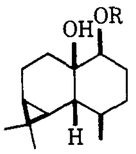
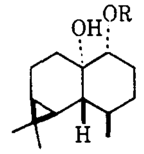
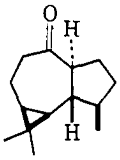
The tosylate **11**, mp 135–136°, [α]D −12° ($\mathrm{CHCl_3}$), prepared from the isomeric diol **10**, has nmr absorption at δ 0.89 (3 H, doublet, J = 6 cps), while the corresponding methyl doublets are present at δ 1.18 in the diol **8** and at δ 1.15 in the tosylate **9**, respectively. The paramagnetic shifts observed[10] in the latter two compounds demand a 1,3-*cis*-diaxial relationship between methyl and tertiary hydroxyl groups, and this is only possible if the major glycol is the *cis*-decalin **8** and the minor glycol the *trans*-decalin **10**. Rearrangement of the tosylate **11** with 1 equiv of potassium *t*-butoxide in *t*-amyl alcohol followed by immediate condensation of the sensitive ketone with methylenetriphenylphosphorane gave a new hydrocarbon **14**, [α]D −40° ($\mathrm{CHCl_3}$).


8, R=H
9, R=$\mathrm{C_7H_7SO_2}$


10 R=H
11, R=$\mathrm{C_7H_7SO_2}$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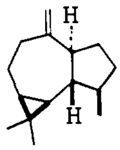
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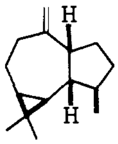
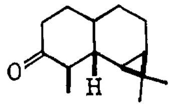

14

In another series of reactions the tricyclic ketone **15**[11] was transformed to the mesylate **16** which on exposure to potassium *t*-butoxide in hot *t*-butyl alcohol afforded a mixture of isomeric olefins from which epi-alloaromadendrene (**17**), [α]D +42° (EtOH), could be isolated by vapor phase chromatography.[12] The two enantiomers **14** and **17** were identical in vapor chromatographic behavior and infrared and mass spectra. This alternate synthesis left no doubt that the synthetic hydrocarbons **13** and **14** as well as their precursors have the configurations indicated, and as a corollary the previously proposed[1,2,7] stereochemistry of aromadendrene required revision. To provide new evidence on this point it was decided to synthesize hydrocarbon **22**.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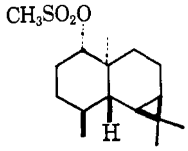
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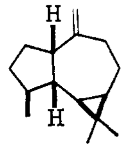
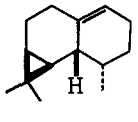

17

The tricyclic aldehyde **5** was transformed to the corresponding hydrocarbon **18** (77%), [α]D −188° ($\mathrm{CHCl_3}$), by the sequence of reactions already used for the preparation of its epimer **7**. Oxidation with osmium tetroxide yielded a single diol **19** (86%), mp 124.5–125.5°, [α]D −9° ($\mathrm{CHCl_3}$), which was converted to the tosylate **20** (89%), mp 129.5–130.5°, [α]D −21° ($\mathrm{CHCl_3}$). The nmr spectra of both diol **19** and tosylate **20** reveal normally shielded secondary methyl groups (doublets at δ 0.87 and 0.83, respectively) demanding the presence of *cis*-decalins. When a solution of the tosylate **20** in chloroform was allowed to remain in contact with activated alumina, the ketone **21**, mp 82.5–83.5°, [α]D +4° ($\mathrm{CHCl_3}$), was formed quantitatively. Its infrared and mass spectra were identical with those of apoaromadendrone, [α]D −4° ($\mathrm{CHCl_3}$), and the two compounds were not separable by chromatographic techniques. When the tosylate **20** was rearranged by treatment with 1 equiv of potassium *t*-butoxide in *t*-butyl alcohol-OD, the resulting ketone **21** contained only 8.5% of one deuterium atom, thus confirming the presence of a substituted *trans*-bicyclo[5.3.0]decane. Condensation of the synthetic ketone **21** with methylenetriphenylphosphorane gave (−)-aromadendrene (**22**), [α]D −11° (EtOH), whose infrared and mass spectra were indistinguishable from those of aromadendrene, [α]D +9° (EtOH).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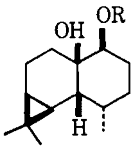
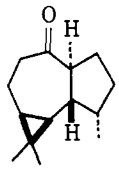

19, R=H
20, R=$\mathrm{C_7H_7SO_2}$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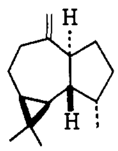
22

The synthesis just described leaves no doubt that natural aromadendrene is actually the C-4 epimer of structure **1**, but the source of error in the earlier deductions[1,2,7] has not yet been identified.

