2$, 260.1269; found, 260.1263.

Anal. Calcd. for $C_{13}H_{24}OS_2$: C, 60.0; H, 9.3; Found: C, 59.8; H, 9.4.

Undecan-2,5-dione

(*a*) A solution of **3***b* (460 mg) in methanol–ethanol (2:1, 3 ml) was treated with a solution of chloramine T (1.128 g) in 80% methanol (5 ml) at room temperature for 2 min. Water was added and the resulting mixture was extracted with ether (80 ml). The extract was washed with 10% potassium hydroxide, water, and dried. Evaporation of the organic solution yielded undecan-2,5-dione (226 mg, 67.3%) which was homogeneous on t.l.c. I.r. ν 1710 cm^{-1}; n.m.r. (CCl$_4$) τ 7.43 (4H, s), 7.62 (2H, t, $J = 6.5$ Hz), 7.90 (3H, s), 9.10 (3H, t, $J = 5$ Hz); mass spectrum *m*/*e* 184 (M$^+$).

(*b*) To a solution of **3***b* (130 mg) in 75% aqueous acetonitrile (8 ml) was added ceric ammonium nitrate (1.10 g) in portions. After swirling at room temperature for 5 min, the reaction mixture was poured into water and extracted with ether (80 ml). The ethereal solution was washed thrice with water (until colorless), dried, and evaporated. The crude product, virtually homogeneous on t.l.c., was filtered through a short column of alumina (1.5 g) with benzene as eluent to give pure undecan-2,5-dione (73 mg, 80%).

Dihydrojasmone

A mixture of undecan-2,5-dione (210 mg), 0.5 *N* sodium hydroxide (2.0 ml), and ethanol (1.0 ml) was refluxed under nitrogen for 5 h. The cooled mixture was acidified with dilute hydrochloric acid and extracted with ether. The crude product was eluted through a short column of neutral alumina with ether–benzene mixture (1:9) to furnish pure dihydrojasmone (158 mg, 83%). I.r. ν 1705, 1650 cm^{-1}; n.m.r. (CDCl$_3$) τ 7.96 (3H, s), 9.13 (3H, t, $J = 5$ Hz); mass spectrum *m*/*e* 166 (M$^+$). Semicarbazone m.p. 174–175° (lit. (2*a*) m.p. 173–175°).

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1. (*a*) S. M. WEINREB and R. J. CVETOVICH. Tetrahedron Lett. 1233 (1972); (*b*) W. F. BERKOWITZ. J. Org. Chem. **37**, 341 (1972); (*c*) J. E. MCMURRY and J. MELTON. J. Am. Chem. Soc. **93**, 5309 (1971); (*d*) G. STORK, G. L. NELSON, F. ROUESSAC, and O. GRINGORE. J. Am. Chem. Soc. **93**, 3091 (1971); (*e*) G. BÜCHI and B. EGGER. J. Org. Chem. **36**, 2021 (1971); (*f*) J. E. MCMURRY and T. E. GLASS. Tetrahedron Lett. 2575 (1971); (*g*) J. FICINI, J. d'ANGELO, J. P. GENÊT, and J. NOIRÉ. Tetrahedron Lett. 1569 (1971): (*h*) M. FÉTIZON and J. SCHALBAR. La France et ses parfums. **12**, 330 (1969); (*i*) K. SHISHIDO and Y. KAWASHIMA. Japan 7014779 (Patent); Chem. Abstr. **73**, 120 181*p* (1970); (*j*) L. CROMBIE, P. HEMESLEY, and G. PATTENDEN. J. Chem. Soc. C, 1024 (1969); (*k*) G. BÜCHI and H. WÜEST. J. Org. Chem. **31**, 977 (1966); (*l*) T. YOSHIDA, A. YAMAGUCHI, and A. KOMATSU. Agri. Biol. Chem. **30**, 370 (1966); (*m*) K. SHISHIDO, Y. KAWASHIMA, and T. ISHIDA. Perfum. Essent. Oil Rec. **57**, 364 (1966); (*n*) G. STORK and R. BORCH. J. Am. Chem. Soc. **86**, 936 (1964); (*o*) J. H. AMIN, R. K. RAZDAN, and S. C. BHATTACHARYYA. Perfum. Essent. Oil Rec. **49**, 502 (1958); (*p*) S. H. HARPER and R. J. D. SMITH. J. Chem. Soc. 1512 (1955); (*q*) L. CROMBIE and S. H. HARPER. J. Chem. Soc. 869 (1952); (*r*) H. HUNSDIECKER. Ber. **75**, 460 (1942).

