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### The Solvolysis of 5,5-Diphenylcyclononyl *p*-Toluenesulfonate. A Reinvestigation

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Reinvestigation of the acetolysis of 5,5-diphenylcyclononyl tosylate (1) has confirmed the absence of any transannular processes and deamination of the corresponding amine 16 gave a similar result. Tri-fluoroacetolysis of 1 caused extensive transannular hydride migration but no phenyl migration. The former may be due to secondary acid-catalyzed rearrangements.

Une étude concernant l'acétolyse du tosylate du diphényl-5,5 cyclononyle (1) a confirmé l'absence de tout processus *trans* annulaire; la désamination de l'amine 16 correspondante conduit à un résultat similaire. La trifluoroacétolyse de 1 provoque une forte migration *trans* annulaire d'hydrure mais aucune migration de phényle. Ceci peut être dû à une transposition acido catalysée secondaire.

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The facility with which transannular rearrangements occur in medium-sized ring compounds is well documented (1, 2). However, in spite of the efforts made by several groups, the only established case of transannular migration of a group *other than hydride* in such compounds is found in the formation (1%) of 1,5-diphenylcyclooctene from 5,5-diphenylcyclooctyl tosylate in trifluoroacetic acid (3). The lack of other examples is intriguing when considered in the light of data for 1,2-migrations where phenyl migration is a more facile reaction than that involving hydride (4).

A maximum on the graph of total ring strain vs. ring size (5) indicates that a nine-membered ring might be expected to provide the most favorable situation for rearrangement in the medium-ring series. The solvolytic behavior of cyclononyl tosylate has been well investigated (1, 6) and Blomquist and Hallam have reported the kinetics and product distribution obtained from the acetolysis of 5,5-diphenylcyclononyl tosylate (1) (7). It was concluded by these workers

that the latter compound gave no products of transannular rearrangement, nor was anchimeric assistance involved in the reaction. However, the analytical techniques available at the time were such that the presence of a minor component in the solvolysis mixture could have been overlooked. In addition, the effect of solvent on the products formed from 5,5-diphenylcyclooctyl tosylate (3) suggested that a study of the effect of solvent on the solvolysis of 1 would be useful.

Many comparisons have been drawn between deamination and solvolytic reactions (8). The results of these comparisons can be summarized in part by noting that both the ratio of substitution to elimination reactions and the amount of rearrangement are found to be larger in deamination reactions. Further, since bimolecular substitution reactions with medium-ring substrates are slow compared to carbonium ion reactions, and since the only protons in the favorable trans-coplanar arrangement for concerted elimination in the diazonium cation intermediates are sterically inaccessible to an external base, virtually all products in the deamination of medium-ring amines are derived from carbonium ion intermediates (1). In contrast, it has recently

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## CANADIAN JOURNAL OF CHEMISTRY. VOL. 49, 1971 TABLE 1. Percentage yields of products from the reactions of 1 and 16

| Compound | Conditions | 2  | 3  | 4  | 5   | 12 | 13 | 14 | 15 |
|----------|------------|----|----|----|-----|----|----|----|----|
| 1        | HOAc       | 38 | 31 | 15 | 16  |    |    |    |    |
| 1        | TFA*       |    | -  |    | 9   | 47 | 17 | 7  | 15 |
| 16       | HOAc/RONO  | 23 |    | 14 | 46† |    |    |    |    |

\*Buffered with 0.3 M sodium trifluoroacetate. †Analyzed as the acetate; 17% alcohol formed not analyzed.



been noted (9–11) that partitioning of the carbonium ions in solvolysis reactions with E1 mechanisms may vary with the nature of the leaving group. It appears that a substantial portion of the proton removal from the  $\beta$ -carbon is effected by the counter ion, affording a route for elimination which is not available in the deamination reaction. With these concepts in mind we prepared 5,5-diphenylcyclononyl amine (16) and compared the products of its deamination with those of the solvolytic reactions of 1.

