approximately 25% yield. However, the cleavage of **12** could result from a retro-pinacol reaction,[2b] and hence this may be an unfair comparison. Nevertheless, it serves as a good reminder that predictions of reductive cleavage must be made cautiously.

While the reductive cleavage described for **1** and **2** is useful in distinguishing head-to-head and head-to-tail dimers of the type shown by **1, 2, 5,** and **6,** it is also useful as a stereospecific synthesis of β,β'-linked hydrocarbon types illustrated by **3** and **4,** which are otherwise difficult to obtain as pure hydrocarbons. Since a single product was obtained in the preparation of **3,** we assume that the positions β to the aromatic rings of **1** are not involved. This permits the stereochemical assignment shown for **3,** mp 84–85 °C,[5] and hence suggests the meso configuration for hydrocarbon **13,** mp 118–119 °C.[14]

Experimental Section

Li–NH$_3$ Reductive Cleavage of *cis,anti,cis*-5,6,6a,-6b,7,8,12b,12c-Octahydrodibenzo[*a,i*]biphenylene (1) to 1,1′,-2,2′,3,3′,4,4′-Octahydro-2,2′-binaphthyl (3). To a solution of 2.0 g (7.2 × 10^{-3} mol) of **1,**[3] mp 71–72 °C, in 10 ml of dry ether and 50 ml of ammonia was added 0.11 g (1.57 × 10^{-2} g-atom) of lithium in small pieces. After addition, the blue color persisted. After 1 h, the reaction was quenched with anhydrous ammonium chloride, ammonia was allowed to evaporate, and 200 ml of water was added to the residue. The reaction mixture was extracted (ether, 3 × 100 ml) and the organic layer was washed with 50-ml portions of 10% sulfuric acid, Claisen's alkali,[16] and water. The ether layer was dried ($MgSO_4$) and concentrated to give 1.95 g of a crystalline product, mp 73–78 °C. GC analysis[17a] of the product showed less than 2% of unreacted **1** and a major peak corresponding to **3.**[5b] Recrystallization of the crude product from isohexane gave 1.2 g (60% yield) of white needles, mp 84.5–85 °C. A second crop of 0.5 g of less pure material was obtained by concentration of the mother liquor. The total yield was 85%. The product had an identical ^{1}H NMR spectrum and undepressed melting point on mixing with a known sample of **3.**[5b]

Li–NH$_3$ Reductive Cleavage of 4bβ,4cα,9,9aα,9bβ,10-Hexahydrocyclobuta[1,2-*a*:4,3-*a′*]diindene (2) to 2,2′-Biindanyl (4). To a solution of 1.0 g (4.3 × 10^{-3} mol) of the photodimer **2,**[4] mp 110 °C, in 10 ml of ether and 50 ml of ammonia was added 0.65 g (9.3 × 10^{-3} g-atom) of lithium. The reaction and product isolation was carried out as described above to give 1.0 g of a solid. GC analysis[17b] of this solid showed a major peak and no unreacted **2.** Recrystallization of the product from acetone gave 0.8 g (80% yield) of white crystals of **4:** mp 165–167 °C (lit.[6a] mp 165–166.5 °C); ^{1}H NMR ($CDCl_3$) δ 7.10 (m, 8, ArH), 3.20–2.90 (m, 4, $ArCH_2$), 2.83–2.30 (m, 6, Ar$\mathbf{CH_2CH}$); mass spectrum (70 eV) *m/e* 234.

Hydrogenation of 1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-binaphthyl-1,1′-diol (12) to 1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-binaphthyl (7). A solution of 15 g (0.051 mol) of the pinacol **12**[13] in 500 ml of acetic acid and 1.5 g of 10% Pd/C was shaken in a Parr hydrogenation vessel under a 50-psig hydrogen atmosphere at 60–70 °C for 43 h. The reaction mixture was filtered and concentrated under reduced pressure. The crude hydrogenation product was purified by chromatography on basic alumina using isohexane. The combined hydrocarbon fractions were distilled using a Kugelrohr apparatus at 160–170 °C (0.2 mm) to give 3.5 g (0.013 mol, 26% yield) of a clear, colorless oil:[8a,17c] ^{1}H NMR ($CDCl_3$) δ 7.31–6.86 (m, 8, ArH), 3.72–3.20 (m, 2, ArCH), 2.65 (t, 4, $ArCH_2$), $J = 4$ Hz, and 2.13–1.04 (m, 8, $ArCH_2\mathbf{CH_2CH_2}$); mass spectrum (70 eV) *m/e* 262.