Acknowledgment. We are indebted to the National Institutes of Health (GM 09686) and to Firmenich & Cie, Geneva, for generous financial support.

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(10) R. F. Zürcher, *Helv. Chim. Acta*, **46**, 2054 (1963).

(11) R. B. Bates, G. Büchi, T. Matsuura, and R. R. Shaffer, *J. Am. Chem. Soc.*, **82**, 2327 (1960).

(12) G. Büchi, J. Kagan, T. Mukai, and A. Zschocke, to be published.

(13) National Institutes of Health Postdoctoral Fellow, 1964–1966.

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Received August 1, 1966

Organic Photochemistry. XVII.[1] Competition between Phenyl Migration, Type A Skeletal Rearrangement, and a New Rearrangement in 4,5-Diphenylcyclohexenone

Sir:

Two general types of photochemical cyclohexenone rearrangements are known. The first, conveniently termed "type A,"[2] involves skeletal change (note eq

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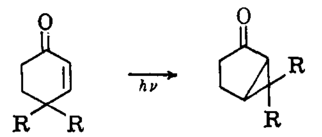
(1) For paper XVI of the series note H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Am. Chem. Soc.*, in press.

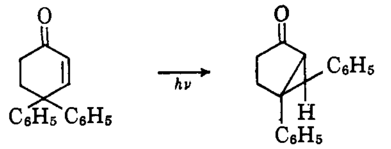
(2) (a) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 159 (1966); (b) *ibid.*, **88**, 1965 (1966).

1). Gardner,[3] Chapman,[4] Jeger,[5] and Zimmerman[2] and their co-workers have provided examples. Although skeletally similar to the rearrangement of dienones, the type A transformation of enones is an inefficient process relative to the dienone rearrangement.[2]



(1)

We reported the second rearrangement which proceeds with phenyl migration.[6]



(2)

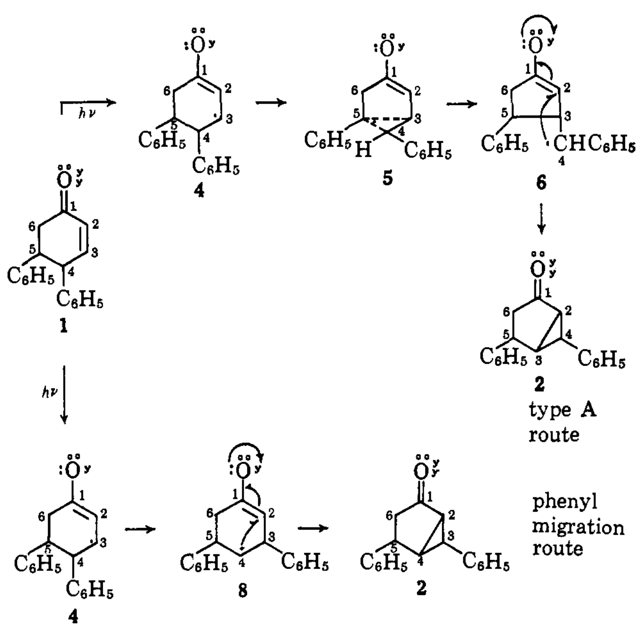
The case of 4,5-diphenylcyclohexenone seemed worthy of investigation since either type A or phenyl migration rearrangements were *a priori* possibilities. Our studies (a) cast light on the factors controlling the relative efficiencies of the competing processes and (b) led to observation of a third and new rearrangement of intrinsic and mechanistic interest.

4,5-Diphenylcyclohexenone (**1**), mp 97.0–97.5°, was synthesized.[7] On irradiation in *t*-butyl alcohol it gave 40–45% of 4,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**), mp 90.0–90.5°, and 8–10% of 2-(*cis*-styryl)-3-phenylcyclobutanone (**3**), mp 65.0–66.0°. The structures of **2** and **3** were established by spectral and degradative evidence.[7]

