

$$\langle \Delta H^2 \rangle = (3/5) \hbar^2 \gamma^2 I(I+1) N \sum_j \sum_k (1/r_{jk})^6 \quad (1)$$

in which  $r_{jk}$  is the separation distance between dipoles  $j$  and  $k$  of magnetogyric ratio  $\gamma$  and spin  $I$ .

In the present case, chemical and physical arguments suggest reasonable models for the CF structure to be infinite arrays of either cyclohexane boats or chairs. This assumption made, one can calculate theoretical  $^{19}\text{F}$  second moments for each structure and compare them with the experimentally measured quantity.

As is illustrated in Table I, the experimental second moment<sup>15</sup> of  $24.2 \pm 1.3 \text{ G}^2$  is consistent only with the boat model of CF. Second-moment values for the chair model are approximately 50% of the measured quantity.

The relatively large difference in second-moment values for the two structures arises from the 1,4 flagpole interaction found only in the boat, in which fluorines separated by 1.63 Å contribute 16.9  $\text{G}^2$  to the theoretical value. Since all fluorines have magnetically equivalent environments, this significant contribution is unaffected by averaging over the complete fluorine array. Only for a case of multiple fluorine environments, as in a hybrid boat-chair structure, would its impact diminish.

If CF does indeed exist in the boat rather than the chair modification, thorough investigation of the X-ray diffraction pattern should reveal the existence of an orthorhombic unit cell with approximate unit cell constants<sup>16</sup>  $a_0 = 2.51$ ,  $b_0 = 5.13$ , and  $c_0 = 6.16 \text{ Å}$  rather than the previously assumed hexagonal cell<sup>16</sup> of  $a_0 = 2.51$  and  $c_0 = 6.16 \text{ Å}$ . Significantly, lines found for CF after tetrahedral anvil pressing<sup>2</sup> at 2.57, 1.72, and 1.29 Å, are assignable as (020), (030), and (040) reflections in the orthorhombic cell.<sup>17</sup> As interconversion of chair and boat forms involves C-F bond rupture, it is reasonable to assume that the boat structure was present both before and after pressing.

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- A Varian 4200 spectrometer interfaced to a PDP 8/e minicomputer through a PAR 129 lock-in amplifier was used for data collection. Double integration using the trapezoidal rule gave a second moment of  $24.2 \pm 1.3 \text{ G}^2$  for  $\text{CF}_{1.06}$  at 8 MHz. Assuming a Gaussian line shape model, we may calculate the second moment directly from the measured line width. For five runs in the frequency range 3.76–16 MHz, we obtain second-moment values of  $18.0 \pm 0.7 \text{ G}^2$  for  $\text{CF}_{1.06}$  and  $20.8 \pm 1.6 \text{ G}^2$  for  $\text{CF}_{1.15}$ .
- We assume a carbon-carbon bond length of 1.54 Å, a carbon-fluorine length of 1.4 Å, tetrahedral coordination about carbon atoms, and an AA stacking of layers. With these assumptions, the value of  $a_0$  must be adjusted to assign the 2.22 Å line in either the orthorhombic or hexago-

nal system. The indexing of (001) reflections is the same in either the orthorhombic or hexagonal system, and, as mentioned,<sup>5</sup>  $c_0$  is a function of fluorine composition.

- Furthermore, if we adjust  $a_0$  to be 2.46 Å (which does not affect (0k0) reflections), we may index the lines<sup>2</sup> at 2.23, 1.86, and 1.64 Å as (110), (102), and (031) reflections in an orthorhombic cell. The remaining line<sup>2</sup> at 3.24 Å is not easily indexed into either a hexagonal or an orthorhombic system within the constraints of AA stacking.
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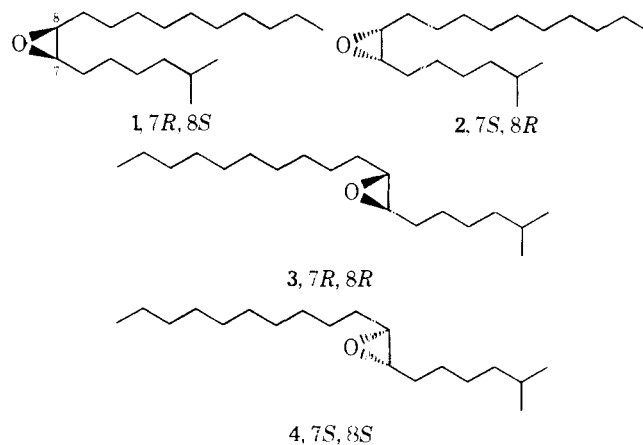
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## Synthesis and Activity of Optically Active Disparlure