Reaction of 12 with Sodium–Ammonia. A solution of 0.8 g (0.0027 mol) of **12,** mp 185–189 °C (lit.[13] mp 191 °C), in 50 ml of THF was added to a solution of 50 ml of ammonia and 0.5 g (0.22 g-atom) of sodium. After 1 h, the reaction was quenched by addition of solid ammonium chloride and the products isolated as previously described. The resulting oil was analyzed by GC[17c] and shown to contain 25% tetralin.

Acknowledgments. We thank the Contraceptive Development Branch, Center for Population Research, National Institute of Child Health and Human Development (Contract No. N01-HD-2846), for partial support. We also thank Continental Oil Co. for some financial assistance.

Registry No.—**1,** 42182-84-3; **2,** 23358-17-0; **3,** 61158-73-4; **4,** 39060-95-2; **7,** 1154-13-8; **12,** 3073-53-8; tetralin, 119-64-2; lithium, 7439-93-2; ammonia, 7664-41-7; sodium, 7440-23-5.

References and Notes

(1) (a) Research Associate, Oklahoma State University; (b) Graduate Research Assistant, Oklahoma State University; (c) Graduate Research Assistant, Oklahoma State University, and Continental Oil Co. Fellow, 1975; (d) Department of Chemistry, University of Oklahoma; (e) Department of Chemistry, Oklahoma State University.

(2) (a) R. L. Augustine, Ed., "Reduction", Marcel Dekker, New York, N.Y., 1968; (b) A. J. Birch and G. Subba Rao, *Adv. Org. Chem.,* **8,** 1–65 (1972).

(3) J. E. Burks, Jr., D. van der Helm, T. K. Dobbs, L. L. Ansell, P. H. Ruehle, and E. J. Eisenbraun, *Acta Crystallogr.,* submitted.

(4) (a) W. Metzner and D. Windisch, *Justus Liebigs Ann. Chem.,* **730,** 111 (1970); (b) J. Bowyer and Q. N. Porter, *Aust. J. Chem.,* **19,** 1455 (1966).

(5) (a) L. Reggel, H. W. Sternberg, and I. Wender, *Nature (London),* **190,** 81 (1961); (b) E. J. Eisenbraun, R. C. Bansal, D. V. Hertzler, and W. P. Duncan, *J. Org. Chem.,* **35,** 1265 (1970).

(6) (a) W. Lüttke and J. Grussdorf, *Chem. Ber.,* **98,** 140 (1965); (b) F. Fichter and H. Stenzl, *Helv. Chim. Acta,* **22,** 425 (1939).

(7) (a) J. Dekker and T. G. Dekker, *J. S. Afr. Chem. Inst.,* **28,** 122 (1975); (b) Alternate synthesis, this laboratory.

(8) (a) Unpublished work, this laboratory. We assume to have a mixture of meso and *dl* isomers. (b) Hydrocarbons **1** and **2** were separately treated with potassium *tert*-butoxide in anhydrous dimethyl sulfoxide at room temperature for 2.5 h and recovered unchanged.

(9) C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.,* **56,** 1133 (1934).

(10) Reference 2a, p 106.

(11) J. L. Marshall and T. K. Folsom, *Tetrahedron Lett.,* 757 (1971).

(12) von F. Gerson and B. Weidmann, *Helv. Chim. Acta,* **49,** 1837 (1966).

(13) E. B. Barnett and C. A. Lawrence, *J. Chem. Soc.,* 1104 (1935).

(14) (a) W. Hückel and M. Wartini, *Justus Liebigs Ann. Chem.,* **686,** 40 (1965); (b) R. C. Bansal, Ph.D. Thesis, Oklahoma State University, 1966; (c) P. Markov, D. Lasarov, and C. Ivanov, *Justus Liebigs Ann. Chem.,* **704,** 126 (1967).

(15) ^{1}H NMR spectra were obtained on a XL-100 Varian instrument. GC analyses for the hydrocarbons were obtained with a Hewlett-Packard Model 5750 apparatus fitted with a hydrogen-flame detector using helium as carrier gas. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and were uncorrected.