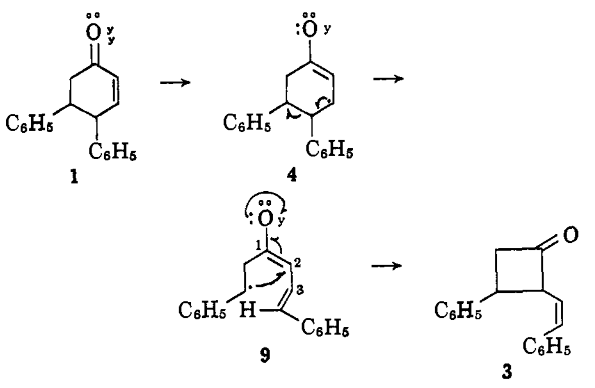
As is apparent from Chart I, both a type A rearrangement and the phenyl migration route lead to the same product, **2**. However, a skeletal difference exists. The type A reaction interchanges C-3 and C-4 (cyclohexane numbering for consistency) of the six ring while with phenyl migration no such skeletal change occurs. Enone **1** was labeled at C-3 and, after photolysis in ethanol,[8] photoketone **2** was subjected to a degradation which disected C-3 of the six ring as benzaldehyde and C-4 as iodoform. The radiocarbon was found 1.39 ± 0.03% in the benzaldehyde and 98.61 ± 0.03% in the iodoform. This shows that the reaction goes mainly by the type A route (98.6%) and to a small but real (1.4%) extent by the phenyl migration mechanism.

In sensitized runs in which the acetophenone was calculated to absorb at least 96% of the light, the same product distribution was observed. The enone concentration, 0.002 *M*, was sufficiently low that acetophenone singlet could not survive long enough to collide with enone molecules and excite these to enone singlets but sufficiently large to allow acetophenone triplets to collide with enone prior to decay. These results showed that photoketone **2** and the cyclobutanone **3** were triplet-state photochemical products, for it would be exceedingly fortuitous for two different excited states to give the same product distribution.

Chart I



The photochemical reaction forming 2-(*cis*-styryl)-3-phenylcyclobutanone (**3**) is a mechanistically plausible process using reasoning of the type outlined by us earlier.[9] We note that after ring opening[10] of the n–π* excited state (note eq 3) attack of the odd electron center of C-5 on C-2 rather than on C-3 affords the cyclobutanone photoproduct **3**.



(3)

We find four factors contributing to the preference for type A rearrangement by 4,5-diphenylcyclohexenone relative to the preference for phenyl migration exhibited by the 4,4-diphenyl isomer.[6] First, inspection of Chart I reveals that the phenyl migration route leads, after migration, to **8**, in which the odd electron is localized[11] on C-4. In the 4,4-diphenylcyclohexenone example a phenyl group remains behind to delocalize the odd

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[3] W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Am. Chem. Soc.*, **84**, 2268 (1962).

[4] O. L. Chapman, T. A. Rettig, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963).

[5] B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963).

[6] H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964).

[7] The syntheses and degradations will be reported in our full paper; acceptable analyses were obtained on all compounds.

[8] The photolysis in ethanol gave 20–25% of photoketone **2** together with ethoxy- and hydroxyethylethanol adducts, some of which were isolated. No photoisomer **3** was obtained.

[9] (a) H. E. Zimmerman, 17th National Organic Chemistry Symposium, Bloomington, Ind., 1961, Abstracts, p 31; (b) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (c) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); **84**, 4527 (1962).

[10] It is possible that species **9** is never engendered with C-5 free but rather that C-5 slithers along from C-4 to C-3 to C-2 where it is firmly bound.

[11] This is an oversimplification. 2,4 Bonding seems likely to be concerted with generation of this species.

electron. This effect must be felt to some extent at the beginning of rearrangement with a lowering of the potential energy surface. Second, there is more relief of strain by migration of one of the geminal phenyl groups of the 4,4-diphenyl enone. Third, in the 4,4-diphenyl enone at least one phenyl group is axial and in a conformation to migrate; the 4,5 isomer appears to be *trans* and has no axial group. The fourth factor is the extra delocalization of the odd electron by the phenyl at C-5 of species **5** (or **9**). It is probably this extra stabilization which gives species **5** (or **9**) the possibility of migration beyond C-3 to C-2, leading to the cyclobutanone product.

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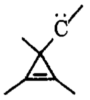
Received June 10, 1966

A Cyclopropenylcarbene–Cyclobutadiene Rearrangement[1]

Sir:

Recently there has been much interest in derivatives of cyclopropenylcarbene (I) because of the apparent use of such molecules as possible precursors to the as yet unknown tricyclo[1.1.0.0^{2,4}]butane system.[2] We wish to report the formation of the chlorotrimethylcyclopropenylcarbenoid V and its rearrangement to a transient cyclobutadiene derivative.

