search Fund, administered by the American Chemical Society, for support of this work.

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A Synthesis of 3,7-Dimethylpentadec-2-yl Acetate. The Sex Pheromone of the Pine Sawfly *Neodiprion lecontei*[1]

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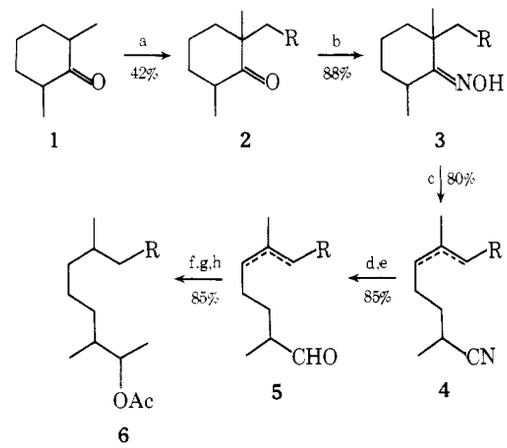
Received August 26, 1976

The sawflies are ubiquitous in North America and include in their host selection a great diversity of plant groups. Many species (e.g., *Diprion hercyniae* and *Neodiprion lecontei*) are among the worst defoliators of spruce and pine forests as a result of feeding by the caterpillar-like larvae on coniferous needles.[2] Recently Coppel and co-workers[3] identified 3,7-dimethylpentadec-2-yl acetate (**6**) as the major component of the sex pheromone produced by female *Neodiprion lecontei*. We report below a facile synthesis of racemic **6** starting with commercial 2,6-dimethylcyclohexanone (**1**).

In the synthesis outlined in Scheme I (R = *n*-heptyl), the

Scheme I



a, NaH, *n*-$C_8H_{17}I$/THF; b, NH_2OH·HCl, NaOAc/EtOH; c, *p*-TsCl/pyridine, reflux; d, DiBALH/hexane, −78°C; e, H_3O^+; f, MeMgI/Et_2O; g, Ac_2O; h, PtO_2/HOAc, H_2.

key step, a Beckmann fragmentation of the oxime **3**[4] to the isomeric olefinic nitriles **4**, proceeded in 90% yield when **3** reacted with 2 equiv of *p*-TsCl in refluxing pyridine.[5] The synthesis was completed by standard procedures as shown to give the acetate **6** in 59% overall yield from the ketone **2**.

Experimental Section

2,6-Dimethyl-2-*n*-octylcyclohexanone (2). A flame-dried 250-ml three-neck flask fitted with a magnetic stirrer, condenser, addition funnel, nitrogen inlet, and gas bubbler was charged with 4.5 g (90 mmol) of 50% NaH. After the mineral oil was removed with 2 × 20 ml of ether, 90 ml of THF (freshly distilled from Na) and 10 ml of DMF was added. The mixture was heated to reflux and 9.45 g (75 mmol) of 2,6-dimethylcyclohexanone was added dropwise. When hydrogen evolution had ceased, the mixture was cooled to 25 °C and 17.5 g (73 mmol) of 1-iodooctane added in one portion. After stirring at ambient temperature for 1 h, the mixture was refluxed for a further 1 h whereupon 50 ml of 3 M H_2SO_4 was added and refluxing continued for 3.5 h. After cooling, the organic layer was separated, diluted with 100 ml of ether, and washed with 2 × 100 ml of H_2O. After drying over $MgSO_4$, the solvent was removed in vacuo and the residue distilled via short path to give 3.34 g (36%) of the starting ketone **1** and 7.31 g (42%) of **2**: bp 117–120 °C (0.1 mm); IR (CCl_4) 1710 cm^{-1}; NMR (CCl_4) δ 0.85 (distorted t, 3 H), 0.92 (d, 3 H, J = 7 Hz), 0.92, 1.08 (2 sharp singlets, 3 H), 1.26 (br s, 14 H), 1.0–2.0 (br, 7 H); *m/e* (rel intensity) 238 (M^+, 22), 126 (100).

2,6-Dimethyl-2-*n*-octylcyclohexanone Oxime (3). A mixture of 5.96 g (25 mmol) of ketone **2**, 10.4 g (150 mmol) of NH_2OH·HCl, 20.6 g (150 mmol) of NaOAc·$3H_2O$, and 20 ml of EtOH was refluxed for 48 h. After 150 ml of H_2O was added, the product was extracted into 2 × 40 ml of ether, dried over $MgSO_4$, and concentrated in vacuo. Methanol (15 ml) was added and the mixture refrigerated overnight. The crystalline product was collected by suction filtration and washed with cold methanol to give 2.05 g of oxime, mp 79–81 °C. The filtrate and washings were combined and concentrated in vacuo and the resultant oil was distilled via short path to give 3.51 g of the oxime as a colorless, viscous oil, bp 127–130 °C (0.1 mm). The combined yield of oximes was 5.56 g (88%). The data for the crystalline oxime are presented below: IR (CCl_4) 3400 cm^{-1}; (broad); NMR (CCl_4) δ 9.9 (s, 1 H), 1.3 (br s, 14 H superimposed on d, 3 H), 1.1 (s, 3 H), 0.9 (distorted t, 3 H), 1.2–2.0 (br, 7 H); *m/e* (rel intensity) 253 (M^+, 6), 236 (5), 141 (100), 126 (22).