(16) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, N.Y., 1967, p 153.

(17) (a) An 8 ft × 0.25 in. column of 80–100 mesh Chromosorb G coated with 7% UC W-98 at 230 °C was used; (b) ref 17a at 190 °C; (c) a 6 ft × 0.25 in. column of 80–100 mesh, AW-DMCS-treated Chromosorb G coated with 3.5% *N,N′*-bis(*p*-methoxybenzylidine)-α,α'-bitoluidine at 220 °C was used.

Reactions of Enones with the New Organocuprates, $LiCu_2(CH_3)_3$, $Li_2Cu_3(CH_3)_5$, and $Li_2Cu(CH_3)_3$

Eugene C. Ashby,* J. J. Lin, and John J. Watkins

School of Chemistry, Georgia Institute of Technology,
Atlanta, Georgia 30332

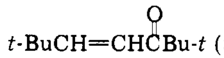
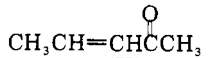
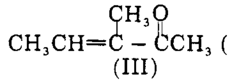
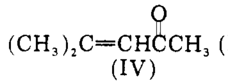
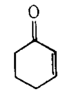
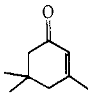
Received August 25, 1976

It has been reported that a mixture of $(CH_3)Li$ and $LiCu(CH_3)_2$ provides unusually stereoselective methylation of 4-*tert*-butylcyclohexanone compared to CH_3Li alone.[1] It was suggested that a highly reactive cuprate having the stoichiometry $Li_2Cu(CH_3)_3$ or $Li_3Cu(CH_3)_4$ is formed when CH_3Li and $LiCu(CH_3)_2$ are allowed to react and that reaction of these species with the ketone would explain the observed results. We have recently obtained direct evidence for the existence of $LiCu_2(CH_3)_3$ and $Li_2Cu(CH_3)_3$ in both dimethyl ether and tetrahydrofuran and indirect evidence for the species $Li_2Cu_3(CH_3)_5$ and $Li_2Cu(CH_3)_3$ in diethyl ether by low-temperature NMR.[2] All of the cuprates appear to be single species in solution except $Li_2Cu(CH_3)_3$ which has been shown to exist as an equilibrium mixture. Since $LiCu(CH_3)_2$ has proven to be an excellent conjugate methylating agent for α,β-unsaturated carbonyl compounds, it was considered to be important to evaluate these new cuprates as conjugate methylating agents.

$$LiCu(CH_3)_2 + CH_3Li \rightleftharpoons Li_2Cu(CH_3)_3 \tag{1}$$

Six enones (I–VI) were chosen to react with $LiCu(CH_3)_2$, $LiCu_2(CH_3)_3$, and $Li_2Cu(CH_3)_3$ in THF and $LiCu(CH_3)_2$, $Li_2Cu_3(CH_3)_5$, and $Li_2Cu(CH_3)_3$ in Et_2O solvent. The results of these reactions are shown in Tables I and II. In THF solvent

Table I. Methylation of Enones with $LiCu(CH_3)_2$, $LiCu_2(CH_3)_3$, and $Li_2Cu(CH_3)_3$[a] in THF at Room Temperature