Acetolysis of 1 in unbuffered acetic acid for 12 half-lives, followed by hydride reduction of the product according to the original procedure (7) afforded the products shown (Chart 1) in the amounts indicated in Table 1. These were identified by their molecular weights (mass spectra) and spectral characteristics. Gas chromatographic comparison of the acetolysis mixture with an authentic sample of 1,5- and/or 1,6-diphenylcyclononene (6), the expected product of phenyl migration, showed the absence of a detectable amount (1%) of **6** in the mixture. The preparation of **6** from 5-phenylazelanitrile is shown in Chart 2.

Repetition of the experiment in buffered trifluoroacetic gave the products shown in Chart 3. The yields are shown in Table 1. Again, none of the compound 6 could be detected. The results of the deamination of 5,5-diphenylcyclononyl amine (16) in acetic acid are summarized in Chart 4 and Table 1.



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### Discussion

The data on which the distinction between 2, 3, and 4 rest are worthy of some discussion. The n.m.r. spectrum of 4 shows two envelopes centered at  $\delta$  2.2 and 1.5 with relative areas of 8:4. The spectrum of 2 shows more complex and broad absorptions centered at  $\delta$  2.2 and 1.2. The chemical shift of the bulk of the high-field part of the spectrum of 2 suggests that the protons are separated from the olefinic bond and the aromatic nuclei by a larger distance than similar protons in 4. Hence, the structural assignments were made on the basis of the relative symmetry of the two spectra and the chemical shifts of the methylene protons in the two compounds. However, when the signals near  $\delta$  2.2 were irradiated, the olefinic protons in both 2 and 3 collapsed to give singlets whereas 4 afforded two doublets (J = 11 Hz)separated by 17 Hz. It appears that the structural assignments require the reverse to be true. This olefinic non-equivalence can be rationalized by the existence of 4 mainly in an asymmetric conformation, but the same explanation may apply to the case of the methylene protons, in which case the structural assignments for 2 and 3, and 4, must be reversed. The remainder of the structures seem secure on the basis of their spectra.

Because of the known isomerization of olefins by acetic and trifluoroacetic acids, the stability of a mixture of olefins 2, 3, and 4 to the reaction conditions was determined. In acetic acid, very little isomerization was noted, but a significant amount (18%) of addition did occur. The reverse was true in trifluoroacetic acid where little addition, but significant isomerization to 12 and 13 occurred, with concurrent disappearance of 3. Under deamination conditions, 3 was completely isomerized into 2.

It is difficult to draw conclusions from the results in trifluoroacetic acid, since the olefins would be present initially in a homogeneous state in the reactions, whereas the isomerization experiments were heterogeneous throughout. A similar problem has been reported previously (3).

### Conclusion

From the results of these experiments, it seems clear that, at least in acetic acid, the presence of the *gem*-diphenyl moiety restricts the conformations of 1 to those in which *both* hydride and phenyl transannular migrations are unfavorable. This is in agreement with the previous work (7). In trifluoroacetic acid, the results are not so clear with regard to hydride migrations since the olefin stability tests indicate that secondary rearrangements may account for the observed product distribution.

### Experimental

Melting points are uncorrected. The i.r. spectra were obtained on a Beckman IR-12 in 10% (w/w) carbon tetrachloride solution. Unless otherwise noted, n.m.r. spectra were recorded on a Jeolco JNM-C60HL instrument in 10% (w/v) carbon tetrachloride solution and shifts are in  $\delta$  units relative to tetramethylsilane. Small samples were accumulated on a Jeolco JRA-1 spectrum accumulator. The u.v. spectra were recorded on a Beckman DK-1 in cyclohexane. The mass spectra were obtained from Morgan Schaeffer Corp., Montreal. The g.l.c. analyses were carried out on an F and M Model 720 Gas Chromatograph utilizing one of the following columns: A, 10 ft  $\times$  0.25 in. XE-60 (Silicone gum nitrile); B, 6 ft  $\times$  0.25 in. QF-1; C, 6 ft  $\times$  0.25 in. Carbowax 20M; all 10% on 60-80 mesh Chromosorb W. Area measurements were made by planimeter. Except as noted the drying agent was magnesium sulfate. Liquid column chromatography was performed using Fisher certified neutral alumina, Brockman Activity 1 (80-200 mesh). Composition of mixtures are stated in terms of moles unless otherwise noted.