Beckmann Fragmentation of Oximes 3. A mixture of 4.00 g (15.8 mmol) of the crystalline oxime **3** and 6.83 g (35.6 mmol) of *p*-toluenesulfonyl chloride in 10 ml of pyridine was refluxed for 2.5 h. After cooling to 25 °C, 1 ml of H_2O was added and the mixture stirred for 10 min whereupon the dark brown solution was poured into 100 ml of water and extracted with 3 × 25 ml of hexane. The combined hexane layers were washed with 2 × 25 ml of H_2O, dried over $MgSO_4$, and concentrated in vacuo. The resultant brown oil was distilled via Kugelrohr to give 3.35 g (90%) of the isomeric olefinic nitriles **4**: bp 125–130 °C (bath) (0.1 mm); IR (CCl_4) 2240 cm^{-1}; NMR (CCl_4) δ 5.0 (m, 1 H), 2.4 (sextet, 1 H), 2.0 (m, 2 H), 2.0 (m, 2 H), 1.65 (br s, 3 H), 1.0–1.7 (br, 6 H), 1.3 (br s, 10 H, superimposed on d, 3 H), 0.85 (distorted t, 3 H); *m/e* (rel intensity) 235 (M^+, 51), 220 (33), 207 (80), 150 (79), 126 (64), 107 (100).

Reduction of the Nitriles 4 to the Aldehydes 5. To a magnetically stirred solution of 3.35 g (14.2 mmol) of the nitriles **4** in 20 ml of hexane was added dropwise at −78 °C 2.80 ml (2.22 g, 15.6 mmol) of DiBALH in 3 ml of hexane. After stirring at −78 °C for an additional 30 min, the cooling bath was removed and stirring continued at ambient temperature for 2 h. The mixture was carefully poured into 35 ml of rapidly stirred 3 M H_2SO_4. After 1 h, the organic layer was washed with 2 × 25 ml of H_2O, dried over $MgSO_4$, and concentrated in vacuo and the residue was distilled via Kugelrohr to give 2.86 g (85%) of the aldehydes **5** as a colorless oil: bp 110–115 °C (bath)(0.1 mm); IR (CCl_4) 2820, 2720, 1720, 1640 cm^{-1}; NMR (CCl_4) δ 9.5 (d, 1 H, J = 2 Hz), 5.0 (m, 1 H), 2.2 (sextet, 1 H), 2.0 (distorted t, 2 H), 1.6 (br s, 3 H), 1.25 (br s, 10 H), 1.05 (d, 3 H, J = 7 Hz), 0.85 (distorted t, 3 H); *m/e* (rel intensity) 238 (M^+, 27), 180 (100), 126 (45).

3,7-Dimethylpentadec-2-yl Acetate (6). To a magnetically stirred solution of MeMgI [prepared from 1.42 g (10.0 mmol) of MeI and 0.36 g (15.0 g-atoms) of Mg in 10 ml of Et_2O] was added 1.70 g (7.15 mmol) of aldehyde **5** in 3 ml of Et_2O. After stirring at 0 °C for 10 min, 2.00 g (20 mmol) of Ac_2O was added dropwise. After addition was compete, stirring was continued for 15 min, whereupon 20 ml of aqueous NH_4Cl was added. The organic layer was washed with 2 × 10 ml of H_2O, dried over $MgSO_4$, and concentrated in vacuo.

The crude product from above in 15 ml of HOAc was reduced over Pt (15 mg of PtO_2) at 15 psi H_2. The catalyst was removed by filtration and the solvent removed in vacuo. The residue was distilled via Kugelrohr to give 1.88 g (88%) of **6** as a colorless oil: bp 130–135 °C (bath)(0.1 mm); IR (CCl_4) 1740, 1240 cm^{-1}; NMR (CCl_4) δ 4.8 (m, 1 H), 1.95 (s, 3 H), 1.25 (br s, 18 H), 1.0–1.5 (m with Me doublets superimposed, 13 H), 0.9 (distorted t, 3 H); MS^3 *m/e* (rel intensity) 298 (M^+, 13), 238 (100).

The distilled product showed one major component (>95%) by VPC analysis on a 4 ft × 0.25 in. 10% SE-30/Chromosorb P column at 180 °C. The VPC retention time, IR, and mass spectra of **6** as prepared above were identical with those of an authentic sample kindly provided by Professor Coppel.[3]

Acknowledgment. We wish to thank the Research Corporation and State University of New York at Binghamton (Biomedical Research Support Grant) for generous financial support. We also thank Jon Stickles and John Soderquist for technical assistance.