Expt	Cuprate reagent[b]	Enone[c]	Molar ratio of reagent to enone	Reaction time, h	Enone recovered, %	Product, %: 1,4 methylation	Product, %: 1,2 methylation
1	$LiCu(CH_3)_2$	 $t\text{-BuCH=CH}\overset{O}{\overset{\|}{\text{C}}}\text{Bu-}t$ (*trans*) (I)	3:1	3	5	95[d]	0
2	$LiCu_2(CH_3)_3$	(I)	3:1	3	20	82	0
3	$Li_2Cu(CH_3)_3$	(I)	2:1	3	0	108	0
4	$LiCu(CH_3)_2$	 $\text{CH}_3\text{CH=CH}\overset{O}{\overset{\|}{\text{C}}}\text{CH}_3$ (II)	3:1	3	7	93[e]	0
5	$LiCu_2(CH_3)_3$	(II)	3:1	3	11	90	0
6	$Li_2Cu(CH_3)_3$	(II)	2:1	3	11	93	0
7	$LiCu(CH_3)_2$	 $\text{CH}_3\text{CH=}\overset{\text{CH}_3}{\overset{\vert}{\text{C}}}-\overset{O}{\overset{\|}{\text{C}}}\text{CH}_3$ (III)	3:1	3	44	56[f]	0
8	$LiCu_2(CH_3)_2$	(III)	3:1	3	95	0	0
9	$Li_2Cu(CH_3)_3$	(III)	2:1	3	48	52	0
10	$LiCu(CH_3)_2$	 $(\text{CH}_3)_2\text{C=CH}\overset{O}{\overset{\|}{\text{C}}}\text{CH}_3$ (IV)	3:1	3	49	51[g]	0
11	$LiCu_2(CH_3)_3$	(IV)	3:1	3	66	30	0
12	$Li_2Cu(CH_3)_3$	(IV)	2:1	5	30	8	59[i]
13	$LiCu(CH_3)_2$	 (V)	3:1	3	0	100[h]	0
14	$LiCu_2(CH_3)_3$	(V)	3:1	3	0	103	0
15	$Li_2Cu(CH_3)_3$	(V)	2:1	3	0	95	0
16	$LiCu(CH_3)_2$	 (VI)	3:1	5	100	0	0
17	$LiCu_2(CH_3)_3$	(VI)	3:1	5	100	0	0
18	$Li_2Cu(CH_3)_3$	(VI)	2:1	5	100	0	0

[a] $Li_2Cu(CH_3)_3$ is in equilibrium with $LiCu(CH_3)_2$ and CH_3Li. [b] Registry no.: $LiCu(CH_3)_2$, 15681-48-8; $LiCu_2(CH_3)_3$, 61303-82-0; $Li_2Cu(CH_3)_3$, 61278-42-0. [c] Registry no.: I, 20859-13-6; II, 625-33-2; III, 565-62-8; IV, 141-79-7; V, 930-68-7; VI, 78-59-1. [d] Registry no., 61267-93-4. [e] Registry no., 61267-94-5. [f] Registry no., 61267-95-6. [g] Registry no., 61267-96-7. [h] Registry no., 61267-97-8. [i] Registry no., 21981-08-8.

Table II. Methylation of Enones with $LiCu(CH_3)_2$ and $Li_2Cu(CH_3)_3$ in Et_2O at Room Temperature

Expt	Cuprate reagent	Enone	Molar ratio of reagent:enone	Reaction time, min	Enone recovered, %	Product, %: 1,4 methylation	Product, %: 1,2 methylation
19	$LiCu(CH_3)_2$	I	1:1	10	37	63	0
20	$LiCu(CH_3)_2$	I	3:1	10	0	100	0
21	$Li_2Cu_3(CH_3)_5$	I	1:1	10	0	105	0
22	$Li_2Cu(CH_3)_3$	I	2:3	10	0	53	47[a]
23	$LiCu(CH_3)_2$	II	3:1	10	3	97	0
24	$Li_2Cu_3(CH_3)_5$	II	1:1	10	0	108	0
25	$Li_2Cu(CH_3)_3$	II	2:1	10	0	96	3[b]
26	$LiCu(CH_3)_2$	III	3:1	10	6	94	0
27	$Li_2Cu_3(CH_3)_5$	III	1:1	10	0	95	0
28	$Li_2Cu(CH_3)_3$	III	2:1	10	0.5	14	86[c]
29	$LiCu(CH_3)_2$	IV	3:1	10	17	82	1
30	$Li_2Cu_3(CH_3)_5$	IV	1:1	10	6	96	0
31	$Li_2Cu(CH_3)_3$	IV	2:1	10	2	19	79
32	$LiCu(CH_3)_2$	V	1:1	1	9	91	0
33	$Li_2Cu_3(CH_3)_5$	V	1:1	10	0	95	0
34	$Li_2Cu(CH_3)_3$	V	2:3	1	0	100	0
35	$LiCu(CH_3)_2$	VI	3:1	10	0	100	0
36	$Li_2Cu_3(CH_3)_5$	VI	1:1	10	0	94	0
37	$Li_2Cu(CH_3)_3$	VI	2:1	10	0	3[d]	93[e]

[a] Registry no., 61267-98-9. [b] Registry no., 61267-99-0. [c] Registry no., 61268-00-6. [d] Registry no., 61268-01-7. [e] Registry no., 61268-02-8.

