E. Pyrolysis of Compounds 1 and 4.—The pyrolysis of **1** and **4** was carried out in a 100-ml three-necked flask equipped with thermometer, nitrogen inlet, and condenser. The latter was connected to a $CaCl_2$ U-tube, a three-way stopcock carrying at each end an ascarite U-tube. The weighing of the latter at regular intervals of time permitted us to measure carbon dioxide liberated during the pyrolysis. The residue after the pyrolysis was partially dissolved in cold ether. The insoluble portion was composed of the compounds **2a**, **3a**, and **7**. The filtrate contained aniline, and the products, **2a**, **4**, **5**, **6**, **8**, **10**, small amounts of **3a** and **7** slightly soluble in cold ether. The degradation products were separated quantitatively by column chromatography on alumina of these two portions with hexane, benzene, chloroform, ethanol, and their mixtures as eluents.

Registry No.—**1**, 748-84-5; **2b**, 32974-53-1; **2c**, 32974-54-2; **2d**, 32974-55-3; **2e**, 32974-56-4; **2f**, 13468-08-1; **2g**, 32974-58-6; **2h**, 32974-59-7; **2i**, 32974-60-0; **3c**, 32974-61-1; **3f**, 32974-62-2; **3i**, 5198-55-0; **4**, 33020-71-2; **6**, 150-61-8; **7**, 102-07-8; β-bromoethyl *N*-phenylcarbamate, 32353-12-1; poly(ethylene-*N*-*o*-tolyl-*N'*-phenylurea), 33029-39-9.

The Transannular Neophyl Rearrangement[1,2]

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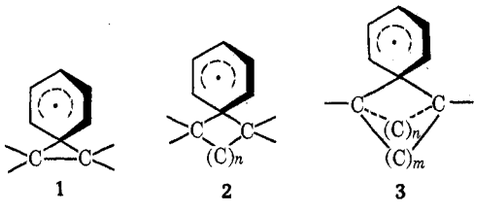
The radical rearrangement in solution of a phenyl group across a cyclohexane ring *via* bicyclo[2.2.1]heptyl and [2.2.2]octyl species has been achieved. This transannular rearrangement did not occur in analogs *via* smaller sized bicyclic species. In these cases the parent structures were retained or ring opening occurred.

The vicinal migration of a phenyl group *via* **1** (the neophyl rearrangement) is well known.[3] Less common, but still recorded,[4] are analogous further rearrangements *via* **2**. It was the intent of the present study to seek phenyl shifts *via* **3**, a process we term

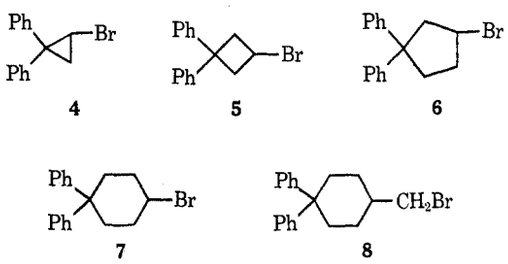


1 **2** **3**

the "transannular neophyl rearrangement."[5] Quite clearly, such rearrangements will be sensitive to the bicyclic ring size of the intermediate; so a series of these were investigated.

Any of several extant free radical processes that exhibited rearrangement *via* **1** or **2** could be chosen for application to **3**. However, in recent years the generation of carbon radicals from the reaction of halides with organotin hydrides has become widespread.[6] This method recommended itself for the present purpose for several reasons: the temperature of the reaction can be varied readily, as can the concentration of the tin hydride. Generally speaking, higher temperatures and lower concentrations of the hydride favor radical rearrangement processes.[7] Also, as one of its best features, the process produces the radical of interest directly and not *via* intervening species.

As precursors to the radicals under study, the series of bromides **4**–**8** was prepared and characterized. The



4 **5** **6**

7 **8**

rationale for using a *gem*-diphenyl function was twofold. First, one of the phenyls is always situated appropriately for migration. Second, the other phenyl group serves as a stabilizer for the radical center formed subsequent to rearrangement. Coincidentally, this second phenyl group serves also as a rearrangement marker through its influence on the nmr spectrum of the product. Secondary bromides sometimes present a problem in their synthesis because carbonium ion rearrangements can occasionally plague the customary routes to them.[8] For this reason, a noncarbonium ion process (eq 1) was chosen to prepare most

$$\underset{\mathbf{11,\ 17,\ 19}}{\mathrm{ROTs}} + \mathrm{LiBr} \xrightarrow[\text{or diglyme}]{\text{acetone}} \underset{\mathbf{5\text{–}7}}{\mathrm{RBr}} + \mathrm{LiOTs} \qquad (1)$$

of those needed for this study. The requisite tosylates were made as shown (eq 2–4). The sequences shown are straightforward and will not be discussed. Details may be found in the Experimental Section. Diagnosis by spectral and chromatographic methods indicated that reaction 1 proceeded without rearrangement in every instance. Bromides **4** and **8** were, however, prepared alternatively (eq 5, 6). In all cases the structures were supported by combustion analytical and spectral data.

One may notice that the transannular neophyl re-

(1) Taken from (a) the Dissertation of R. A. D., 1970; and (b) the M.S. Thesis of K. C. W., 1970.

(2) Presented at the Third Great Lakes Meeting of the American Chemical Society, Northern Illinois University, De Kalb, Ill., June 1969, Abstracts of Papers, paper 58.

(3) *Cf.* R. Kh. Freidlina in "Advances in Free-Radical Chemistry," Vol. 1, G. H. Williams, Ed., Academic Press, New York, N. Y., 1965, pp 249–260.