Sir:

The plain structure of disparlure, the sex attractant emitted by the female gypsy moth (*Porthetria dispar* (L.)), has been established as *cis*-7,8-epoxy-2-methyloctadecane.<sup>1</sup> The natural pheromone is supposed to be optically active, with its chiral centers at C<sub>7</sub> and C<sub>8</sub>. Its absolute stereochemistry, however, remained obscure, because of the small magnitude of the expected optical rotation and the extremely low yield of the pheromone from the insects. This communication describes the synthesis of both enantiomers of disparlure and its trans analog and also their activity on the male moth, in hopes of determination of the absolute stereochemistry of the natural pheromone.



(*S*)-(+)-Glutamic acid,  $[\alpha]^{23\text{D}} +30.9^\circ$  ( $c$  1.0, 6 *N* HCl), was deaminated with nitrous acid in 1 *N* HCl-acetic acid-water (2:3:4) to give a lactone acid (**6**)<sup>2</sup> (80%). As the deamination reaction proceeds with retention of configuration at the chiral center,<sup>3</sup> **6** should have the *S* configuration (the methyl ester of **6**,  $[\alpha]^{12\text{D}} +14.6^\circ$  ( $c$  1.7, MeOH)). **6** was converted with oxalyl chloride in benzene to the acid chloride (**7**), which was condensed with didecylcadmium to yield a lactone ketone (**8**) (34% overall yield from **6**). Reduction of **8** with  $\text{NaBH}_4$  in methanol afforded a diastereomeric mixture of a lactone alcohol (**9** and **10**) (81%). Each diastereomer was isolated in a completely pure state by preparative tlc (silica gel, ethyl acetate-*n*-hexane) followed by repeated recrystallization (ethyl acetate-petroleum ether). **9** was identified as 5-hydroxypentadecan-4-olide with a 4*S*, 5*S* configuration<sup>4</sup> by the following properties: mp  $66.0^\circ$ ;  $[\alpha]^{20\text{D}} +29.2^\circ$  ( $c$  1.2,  $\text{CHCl}_3$ ); mass  $m/e$  256 ( $M^+$ ); nmr ( $\text{CDCl}_3$ )  $\delta$  4.46 (1 H, m), 3.60 (1 H, bm), 2.92 (bs, OH), 2.58 (2 H, m), 2.24 (2 H, m), 0.89 (3 H, a virtually coupling triplet). Data for **10** (mp  $63.5^\circ$ ;  $[\alpha]^{20\text{D}} +14.8^\circ$  ( $c$  1.2,  $\text{CHCl}_3$ ); mass  $m/e$  256 ( $M^+$ );  $\delta$  4.48 (1 H, m), 3.96 (1 H, bm), 2.60 (2 H, m, and 1 H, OH exchangeable with

Table I. Activity of Synthetic Disparlure, Expressed as the Percentage of Insects Responding to the Pheromone

|  | Concentration (g/ml) |                    |                    |                    |                    |                    |                     |
|--|----------------------|--------------------|--------------------|--------------------|--------------------|--------------------|---------------------|
|  | $1 \times 10^{-4}$   | $1 \times 10^{-5}$ | $1 \times 10^{-6}$ | $1 \times 10^{-7}$ | $1 \times 10^{-8}$ | $1 \times 10^{-9}$ | $1 \times 10^{-10}$ |
| (7 <i>R</i> ,8 <i>S</i> )-(+)-Disparlure |                      | 100                | 100                | 60                 | 60                 | 50                 | 30                  |
| Racemic ( $\pm$ )-disparlure             | 100                  | 80                 | 60                 | 40                 | 0                  | 0                  | 0                   |
| (7 <i>S</i> ,8 <i>R</i> )-(–)-Disparlure | 20                   | 0                  | 0                  |                    |                    |                    |                     |

D<sub>2</sub>O), 2.28 (2 H, m), 0.89 (3 H, a virtually coupling triplet)) showed **10** to be the 5*R* epimer<sup>4</sup> of **9**. Starting from **9** or **10**, the enantiomeric pairs of disparlure (**1** and **2**) and of its trans analog (**3** and **4**) were synthesized.