(Table I), $LiCu_2(CH_3)_3$ reacted with enones in the same fashion as $LiCu(CH_3)_2$ to give 100% 1,4-regioselective methylation, but at a slower rate (expt 2, 5, and 11). When the enone was substituted in the α position (enone III), $LiCu_2(CH_3)_3$ did not react under the conditions that $LiCu(CH_3)_2$ gave a 56% yield. On the other hand, $Li_2Cu(CH_3)_3$ has a reaction rate similar to that of $LiCu(CH_3)_2$ in the reactions of β-monosubstituted enones (I, II, III, and V) but gives mostly 1,2 methylation for β-disubstituted enones such as IV (expt 12). Although all three cuprate reagents gave quantitative conjugate alkylation with cyclohexenone (V), none of the three reagents reacted with isophorone (VI).

In Et_2O solvent (Table II), the reactions are much faster than in THF solvent. $Li_2Cu_3(CH_3)_5$ is more reactive than $LiCu(CH_3)_2$ and also provides 100% 1,4 regioselectivity in each case studied as does $LiCu(CH_3)_2$. $Li_2Cu(CH_3)_3$ gives 100% conjugate alkylation for cyclohexenone (V) whereas $LiCu(CH_3)_2$ under the same conditions results in some recovered reactant. However, in diethyl ether, $Li_2Cu(CH_3)_3$ is in general less regioselective than $LiCu(CH_3)_2$. Clearly in the case of $Li_2Cu(CH_3)_3$, CH_3Li is reacting in diethyl ether to form 1,2-addition product.

It appears that the relative rates of $LiCu(CH_3)_2$, $LiCu_2(CH_3)_3$, $Li_2Cu_3(CH_3)_5$, and $Li_2Cu(CH_3)_3$ reaction with enones depends on the steric requirement of the particular enone. When the enone is disubstituted (either β,β or α,β), reaction is much slower than for a monosubstituted enone. For example, $LiCu_2(CH_3)_3$ does not react with III (an α,β-disubstituted enone) in THF whereas $LiCu(CH_3)_2$ effects conjugate addition in 56% yield (expt 7 and 8). On the other hand, $LiCu_2(CH_3)_3$ and $LiCu(CH_3)_2$ react with II (β-monosubstituted enone) in THF at about the same rate (expt 4 and 5). Clearly all of the cuprates react with cyclohexenone (V) at a rapid rate compared to the other enones whereas isophorone (VI) (a β,β-disubstituted enone) does not react with any of the cuprates.

When $Li_2Cu(CH_3)_3$ was allowed to react with IV (a β,β-disubstituted enone) in THF, the reaction involving conjugate addition is apparently slowed down so much that 1,2 addition by the equilibrium concentration of CH_3Li becomes the major reaction. The same phenomenon is observed in diethyl ether (Table II). $Li_2Cu(CH_3)_3$ is affected much more than $LiCu(CH_3)_2$ by disubstitution in the enone. For example, with the least substituted enones (II and V), $Li_2Cu(CH_3)_3$ gives conjugate addition in high yield, whereas with the more sterically hindered enones (I, III, IV, and VI), substantial 1,2 addition takes place.[3,4]

In conclusion, the new organocuprates, $LiCu_2(CH_3)_3$ and $Li_2Cu(CH_3)_3$ in THF and $Li_2Cu(CH_3)_3$ and $Li_2Cu_3(CH_3)_5$ in Et_2O, react with enones in a similar manner compared to $LiCu(CH_3)_2$. Except in the cases of disubstituted enones, $Li_2Cu(CH_3)_3$ gives quantitative conjugate methylation of the enones studied at a comparable or greater rate than $LiCu(CH_3)_2$ provided that the reaction is carried out in THF. On the other hand, poor regioselectivity was observed in diethyl ether. $LiCu_2(CH_3)_3$ gave quantitative regioselectivity in THF and reacted in general more slowly than $LiCu(CH_3)_2$. Since $LiCu_2(CH_3)_3$ is insoluble in diethyl ether, studies were not carried out in this solvent. $Li_2Cu_3(CH_3)_5$ in ether gave excellent results with all of the enones and appeared to react somewhat more rapidly compared to $LiCu(CH_3)_2$.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[5] Other manipulations were carried out in a glove box equipped with a recirculating system using manganese oxide columns to remove oxygen and dry ice–acetone to remove solvent vapors.[6] ^1H NMR spectra were obtained at 60 MHz using a Varian A-60 NMR spectrometer.

