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2. N. Fusetani and K. Hashimoto, *Nippon Suisan Gakkaishi*, **50**, 465 (1984).
3. The ^{13}C NMR(22.5 MHz, CD_3OD, δ_c) data for fatty acid moiety of GV-5(**1**) are as follows: 174.9(s), 174.7(s), 174 (s), 131.4(d), 131.0(d), 130.9(d), 130.1(d), 129.6(d), 129.3 (d), 129.1(d), 128.9(d), 35.3(t), 35.1(t), 34.7(t), 34.5(t), 33.2(t), 32.8(t), 30.9(t), 30.8(t), 30.6(t), 30.4(t), 28.4(t), 27.7(t), 26.8(t), 26.2(t), 26.1(t), 23.9(t), 23.8(t), 14.8(q).
4. T. Taniyama, Ph. D. Dissertation, Graduate School, Osaka University, Osaka 565, Japan, 1988. The structure of the glyceroglycolipid is 1-O-β-D-galactopyranosyl-2′,3′-di-O-acyl-D-glycerol[acyl: linolenate (90%), linolate(8%), palmitate(2%)].
5. H. Kikuchi, Y. Tsukitani, T. Manda, T. Fujii, H. Nakanishi, M. Kobayashi, and I. Kitagawa, *Chem. Pharm. Bull.*, **30**, 3544 (1982), and the structure of the M-5 is 1-O-β-D-galactopyranosyl-2′,3′-di-O-acyl-D-glycerol[acyl; myristate: 8-hexadecenoate: palmitate = 1:10:10).
6. TMS-glycerol and methyl TMS-galactoside were identified by direct GLC comparisons (2% SE-30 on Chromosorb WAW DMCS, 80-100 mesh, 3 mm × 2 m) with authentic samples: TMS-glycerol [column temp. 120°C, carrier gas N_2 at flow rate 25 ml/min., t_R(min.) = 5′18″] and methyl TMS-galactoside [column temp. 170°C, N_2 at flow rate 30 ml/min., t_R(min.) = 8′23″, 9′39″, 11′01″].
7. ^{13}C NMR data (22.5 MHz, D_2O-CD_3OD = 2:1, δ_c) of **2**: 104.4(C-1), 72.1(C-2), 74.0(C-3), 69.9(C-4), 76.4(C-5), 62.2(C-6), 63.6(C-1′), 71.7(C-2′), 71.9(C-3′).
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9. A mixture of fatty acid methyl esters was identified by direct GLC comparison (15% polyethylene glycol succinate on Chromosorb WAW DMCS, 80-100 mesh, 3 mm × 2 m, column temp. 210°C, carrier gas N_2 at flow rate 35 ml/min.) with authentic samples and its ratio was obtained by comparison of peak area for each of the fatty acid methyl esters: t_R(min.) = **a** 2′23″, **b** 4′14″, **c** 11′01″; **a:b:c** = 4:1:9.
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11. GV-4; ^1H NMR(90 MHz, $CDCl_3$, δ): 5.37(triplet like, olefinic protons) 1.26(methylene protons), 0.89(a deformed triplet, terminal methyl protons), ^{13}C NMR (22.5 MHz, $CDCl_3$, δ_c): 180.1(br.s), 130.5(d), 129.2(d), 128.8(d), 128.7(d), 128.3(d), 128.2(d), 127.9(d), 127.6(d), 34.1(t), 33.5(t), 32.0(t), 31.6(t), 29.8(t), 29.4(t), 29.2(t), 27.3(t), 26.6(t), 25.7(t), 24.8(t), 24.6(t), 22.6(t), 14.1(q), and methyl ester of GV-4; ^1H NMR(90 MHz, $CDCl_3$, δ): 5.35(triplet like, olefinic protons), 3.65(s), 1.25(methylene protons), 0.88 (a deformed triplet, terminal methyl protons).
12. Analytical conditions for GLC were the same as described in that of a mixture of fatty acid methyl esters of GV-5[9]: t_R(min.) = **a** 2′24″, **b** 4′19″, **c** 11′03″; **a: b: c** = 2:1:6.
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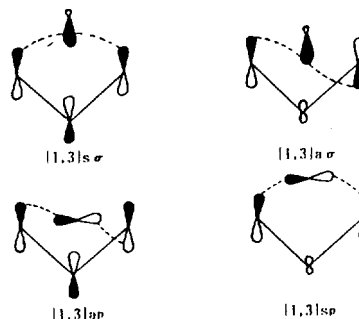
Theoretical Studies on [1,3] Sigmatropic Group Rearrangements[1]

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Sigmatropic rearrangements are not confined to hydrogen atoms.[1,2] Groups of nearly every type have been found to migrate. We report here semiempirical MO theoretical results on the course of such reactions involving migrating groups with lone pairs(F, OH, NH_2, SH, Cl) and those which can migrate by either σ- or p-type interactions (CH_3, NO) between 1,3-2p orbitals of propenyl system. Four types of orbital interactions can be envisaged, since both σ and p type can interact either suprafacially(s) or antarafacially(a) (Scheme 1).

[1,3]sσ [1,3]aσ

[1,3]ap [1,3]sp

Scheme 1

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Table 1. Energy Barriers (ΔH_f : kcal / mol) and Types of 1,3-Sigmatropic Group Rearrangements Investigated in This Work

| X | Method | | Type[a] |
	AM1	MNDO	
CH_3	106.51	123.37	sp
NH_2	75.57	59.01	sp
OH	78.51	82.42	sσ
CN	102.25	91.93	aσ
NO	68.32	53.26	sp,sσ
F	---	102.79	aσ
Cl	---	56.15	sσ
SH	---	57.53	Sσ

[a] s, a, σ, and p denote suprafacial, antarafacial, sigma, and p-type interactions respectively.

Obviously the σ type should result in retention whereas the p type should give inversion of configuration at the migrating group. For neutral, four electron systems, only [1,3] aσ and [1,3] sp shifts are allowed according to the orbital symmetry rules,[3] since normally the interactions are between propenyl-HOMO and migrating group-LUMO in terms of frontier orbital (FMO) theory.[4]

Our MNDO[5,7] and AM1[6,7] computations on the transition states for 1,3-shifts of eight groups have shown that (i) antarafacial processes are sterically unfavorable so that suprafacial processes are favored for relatively large migrating groups ([1,3]sp for CH_3 group), (ii) if a lone pair (nonbonding) level is high compared with the nonbonding level (HOMO) of the propenyl system, the lone pair participate in the migration so that six electrons are involved in the [1,3] shift, for which propenyl-LUMO and migrating group-HOMO interactions become dominant and allowed processes change to [1,3]sσ and [1,3]ap ([1,3]sσ for OH, Cl, and SH groups), and (iii) the activation energy barriers were found to decrease in the order CH_3>F>CN>OH>NH_2>SH $\cong$ Cl>NO (Table 1).

Normal four electron [1,3]aσ process was followed only by CN group, while NO exhibited both aspects of σ- and p-type interactions. Symmetry forbidden processes were found to take place for the two 6 electron systems involving NH_2 and F groups; the former has a p-type lone pair so that it should proceed by [1,3]ap, but due to the large steric repulsion of two H atoms it was forced to go through [1,3]sp, whereas the latter, having a rather low lying lone pair, gave [1,3]a σ i.e., behaved like a four electron system.

We conclude that in [1,3]group rearrangements antarafa-

cial process is always sterically unfavorable and the lone pairs can participate in σ and p type shifts providing two extra electrons to the system so that selection rules can also change.

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