Registry No.—**1**, 2816-57-1; **2**, 61259-60-7; **3**, 61288-74-2; **4** (5-ene), 61259-61-8; **4** (6-ene), 61259-62-9; **5** (5-ene), 61259-63-0; **5** (6-ene), 61259-64-1; **6**, 59056-74-5; 1-iodooctane, 629-27-6; MeI, 74-88-4; Ac_2O, 108-24-7.

References and Notes

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(2) H. H. Ross, "A Textbook of Entomology", 3d ed, Wiley, New York, N.Y., 1965, pp 301–304.
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A Facile Internal Dilactonization of 1,6-Dialkyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]non-7-en-9-one-*endo*-2,5-dicarboxylic Acids

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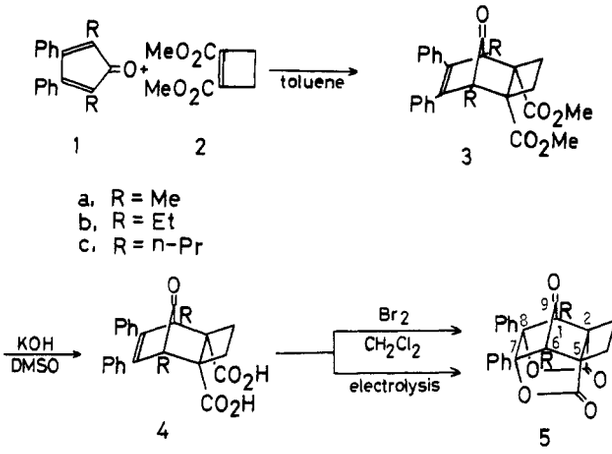
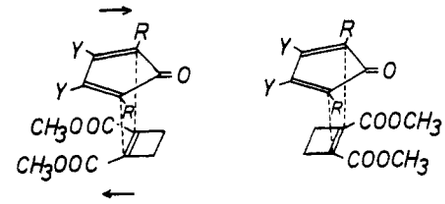
Received June 15, 1976

Although electrophile-induced monolactonization of 2-*endo*-norbornenecarboxylic acid and related compounds is well known,[1] examples involving formation of dilactone are rare.[2] The present note describe the facile formation of dilactones **5** from 1,6-dialkyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]-non-7-en-9-one-*endo*-2,5-dicarboxylic acids (**4**) which were obtained by Diels–Alder reactions[3] of 2,5-dialkyl-3,4-diphenylcyclopentadienones (**1**)[4] with dimethyl Δ^1-cyclobutene-1,2-dicarboxylate (**2**),[5] followed by hydrolysis.



Reaction of **1** with two equimolar amounts of **2** in refluxing toluene for 3–4 days produced the single products in 42–93% yields. The analytical and spectral data are compatible with the 1:1 adduct structure of **3** (see Tables I and II). The ^1H ester methyl resonances which appear at 3.61–3.62 ppm for these adducts are in accord with the *endo*-carbomethoxy assignment.[1c] The endo stereoselectivity can be predicted on the basis of the secondary orbital interactions[6] between carbomethoxy groups and diene systems, as well as the dipole–



dipole interactions[7] between reactants in the transition state of the [4 + 2] cycloaddition.

The dimethyl esters **3** were converted by alkaline hydrolysis in dimethyl sulfoxide at 80 °C to the corresponding dicarboxylic acids **4**, which, on treatment with excess bromine in dichloromethane at room temperature, afforded the corresponding dilactones **5** in 22–26% yields (from **3**). The struc-

Table I. Cycloadducts 3 Derived from Cyclopentadienones 1 and Dimethyl Δ^1-Cyclobutene-1,2-dicarboxylate (2)

Registry no.	Compd[b]	R	Time,[a] days	Yield, %	Mp, °C	IR (KBr), cm^{-1}, $\nu_{C=O}$	^1H NMR, δ ($CDCl_3$) $-COOCH_3$	^1H NMR, δ ($CDCl_3$) Others
61202-87-7	**3a**	Me	3	42	142–144.5	1726 1749 1778	3.62	1.33 (s, 6 H, CH_3) 1.66–2.87 (m, 4 H, $-CH_2CH_2-$) 6.88–7.19 (m, 10 H, aromatic)
61202-88-8	**3b**	Et	3.5	93	126–128.7	1724 1750 1773	3.61	0.77 (t, J = 8 Hz, 6 H, CH_3) 2.05 (q, J = 8 Hz, 4 H, $-CH_2-$) 1.95–2.72 (m, 4 H, $-CH_2CH_2-$) 6.89–7.20 (m, 10 H, aromatic)
61202-89-9	**3c**	*n*-Pr	4	59	120–122	1720 1742 1763	3.62	0.7–2.8 (m, 18 H, n-$CH_3CH_2CH_2-$) 6.63–7.37 (m, 10 H, aromatic)

[a] Time of disappearance of 1, monitored by TLC. [b] Satisfactory analytical data (±0.4% for C, H) for all compounds were submitted for review.