Trimethylcyclopropenium chloride (III), prepared by photolysis of the readily available 3H-pyrazole (II)[3] followed by treatment with anhydrous hydrogen chloride, was allowed to react with a suspension of dichloromethyllithium[4] in tetrahydrofuran at −100°. Treatment of the resulting 3-dichloromethyl-1,2,3-trimethylcyclopropene (IV) with *n*-butyllithium in ether at −20° gave a mixture of four isomeric compounds in 85% yield. Separation by chromatography and examination of the ultraviolet (only end absorption at 210 mμ), infrared, mass, and nmr spectra led to an unambiguous assignment of the tricyclooctadiene ring structure to all four compounds. The number of nonequivalent sets of methyl groups in each isomer was determined by nmr in two different solvents. This information together with the observed long-range coupling between methyl groups attached to the same double bond narrows down the structure assignments to the alternatives listed in Table I. The infrared spectra, which showed weak absorptions for dimethyl-substituted double bonds at 1680 cm^{-1} and stronger bands at 1660 cm^{-1} originating from double bonds with chlorine substitution, confirmed the assignment. With the available data it is impossible to distinguish between the two alternatives in each substitution group as well as to assign either *syn* or *anti* structures to the dimers.[5]



I

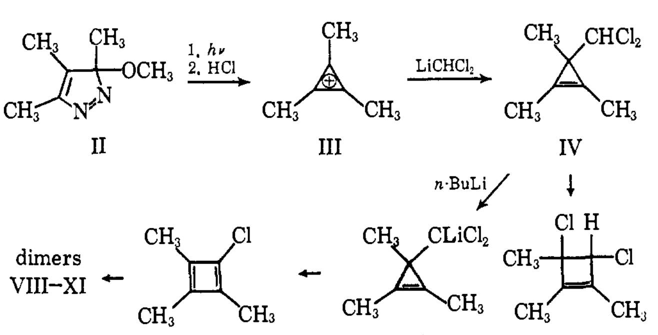
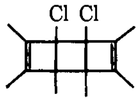
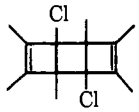
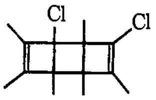
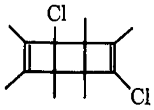
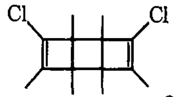
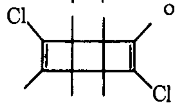


Table I. Chemical Shifts of Methyl Protons of Isomers VIII–XI[a]

	Solvent		Suggested structures[b]
	CS_2	C_6H_6	
VIII	1.20 (6), s 1.55 (12), s	1.28 (6), q (1.2 cps) 1.42 (6), q (1.2 cps) 1.48 (6), s	 or 
IX	1.06 (3), s 1.08 (3), s 1.14 (3), s 1.53 (6), m 1.56 (3), s	0.88 (3), s 1.11 (3), s 1.29 (3), q (1.2cps) 1.33 (3), s 1.36 (3), s	 or 
X	1.07 (3), s 1.10 (3), s 1.50 (3), s 1.55 (6), m 1.59 (3), s	1.70 (3), q (1.2 cps) 1.04 (3), s 1.16 (3), s 1.18 (3), s 1.42 (3), s 1.50 (3), q (1.2 cps) 1.54 (3), q (1.2 cps)	
XI	1.05 (6), s 1.06 (6), s 1.61 (6), s	0.85 (6), s 0.96 (6), s 1.66 (6), s	 or 

[a] Chemical shifts are in parts per million downfield from internal tetramethylsilane. Numbers in parenthesis following the chemical shift values designate the number of protons causing the signal. The multiplicity of the signal is given by s for singlet, q for quartet, and m for unresolved multiplet. [b] Methyl groups are omitted from structures.

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(1) Supported by National Science Foundation Grant GP-4214.

(2) *Cf.* S. Masamune and M. Kato, *J. Am. Chem. Soc.*, **87**, 4190 (1965); **88**, 610 (1966); E. H. White, G. E. Maier, R. Graeve, U. Zirngibl, and E. W. Friend, *ibid.*, **88**, 611 (1966).

(3) G. L. Closs and H. Heyn, *Tetrahedron*, **22**, 463 (1966).

(4) G. Köbrich and W. Drischel, *Angew. Chem. Intern. Ed. Engl.*, **3**, 513 (1964).

(5) It is very likely, however, that all isomers have the same stereochemistry because the crystals appear to be isomorphous and have approximately the same melting points which are not depressed in mixtures. Partly because of the solvent dependence of the chemical shifts and partly because of precedent[6] we presently prefer the *anti* configuration.

(6) *Cf.* R. Criegee, *Bull. Soc. Chim. France*, **5**, 1 (1965), and references cited therein; L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3254 (1965).