Tetrahydropyranyl ether (**11**), prepared (78%) from **9**, was reduced with diisobutylaluminum hydride (1.5 equiv) in toluene at  $-78^\circ$  for 30 min to yield a lactol (**13**)<sup>2</sup> (94%). Wittig reaction between **13** and isobutyldenetriphenylphosphorane (3.5 equiv prepared from isobutyltriphenylphosphonium bromide and dimethylsodium) yielded **14**<sup>2</sup> (77%) which, upon hydrogenation (PtO<sub>2</sub> in ethyl acetate) afforded a C<sub>19</sub> compound (**15**)<sup>2</sup> (98%). The three consecutive reactions upon **15**, which were tosylation (*p*-toluenesulfonyl chloride in pyridine), hydrolysis (acetic acid-water-THF (2:1:1), 40°, 5 hr) affording a tosyl alcohol (**16**), and treatment with 0.25 *N* methanolic KOH, produced (7*R*,8*S*)-disparlure (**1**): liquid;  $[\alpha]^{25}_D +0.6 \pm 0.4^\circ$  (*c* 0.8, CCl<sub>4</sub>); nmr  $\delta$  2.92 (2 H, bs; methines on the epoxy ring), 0.87 (9 H; two secondary methyls, d, *J* = 7 Hz, overlapping a virtually coupling methyl) (75% overall yield from **15**). The product showed the nmr, ir, and mass spectra completely identical with those of an authentic specimen of racemic disparlure.<sup>1a</sup> In parallel, **15** was converted into (7*S*,8*R*)-disparlure (**2**) as in the following. Benzylation (benzyl bromide and NaH in benzene) followed by a hydrolytic removal of the THP group gave a benzyl ether alcohol (**17**),<sup>2</sup> which upon tosylation and subsequent catalytic debenzilation (Pd black in ethanol) yielded a tosyl alcohol (**18**).<sup>2</sup> Epoxidation of **18** with 0.25 *N* methanolic KOH gave the desired product **2**: (Scheme I); liquid;  $[\alpha]^{25}_D -0.7 \pm 0.3^\circ$  (*c* 1.1, CCl<sub>4</sub>) (54% overall yield from **15**). The spectral data unequivocally confirmed the structure.

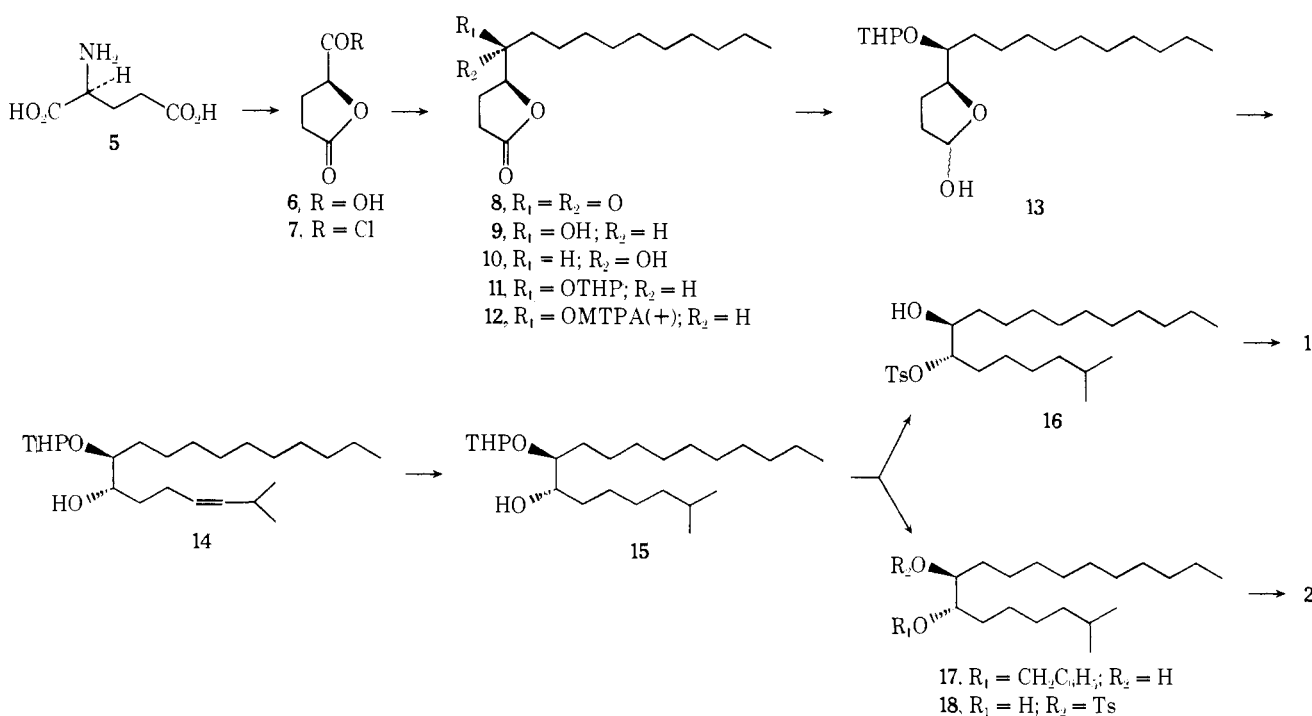
By essentially the same scheme as the one leading to **1**