### 5,5-Diphenylcyclononanol

This compound was prepared by the published (7) procedure except that the ketone was purified by chromatography using methylene chloride followed by recrystallization from cyclohexane at  $-20^{\circ}$ .

### 5,5-Diphenylcyclononyl Tosylate (1)

The method of Brown and Ham (12) was used and a yield of 90% based on the alcohol was common, m.p. 102-104°. This compound was relatively unstable and consequently was never heated above 30° nor kept for long periods of time; i.r.: 1360, 1170 (d), 1090 and 885 (br) cm<sup>-1</sup>; n.m.r. (CDCl<sub>3</sub>): 7.50 (4H, q, J = 8), 7.1 (10H, s), 4.70 (1H, m), 2.42 (3H, s), 2.4–0.9 (14H, m).

### Acetolysis of 5,5-Diphenylcyclononyl Tosylate

The tosylate (1.8 g) was dissolved in 108 ml anhydrous

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acetic acid and stirred at 35° for 36 h (12 half-lives) (7). The solvolysis product was quenched with 300 ml cold water and extracted with four 50 ml portions of ether. The combined ether portions were then washed with five 50 ml portions of water, two 40 ml portions of saturated sodium bicarbonate solution, and dried. After filtering and removing the ether there remained 1.16 g of an amber viscous liquid which was dissolved in 50 ml anhydrous ether, 100 mg lithium aluminum hydride added, and the mixture stirred for 3 h. Water (0.5 ml) was added dropwise, followed by magnesium sulfate (1-2 g). The mixture was stirred for 1 h, filtered, and the ether removed leaving 1.03 g of a colorless oil. This was subjected to column chromatography on 70 g alumina using petroleum ether  $(30-60^\circ)$  (1020 ml) as eluent from which 804 mg of a white solid (fraction 1) was obtained. The eluent was then changed to ether (1200 ml) followed by methylene chloride (1200 ml) but gave a combined total of only 39 mg of white solid (fraction 2). Finally three methanol fractions were collected, combined, and the solvent removed. The residue was dissolved in methylene chloride, filtered in order to remove any column residue, and concentrated, to give 191 mg brown oil (fraction 3). The total amount recovered from the column was 1.03 g.

The three fractions were analyzed by g.l.c. on column  $B(175^{\circ})$ . Fraction I consisted only of compounds 2 and 3 (80%) and 4 (20%), while the second fraction contained a small amount of 5 in addition to 2, 3, and 4. Fraction 3 consisted mainly of compound 5 and other small unidentified compounds (total 1%). The overall distribution was 2 + 3 (68%), 4(15%), and 5(16%). Sufficient quantities of 2 and 3, 4, and 5 were collected by g.l.c. (column A) for spectral examination. Fraction I gave only 2 when subjected to gas chromatography on an acid contaminated column C (205°). The n.m.r. of 3 was obtained by subtraction of the portion due to 2a. Compound 5 was shown by comparison of the i.r., n.m.r., and g.l.c. retention times to be identical to 5,5-diphenylcyclononanol.

Compound 2: i.r. 1653 (w), 1580 (w), 725, 700 cm<sup>-1</sup>; n.m.r. 7.18 (10H, s), 5.68 (2H, t, J = 6), 2.5–0.9 (12H, m).

Compound 3: i.r. (in addition to those of 2) 992 cm<sup>-1</sup>; n.m.r. 7.13 (10H, s), 5.45 (2H, m), 2.5–0.8 (12H, m); u.v. (56:44 mixture of 2 and 3)  $\lambda_{max}$  (C<sub>6</sub>H<sub>12</sub>) 270 (log  $\varepsilon$  2.65), 266 sh (2.67), 263 (2.75), 259 (2.78), 254 (2.79), 249 (2.78), 244 (2.75), 218 inf (4.14) mµ; *m/e* 276 (P), 277 (P + 1, 23.2%), and the following additional prominent peaks: 193 (B), 180, 179, 178, 167, 165, 117, 91, 41.