2. (*a*) E. Wenkert, A. Mueller, E. J. Reardon, Jr., S. S. Sathe, D. J. Scharf, and G. Tosi. J. Am. Chem. Soc. **92**, 7428 (1970); (*b*) J. Katsube and M. Matsui. Agri. Biol. Chem. **33**, 1078 (1969); (*c*) R. T. Dahill. J. Org. Chem. **31**, 2694 (1966); (*d*) A. Takeda, H. Hosisima, and S. Torii. Bull. Chem. Soc. Japan, **39**, 1354 (1966); (*e*) E. Thiele. Ger. (East) Pat. 30 727; Chem. Abstr. **65**, 8789*h* (1966); (*f*) J. L. Erickson and F. E. Collins. J. Org. Chem. **30**, 1050 (1965); (*g*) M. Elliott. J. Chem. Soc. 2231 (1956); (*h*) R. L. Frank, P. G. Arvan, J. W. Richter, and C. R. Vanneman. J. Am. Chem. Soc. **66**, 4 (1944); (*i*) H. Hunsdiecker. Ber. **75**, 455 (1942); (*j*) H. Staudinger and L. Ruzicka. Helv. Chim. Acta, **7**, 245 (1924); (*k*) T. L. Ho. J. Chinese Chem. Soc. (II) **18**, 153 (1971).
3. G. D. Buckley, T. J. Elliott, F. G. Hunt, and A. Lowe. J. Chem. Soc. 1505 (1947).
4. W. F. J. Huurdeman, H. Wynberg, and D. W. Emerson. Tetrahedron Lett. 3449 (1971).
5. T. L. Ho, H. C. Ho, and C. M. Wong. Chem. Commun. In press.

The Photolysis of Tetra(trifluoromethyl)thiophene Vapor[1]

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The photolysis of tetra(trifluoromethyl)thiophene (TTFT) at 2139 Å or by mercury sensitization at 2537Å yields hexafluorobutyne-2 and 1,2,3,4-tetra(trifluoromethyl)5-thiabicyclo[2,1,0]pentene-2 (also called tetra(trifluoromethyl)cyclobutadiene episulfide) as the principal gas phase products. The latter is colored a pale yellow and is stable at room temperature. These results suggest that a possible mechanism for the reaction of photoexcited thiophenes is via the formation of valence bond isomers as intermediates.

La photolyse du tétra(trifluorométhyl)thiophène (TTFT) à 2139 Å ou par sensibilisation par le mercure à 2537 Å, donne l'hexafluorobutyne-2 et le tétra(trifluorométhyl)-1,2,3,4 thia 5 bicyclo[2,1,0] penetène-2 (appelé aussi tétra(trifluorométhyl)cyclobutadiène épisulfure) comme produits principaux de la phase gazeuse. Ce dernier, de couleur jaune pâle, est stable à la température ambiante. Ces résultats laissent penser qu'un mécanisme possible dans la réaction des thiophènes photoexcités, est le passage par les isomères de liaison de valence au stade intermédiaire.

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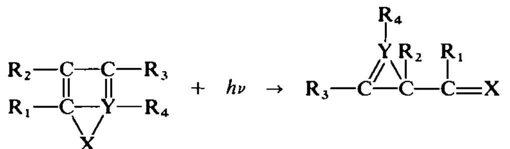
Introduction

The photolysis of a number of five-membered heterocyclic compounds proceeds through the intermediate **1**, (1–8), the reaction being



1

where X is a heteroatom and Y is either carbon or a heteroatom.

Wynberg and his coworkers (9–12) have studied the photolysis of substituted thiophenes in solution and have observed that the substituted groups shift. Labelling experiments have shown that ring carbons move, carrying the substituent groups with them. Such an isomerization could proceed through a ring contracted intermediate or "benzenoid" type valence bond isomer, but Wynberg *et al.* (12) preferred a species involving valence shell expansion of the sulfur atom.

Recent studies (13–15) have shown that the irradiation of solutions of thiophenes or furans in amines leads to the formation of pyrroles. The same pyrroles are formed from furans as from the corresponding thiophenes. This was taken to imply that cyclopropenyl intermediates (ketones or aldehydes for the furan systems, thioketones or thioaldehydes for the thiophene systems) are involved in the reaction.

In an earlier report from our laboratory (16), the photolysis of thiophene was reported. The mechanistic details required that the initially formed electronically excited thiophene pass

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