and **2**, (4*S*,5*S*)-lactone alcohol (**10**) has been converted into an enantiomeric pair of the trans analog of disparlure, *i.e.*, **3** (liquid;  $[\alpha]^{25}_D +27.5 \pm 1.0^\circ$  (*c* 0.5, CCl<sub>4</sub>)) and **4** (liquid;  $[\alpha]^{25}_D -26.6 \pm 0.8^\circ$  (*c* 0.5, CCl<sub>4</sub>)). Spectral data of **3** and **4** were completely identical with each other, showing the following properties: mass *m/e* 282 (M<sup>+</sup>), 264 (M<sup>+</sup> – H<sub>2</sub>O); ir (CCl<sub>4</sub>) 2930, 2860, 1473, 1389, and 1370 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$  2.65 (2 H, bm; methines on the epoxy ring which were shifted to higher field than that of **1**), 1.45 (bm), 1.26 (bs), and 0.86 (9 H, the signals were almost same as those of **1**).

In continuation, the enantiomeric purity of the synthesized compounds was investigated. Since it is a reasonable assumption that no racemization has occurred at any synthetic step later than **9**, the examination was conducted on this compound. It was esterified with (+)- $\alpha$ -methoxy- $\alpha$ -trifluoromethylphenylacetyl (MTPA) chloride<sup>5</sup> in pyridine to the ester (**12**), and, in parallel, the racemized **9** (obtained from the racemized **8** with NaOMe) was similarly esterified. In the nmr spectrum of the latter in CCl<sub>4</sub>, the addition of Eu(DPM)<sub>3</sub> shifted the two  $\alpha$ -methoxyl signals downfield by different degrees, with the shift of the signal of the (4*S*,5*S*) compound ( $\Delta$  1.37 ppm) being smaller than that of the (4*R*,5*R*) diastereomer ( $\Delta$  1.86 ppm) at the reagent/substrate ratio of 0.73 (mole/mole). Under the same conditions, the synthesized **12** was determined to be contaminated with 5.8% of its enantiomer. This percentage represented the enantiomeric ratio in the final products.<sup>6</sup>

The preliminary biological tests were carried out on the Japanese gypsy moth males by two methods. Behavioral observation in the laboratory<sup>7</sup> gave the result shown in Table I, indicating that the synthesized (+)-disparlure was more active than an authentic specimen of racemic disparlure; on

Scheme I



the other hand, the (–) enantiomer showed only weak activity. Similar results were obtained by electroantennogram (EAG) studies.<sup>8</sup> The threshold concentration of the (+) enantiomer was  $1 \times 10^{-7}$  g/ml, which is slightly lower than that of the racemate ( $1 \times 10^{-6}$  g/ml), whereas the (–) enantiomer needed a much higher concentration ( $1 \times 10^{-4}$  g/ml). Interestingly, difference of the activity between both enantiomers is far stronger than the one expected from the enantiomeric composition of synthetic products. The present data, although still preliminary, implicate a chiral receptor system in the olfactory organ of the male insects, and may suggest possibility that the natural pheromone is the (+) enantiomer. Detailed assays will be conducted next summer.

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- (2) Analytical and spectrometric data for all synthetic compounds were in agreement with their structures.
- (3) K. Koga, M. Taniguchi, and S. Yamada, *Tetrahedron Lett.*, 263 (1971).
- (4) Assignment of the absolute stereochemistry on **9** and **10** was done as the result of chemical transformation of the former compound into (7*R*,8*S*)-disparlure, and of the latter into (7*R*,8*R*) trans analog, respectively, through the stereospecific reactions as described in this report.
- (5) J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969).
- (6) The optical purity of **9** was also investigated by converting **9** by oxidation (KMnO<sub>4</sub>) followed by lactonization and methylation into a methyl ester of **6**. Its optical rotation,  $[\alpha]^{25}_D +13.5^\circ$  (*c* 1.39, MeOH), indicated **9** to be contaminated with 4% of its enantiomer.
- (7) The method of B. C. Block (*J. Econ. Entomol.*, **53**, 172 (1960)) was used with a partial modification.
- (8) EAG potentials were recorded from the antenna of a living moth, as in early investigations by D. Schneider (*Z. Vergl. Physiol.*, **40**, 8 (1957)) and by J. Boeckh, H. Sass, and D. R. A. Wharton (*Science*, **168**, 589 (1970)). A glass rod was dipped into a hexane solution of disparlure prepared in the concentrations as shown in the table. Olfactory stimuli were presented by inserting the glass rod into the airstream passing over the antenna of insects.