Compound 4: i.r. 1650 (w), 1598, 1580 (w), 700 cm<sup>-1</sup>; n.m.r. 7.17 (10H, s), 6.0–5.0 (2H, m), 2.6–1.1 (12H, m); u.v.  $\lambda_{max}$  (C<sub>6</sub>H<sub>12</sub>) 270 (log  $\epsilon$  2.79), 265 sh (2.82), 263 (2.88), 259 (2.90), 254 (2.90) 249 (2.88), 244 (2.84), 219 inf (4.52) mµ; m/e 276 (P), 277 (P + 1, 23.2%), and the following additional prominent peaks: 205, 193, 181, 180 (B), 179, 178, 167, 165, 129, 115, 103, 91, 77, 41.

# Trifluoroacetolysis of 5,5-Diphenylcyclononyl Tosylate (1)

The tosylate (4 g) was added to 35 ml trifluoroacetic acid (Eastman highest purity) containing 1.43 g (0.3 M) sodium trifluoroacetate and the mixture was stirred at 5° for 23 h. An aliquot taken after 18 h showed virtually no tosylate in the i.r. spectrum. The mixture was poured

cautiously into 500 ml cold saturated sodium bicarbonate solution and extracted with five 50 ml portions of ether. The combined ether portions were washed twice with 25 ml of water, dried, filtered, and concentrated to give 2.16 g of a brown oil (small 1780  $\text{cm}^{-1}$ , trifluoroacetate). This was dissolved in 150 ml dry ether, 0.15 g lithium aluminum hydride was added, and the mixture stirred magnetically for 30 min. After the dropwise addition of 1 ml of water, the solution was stirred for 30 min, a few grams of magnesium sulfate were added, the mixture filtered through Celite, and the solvent removed to give 1.9 g of an amber oil. This was chromatographed on 70 g alumina using pentane as eluent. Fraction 1 (500 ml) was 1.03 g of a yellow oil, which by g.l.c. on column A (180°) consisted of 12, 13, 14, and 15, (65:24:3:8). Over the next ten 100 ml fractions methylene chloride was added gradually up to 5% by volume and these fractions combined to give 0.31 g yellow oil (fraction 2), which by g.l.c. consisted mainly of the same four compounds in the ratio 30:10:20:37 and a few other peaks (all < 1%). The eluent was then changed to 10:1 ether-methanol to give 0.36 g of a brown oil (fraction 3), which by g.l.c. consisted of mainly 14 and 15 (7 and 17%, respectively) and 45% 5. The total recovery was 1.70 g with the following composition: 12 (47%), 13 (17%), 15 (15%), 5 (9%), with the remainder totalling a maximum of 5% (all individually less than 1%). None of compound 6 could be detected. Sufficient quantities of compounds 12 to 15 were collected for spectral analysis:

Compound 12: i.r., 1598, 1572 (w), 702 cm<sup>-1</sup>: n.m.r. 7.01 (10H, s), 2.66 (4H, m), 1.67 (10H, br s); u.v.  $\lambda_{max}$ (C<sub>6</sub>H<sub>12</sub>) 246 sh (log  $\varepsilon$  3.97) mµ; *m/e* 276 (P), 277 (P + 1, 23.4%), and the following prominent peaks: 115, 105, 91 (B), 77.

Compound 13: i.r., 1600, 1585 (w), 1575 (w), 703 cm<sup>-1</sup>; n.m.r. 7.22 (10H, s), 2.19 (4H, s), 1.48 (10H, br s); u.v.  $\lambda_{max}$  (C<sub>6</sub>H<sub>12</sub>) 245 sh (log  $\varepsilon$  3.68) mµ.