Analytical. Active CH_3 group analysis was carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line and collecting the evolved methane with a Toepler pump.[3] Lithium was determined by flame photometry. Iodide was determined by the Volhard procedure. Copper was determined by electrolytic deposition on a Pt electrode.

Materials. Tetrahydrofuran (Fisher Certified reagent grade) was distilled under nitrogen over $NaAlH_4$ and diethyl ether (Fisher reagent) over $LiAlH_4$ prior to use. Methyllithium in THF and Et_2O was prepared by the reaction of $(CH_3)_2Hg$ with excess lithium metal. Both solutions were stored at −78 °C until ready to use. Cuprous iodide was purified by precipitating from an aqueous KI–CuI solution.[7] The precipitated solid was washed with water, ethanol, and diethyl ether and then dried at room temperature under reduced pressure.

Preparation of Reagents in THF. $LiCu_2(CH_3)_3$. Cuprous iodide (1.53 g, 8.05 mmol) was weighed into a 50-ml round-bottom flask in the drybox, then the flask fitted with a rubber septum. The flask was removed from the drybox, connected by means of a needle to a nitrogen bubbler, and 15 ml of THF added to slurry the solid. The slurry was cooled to −78 °C and 15.1 ml of a 0.802 M solution of methyllithium (12.1 mmol) in THF was added to the flask. Within 5 min all the solid had dissolved and a clear, brown solution was present. ^1H NMR at −96 °C showed the solution to contain only $LiCu_2(CH_3)_3$.[2] Analysis of the solution showed Li, Cu, CH_3, and I to be present in a ratio of 1.49:1.00:1.50:1.02.

$LiCu(CH_3)_2$. Cuprous iodide (1.26 g, 6.62 mmol) was allowed to react with 16.5 ml of 0.802 M methyllithium (13.2 mmol) in THF using the same procedure as was used to prepare $LiCu_2(CH_3)_3$ (see above). All the solid dissolved within 1 min to yield a clear, light brown solution. ^1H NMR at −96 °C showed only one signal at δ −15.7, which corresponded to $LiCu(CH_3)_2$. An analysis of the solution showed Li, Cu, CH_3, and I to be present in a ratio of 2.00:1.00:2.12:0.98.

$Li_2Cu(CH_3)_3$. Cuprous iodide (0.80 g, 4.23 mmol) was allowed to react with 19.0 ml of 0.802 M methyllithium (16.9 mmol) in THF using the above procedure for making $LiCu_2(CH_3)_3$. All the solid dissolved within 1 min to yield a clear, colorless solution. ^1H NMR at −96 °C showed the presence of $Li_2Cu(CH_3)_3$ in equilibrium with $LiCu(CH_3)_2$, and CH_3Li [four signals at δ −1.40, −1.57, −1.73, and −2.08 are observed; signals at δ −1.57 and −2.08 are due to $LiCu(CH_3)_2$ and CH_3Li, respectively, while those at δ −1.40 and −1.73 are due to $Li_2Cu(CH_3)_3$]. An analysis of the solution showed Li, Cu, CH_3, and I to be present in a ratio of 3.82:1.00:3.62:0.94.

Preparation of Reagent in Et_2O. $LiCu(CH_3)_2$. Cuprous iodide (0.53 g, 2.79 mmol) was weighed into a 50-ml round-bottom flask in the drybox, then the flask fitted with a rubber spetum. The flask was removed from the drybox and connected by means of a needle to a nitrogen bubbler, and 5 ml of Et_2O added to slurry the solid. The slurry was cooled to −78 °C and 4.4 ml of 1.27 M solution of methyllithium (5.58 mmol) in Et_2O was added to the flask. All the solid dissolved immediately and a clear, colorless solution formed. ^1H NMR at −96 °C showed only $LiCu(CH_3)_2$ to be present. An analysis of the solution showed Li, Cu, CH_3, and I to be present in a ratio of 1.97:1.00:.96:0.95.