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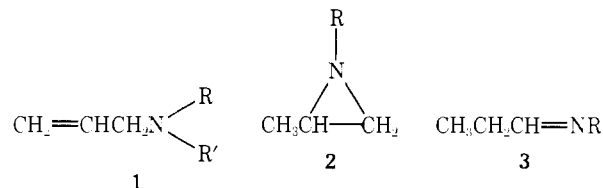
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### Photochemical Transformations. X. Photoreactions of Aliphatic Allylamines<sup>1</sup>

Sir:

In extending our studies<sup>2,3</sup> on the photoreactions of allylic compounds containing heteroatoms, we have discovered several new reactions in the irradiation of allylamines of

general formula **1**. These reactions, which include a new general synthesis of aziridines **2**, are not anticipated from the known photochemistry of simple allylic alcohols, ethers, esters, which are either photoinert (except for cis–trans isomerization) or give hydrogenation products,<sup>3</sup> of allylic halides,<sup>2</sup> or of simple olefins or polyenes.



- a. R = R' = H
- b. R = *n*-Bu; R' = H
- c. R = cyclo-C<sub>6</sub>H<sub>11</sub>; R' = H
- d. R = *t*-Bu; R' = H
- e. R = R' = *n*-Bu

Following the observation<sup>2</sup> that ketones sensitize the photoisomerization of allylic halides to cyclopropyl halides, we attempted similar procedures with allylamine (**1a**) in pentane and in acetonitrile.<sup>4</sup> No isomeric products were formed, but ketone reductions and condensations to give Schiff bases (R<sub>2</sub>C=NCH<sub>2</sub>CH=CH<sub>2</sub>) resulted. No photo-reactions occurred with **1a** in benzene, toluene, or pyridine.

On the other hand, direct irradiation of 0.2 *M* **1a** in cyclohexane (7 hr) or in acetonitrile (6 hr) gave 55 and 31% loss of reactant, forming three products in combined yields of 12 and 23%, respectively.<sup>5</sup> The ratio of the three products was 1:3:3 in both solvents. The minor component was identified as *n*-propylamine (pmr spectrum). The more volatile major product was identified as 2-methylaziridine (**2a**) by nmr and mass spectral comparisons. The third product was not identified, but it was not cyclopropylamine (expected if allylamine behaved analogously to allyl chloride<sup>2</sup>).

Irradiation of a 0.05 *M* solution of *N*-cyclohexylallylamine (**1c**) in cyclohexane gave four products, in combined 61% yield.<sup>6</sup> Loss of **1c** remained nearly constant (quantum yield 0.08) over the first hour (40% loss) but declined thereafter. The product yields were 6:29:14:12. Unlike the latter three, the most volatile component (6% yield) was not basic. It was identified as allylcyclohexane. The 29% product was cyclohexylamine. The 14% yield component was identified as *N*-cyclohexyl-2-methylaziridine (**2c**) by comparison of vpc retention time and ir and nmr spectra to those of an authentic sample.<sup>7</sup> The fourth component was identified as *N*-propylidenecyclohexylamine (**3c**) by comparison of spectral properties (and odor) with those of a sample prepared by condensation of cyclohexylamine and propionaldehyde in anhydrous benzene over 3Å molecular sieves.

Irradiation of **1c** in tetrahydrofuran and acetonitrile gave comparable yields of cyclohexylamine, aziridine **2c**, and Schiff base **3c**. Allylcyclohexane was not produced, but 2-allyltetrahydrofuran was isolated (18% yield) in the THF experiment.

Irradiation of allyl-*n*-butylamine (**1b**) in cyclohexane gave *n*-butylamine, the aziridine **2b**, and the Schiff base **3b**, and that of allyl-*tert*-butylamine (**1d**) in decalin gave *tert*-butylamine, aziridine **2d**, and Schiff base **3d** at rates and with yields comparable to analogous products obtained from **1c**.

When the tertiary amine, *N,N*-di-*n*-butyl-*N*-allylamine (**1e**), which is constitutionally unable to isomerize to aziridine or to Schiff bases by hydrogen migration, was irradiated in cyclohexane (initial  $\phi \sim 0.15$ ), propene,<sup>8</sup> *N*-butylidene-*n*-butylamine,<sup>9</sup> and di-*n*-butylamine<sup>9</sup> were formed in 59, 60, and 40% yields, respectively.

Work has been reported on irradiation of a number of al-