Compound 14: i.r. 1599, 1584 (w), 1574 (w) 702 cm<sup>-1</sup>; n.m.r. 7.13 and 7.00 (10H), 5.79 (1H, t, J = 8.6), 4.22 (1H, m), 2.47 (2H, m), 1.71 (10H, br s); u.v.  $\lambda_{max}$  (C<sub>6</sub>H<sub>12</sub>) 238 sh (log  $\varepsilon$  3.74) mµ; *m/e* 276 (P), 277 (P + 1, 23.1%), and the following additional prominent peaks: 205, 129, 117, 115, 91 (B).

Compound 15: i.r. 1600, 702 cm<sup>-1</sup>; n.m.r. 7.25 (10H, s), 5.85 (1H, d, J = 10), 3.30 (1H, m), 2.3 and 1.68 (12H); u.v.  $\lambda_{max}$  (C<sub>6</sub>H<sub>12</sub>) 274 (log  $\varepsilon$  3.09), 2.67 (3.11), 260 (3.06), 254 (2.97), 224 inf (4.09) mµ; m/e 276 (P), 277 (P + 1, 23.4%), and the following additional prominent peaks: 205, 192, 179, 115, 91 (B).

### 5,5-Dipkenyleyclononylamine (16)

Hydrogenation of the oxime of 5,5-diphenylcyclononanone was extremely slow, while reduction with lithium aluminum hydride gave mainly a secondary amine. To 6.2 g tosylate 1 dissolved in 120 ml dry dimethylsulfoxide was added 1.7 g sodium azide. The solution was stirred magnetically for 5 days at room temperature, poured into 250 ml cold water, and extracted with four 50 ml portions of ether. The combined ether portions were washed in turn with four 25 ml portions of water, dried over sodium sulfate, filtered, and concentrated to give 3.5 g of azide (i.r. 2100 cm<sup>-1</sup>). This was dissolved in 150 ml dry tetrahydrofuran, 2.0 g lithium aluminum hydride added, and the mixture heated to reflux for 2 h,

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then left stirring overnight. After the addition of 2 ml of water, 2 ml of 15% sodium hydroxide was added, followed by 6 ml of water. The resulting solid was filtered and the filtrate dried with sodium sulfate. After removal of solvent there remained 3.6 g of a colorless viscous oil. This was dissolved in 40 ml 95% ethanol and 80 ml of a saturated ethanolic picric acid solution added. The solution was heated to reflux, left overnight, and the picrate filtered and dried (dec. 236–238°).

Anal. Calcd. for  $C_{27}H_{30}N_4O_7$ : C, 62.06; H, 5.79; N, 10.72. Found: C, 62.15; H, 5.72; N, 10.60.

The picrate was dissolved in 400 ml of 5% sodium hydroxide solution (heated) and the amine extracted with three 100 ml portions of ether. The ether fractions were combined and washed with a small portion of 5% sodium hydroxide solution, then passed through about 50 g Rexyn 201 ion exchange resin, followed by 200 ml of ether. The ether solution was dried with sodium sulfate, filtered, and concentrated. The pure amine was dried under reduced pressure at  $100^{\circ}$  in a drying tube to give 1.45 g white solid, m.p. 95–96°, which turned brown on exposure to air. The overall yield was 38%, i.r.  $3320 \text{ cm}^{-1}$ ; n.m.r. 7.27 (10H, s), 2.73 (s, 10), 3.7 (1H, m), 2.6–0.5 (16H, m).

Anal. Calcd. for  $C_{21}H_{27}N$ : C, 85.95; H, 9.27. Found: C, 85.73; H, 8.99.

Acetamide: m.p.  $233-235^{\circ}$  (from ethyl acetate – cyclohexane). i.r. (KBr) 3280, 2940, 1640, 1560, 1490, 1450, 750, 705 cm<sup>-1</sup>; *m/e* 335 (P), 276, 206, 205, 193, 168, 167, 166, 140, 129, 127, 117, 115, 114, 100, 91 (B), 70, 60, 57, 56, 44, 43.