$Li_2Cu_3(CH_3)_5$. Cuprous iodide (0.380 g, 2.0 mmol) was allowed to react with 3.5 ml of 0.95 M solution of methyllithium (3.3 mmol) in Et_2O using the same procedure as was used to prepare $LiCu(CH_3)_2$ (see above). Most of the solids dissolved immediately to give a clear, light pink solution, but a small amount of a yellow solid (methylcopper) remained. An analysis of the solution showed Li, Cu, CH_3, and I to be present in a ratio of 5.21:3.00:5.09:3.03. If all of the iodide is assumed to be present as LiI, then the organocopper species would have a Li:Cu:CH_3 ratio of 2.18:3.00:5.09. This indicates the presence of the complex $Li_2Cu_3(CH_3)_5$. This compound was indeed shown to be present by NMR studies.[2]

$Li_2Cu(CH_3)_3$. Cuprous iodide (0.57 g, 2.97 mmol) was allowed to react with 9.36 ml of 1.27 M solution of methyllithium (11.9 mmol) in Et_2O using the same procedure as was used to prepare $LiCu(CH_3)_2$ (see above). All the solid dissolved immediately and a clear, colorless solution remained. ^1H NMR at −96 °C showed $Li_2Cu(CH_3)_3$, $LiCu(CH_3)_2$, and CH_3Li to be present.[2] An Analysis of the solution a showed Li, Cu, CH_3, and I to be present in a ratio of 3.82:1.00:3.88:1.02.

General Reactions of Enones. A 10-ml Erlenmeyer flask with a Teflon-coated magnetic stirring bar was dried in an oven and allowed to cool under nitrogen flush, then sealed with a rubber septum and connected by means of a needle to a nitrogen-filled manifold equipped with a mineral oil filled bubbler. The cuprate reagent (ca. 0.1–0.5 mmol) was syringed into the flask, then the calculated amount of enone (in THF or Et_2O solvent with internal standard, n-$C_{12}H_{26}$ or n-$C_{14}H_{30}$) was added to the stirred reagent. After the designated reaction time, the reaction was quenched by H_2O slowly and dried by $MgSO_4$. A 10-ft 5% Carbowax 20M on Chromosorb W column was used to separate the 1,4 and 1,2 methylation products of enone I (120 °C), enone II (90 °C), enone III (100 °C), enone IV (100 °C), enone V (100 °C), and enone VI (100 °C). Authentic samples of 1,2-addition products were prepared by reaction of the enone with MeLi. The yield percent for each reaction with $LiCu(CH_3)_2$ was normalized by 100% yield = enone recovery % + 1,2 product % + 1,4 product %. The yield percents for other reactions were based on the $LiCu(CH_3)_2$ reaction.

Acknowledgment. We are indebted to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

References and Notes

(1) T. L. Macdonald and W. C. Still, *J. Am. Chem. Soc.*, **97**, 5280 (1975).
(2) E. C. Ashby and J. J. Watkins, *J. Chem. Soc., Chem. Commun.*, in press.
(3) Professor Still has informed us that the reference to low-temperature 1,4 addition of cuprates to isophorone was erroneously included and should be ignored.
(4) W. C. Still and T. L. Macdonald, *Tetrahedron Lett.*, 2659 (1976).
(5) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(6) E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, **51**, 65 (1974).
(7) G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, **7**, 9 (1963).

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

Philip J. Kocienski* and J. M. Ansell

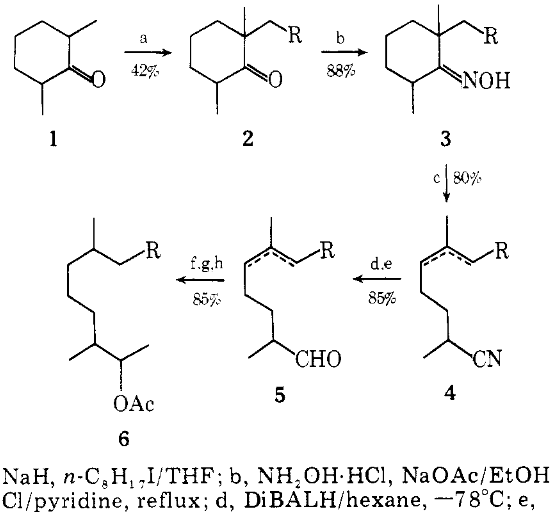
Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

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 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**.

Scheme I



a, NaH, *n*-$C_8H_{17}I$/THF; b, $NH_2OH \cdot HCl$, 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.

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 $NH_2OH \cdot HCl$, 20.6 g (150 mmol) of $NaOAc \cdot 3H_2O$, 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]