Anal. Calcd. for C<sub>23</sub>H<sub>29</sub>NO: C, 82.34; H, 8.71; N, 4.17. Found: C, 82.30; H, 8.49; N, 4.39.

### Deamination of 5,5-Diphenylcyclononylamine

An attempt with sodium nitrite and trifluoroacetic acid gave large amounts of aromatic nitration (i.r., strong 1525 and 1350 cm<sup>-1</sup>), possibly from the dinitrogen tetroxide produced. Substitution of isoamyl nitrite in trifluoroacetic acid gave an unknown solid, m.p. 190-195°, with a large increase in weight and no olefin after an hour at reflux. Hence glacial acetic acid was used. Amine 16 (0.54 g) was dissolved in 10 ml glacial acid in a 25 ml two-neck flask equipped with a septum and condenser with calcium chloride drying tube. Using a syringe, 290 µl (1.1 equiv) of freshly distilled isoamyl nitrite was added and the solution heated at reflux (bath 130°) with magnetic stirring for 5 h, then cooled and left stirring overnight. The solution was poured into 25 ml cold water, extracted with three 25 ml portions of ether, which in turn were combined and washed with two portions of water and saturated sodium bicarbonate solution, then dried. After filtration and ether removal there remained 0.8 g of a brown viscous oil (i.r., strong 1735 cm<sup>-1</sup>). This was chromatographed on 40 g alumina. Fraction 1 (petroleum ether, 560 ml) gave 0.17 g of amber product which by g.l.c. (column A) and n.m.r. was shown to be a 62:38 mixture of compounds 2 and 4. While slowly increasing the amount of methylene chloride up to 50%, 1050 ml were collected to give 0.25 g of an amber oil, which was identical by i.r. and n.m.r. (mixed with authentic) to 5,5-diphenylcyclononyl acetate (7) (decomposed under g.l.c. conditions). Recrystallization from petroleum ether (30-60°) gave the acetate as a white solid, m.p.  $98-100^{\circ}$ , (undepressed with authentic material). Elution with pure methylene chloride (350 ml) gave 0.1 g brown oil which by i.r. and n.m.r. was shown to be a 50:50 mixture (80:20 by weight) of 5,5-diphenyl-cyclononanol 5 and isoamyl alcohol. Hence, the overall yield was 0.50 g which consisted of 37% olefin, 46% acetate, and 17% alcohol.

### 5-Phenylazelanitrile (7)

This compound was synthesized by the method of Cope and Kinnel (13) using the reported dimethylsulfoxide method of nitrile synthesis rather than refluxing ethanol.

### Dimethyl 5-Phenylazelate (8)

The dinitrile 17 (23 g) was hydrolyzed by heating at reflux for 16 h in 200 ml concentrated hydrochloric acid. The cooled solution was made basic with 15% sodium hydroxide, extracted with several portions of ether, then acidified to pH 2.

Extraction with ether gave 25 g of an amber liquid which was dissolved in 175 ml methanol and heated at reflux for 6 h in the presence of 10 ml concentrated sulfuric acid. The cooled solution was poured into water and extracted with three 150 ml portions of ether. The combined ethereal extracts were washed with saturated brine, dried, and evaporated. The residue was distilled and the fraction boiling from  $185-191^{\circ}$  (2.5 mm) was collected ( $n_{\rm D}^{23} = 1.4950$ ) to give diester **8** (21.4 g) in 67% yield.

### 5-Phenylcyclononanone (10)

Diester 8 (15.8 g) was cyclized in the same manner used in the preparation of 1 (7). The crude acyloin 9 (2.6 g) was isolated by distillation (b.p.  $149-158^{\circ}$  (0.2 mm)). This material was reduced by the same method used in the preparation of 1 and the product purified by column chromatography on 50 g of alumina. Elution with petroleum ether gave 0.4 g of hydrocarbon. The solvent was then changed gradually to pure methylene chloride and elution continued until a dark band was about to be eluted. Concentration of the fraction gave 0.6 g of a brown liquid which was purified by g.l.c. collection (8 ft × 0.5 in. 10% XE-60, 230°). The ketone 10 (0.34 g) was obtained in 3% yield from diester 8. i.r.: 1704 cm<sup>-1</sup>; n.m.r. 7.21 (5H, s), 2.43 (5H, m), 1.80 (10H, m).

Anal. Calcd. for  $C_{15}H_{20}O$ : C, 83.28; H, 9.32. Found: C, 82.98; H, 9.23.

### 1,5-(1,6)-Diphenylcyclononene (6)

To a solution of phenyl lithium prepared from 0.8 g each of bromobenzene and lithium wire (high sodium content) in 10 ml dry ether, 0.3 g of ketone **10** in 5 ml dry ether was added slowly. The solution was heated at reflux for 1 h, cooled and stirred for 2 h, then 15 ml water added. The aqueous layer was separated, extracted twice with 15 ml of ether, and the combined organic phases dried over sodium sulfate. After filtration and solvent removal there remained 0.5 g of a brown oil (i.r., strong OH), which was dissolved in 100 ml dry benzene containing a few crystals of iodine. The solution was heated at reflux for 26 h under a Dean–Stark water trap, then cooled and washed with 10 ml of saturated sodium thiosulfate solution, two 5 ml water portions,

and dried over sodium sulfate. The brown liquid (0.4 g) obtained was purified by preparative g.l.c. (8 ft  $\times$  0.50 in. 10% SE-30, 225°). The olefin had a retention time of about 40 min.

Compound 6: i.r. 1665 (w), 1642 (w), 1600, 701 cm<sup>-1</sup>; n.m.r. 7.27 and 7.13 (10H). 5.85 (1H, t, J = 8.6), 3.0–2.1 (5H, m), 1.70 (8H, m); u.v.  $\lambda_{max}$  (C<sub>6</sub>H<sub>12</sub>) 293 inf (log  $\varepsilon$  2.31), 241 (3.86) mµ.

Anal. Calcd. for C<sub>21</sub>H<sub>24</sub>: C, 91.25; H, 8.75. Found: C, 90.98; H, 8.73.

### Olefin Stability Tests

To 1.8 ml trifluoroacetic acid containing 70 mg (0.3 M) sodium trifluoroacetate and 80 mg p-toluenesulfonic acid (1 equiv) was added 100 mg of an olefin mixture consisting of 45% 2, 45% 3, and 10% 4. This was stirred in a sealed vial for 23 h at 5° (heterogeneous throughout), poured into 15 ml saturated sodium bicarbonate solution, and extracted with ether. The ether layers were washed with water and dried over sodium sulfate. After filtration and solvent removal, the residue (i.r. small 1780 cm<sup>-1</sup>) was shown by g.l.c. to consist of 27% 12, 8% 13, 54% 2 (no 3 in i.r.), and 11% 4. Small amounts of 14 and 15 would have been obscured under the last two peaks and hence could not be detected.

After heating the same olefin mixture in 1 ml of glacial acetic acid containing 35 mg (1 equiv) *p*-toluenesulfonic acid at  $35^{\circ}$  for 35 h, the solution was worked-up in analogous manner. By i.r. and n.m.r. comparison of a mixture of known concentration, the product was estimated to contain 18% (23% by weight) of the acetate of 1.

About 20 mg of the olefin **6** was dissolved 0.5 ml glacial acetic acid with 19  $\mu$ l isoamyl nitrite, and the solution heated at reflux (130°) for 5 h, then left stirring overnight. After an identical work-up to that of the deamination product, the residue (i.r., strong 1740 cm<sup>-1</sup>, acetate) was estimated by n.m.r. to be about 35% of the mixture.

Treatment of a 42 mg sample of the same olefin mixture used in the trifluoroacetolysis test in the same manner as the olefin 6 above resulted in complete isomerization of 3 to 2 (no 3 detectable by i.r. nor n.m.r.), with the formation of only a small amount of acetate. The financial assistance from the National Research Council of Canada is gratefully acknowledged. We also thank Mr. D. Hill for technical assistance.

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