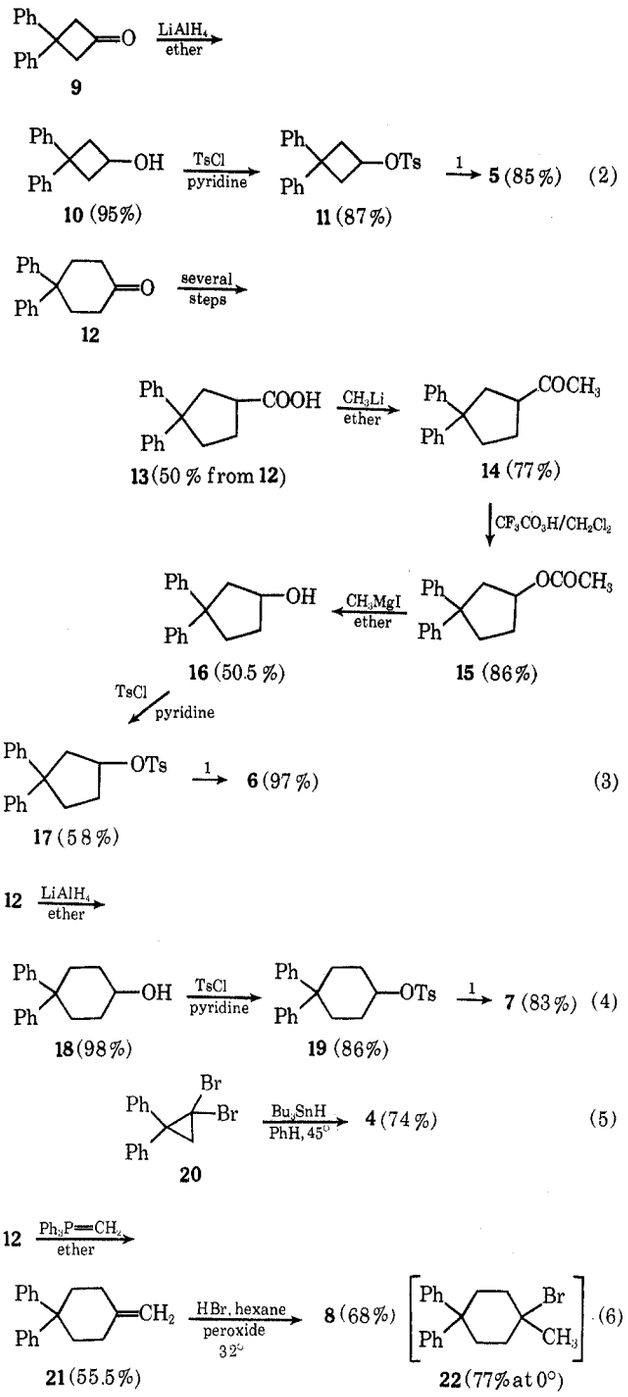
(4) S. Winstein, R. Heck, and S. Lapporte, *Experientia*, **12**, 138 (1956).

(5) Although perhaps properly applied only to the rearrangement of the β-phenylisobutyl ("neophyl") radical itself, the term "neophyl rearrangement" is used here for the radical migration of an aromatic group from a carbon atom origin to any other carbon atom terminus.

(6) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 229 (1968).

(7) L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

(8) *Cf.* J. Cason and J. S. Correia, *J. Org. Chem.*, **26**, 3645 (1961).



arrangement in the systems represented by **4**–**8** would engender a particular bicyclic intermediate Ar$_1$[*x.y.z*][9,11] as shown (eq 7). For reference, the strain energies, measured and/or calculated, for the bicycles of concern are collected in Table I. Although the

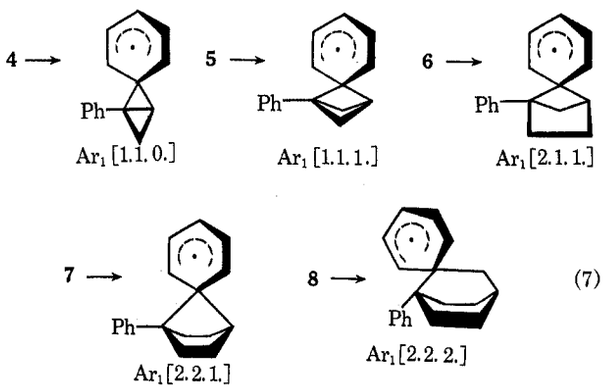


TABLE I

Bicyclo-	Strain energy, kcal mol^{-1}
[1.1.0]butane	66.5,[a] 64.7[b]
[1.1.1]pentane	92.23[c]
[2.1.1]hexane	44.64[c]
[2.2.1]heptane	17.55,[a] 17.95[c]
[2.2.2]octane	11.01,[a] 13.22[c]

[a] P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970). [b] K. B. Wiberg, *Rec. Chem. Progr., Kresge-Hooker Sci. Libr.*, **26**, 143 (1965). [c] N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971).

Ar$_1$[*x.y.z*] intermediates are perhaps not exactly comparable to these bicyclic species,[12] the trend in the values in Table I allows at least a qualitative comparison. So some simple deductions from these data may be mentioned. In both **7** and **8**, for example, transannular rearrangement obviously requires a boat conformation in the rearranging radical (eq 8, 9). Plausibly, the initially formed radicals **7**· and **8**· are predominantly chairlike more than boatlike[13] and energy must be expended to convert them to **7′**· and **8′**·. The energy required for the change **7**· → **7′**· is presumably not great, however, because boat and chair conformers of cyclohexanone (a passable model for a cyclohexyl radical) are easily interconvertible.[14] If this be so, then only a modest further energy expenditure would be necessary to accommodate the strain involved in the transannular phenyl shift. For the change **8**· → **8′**·, the energy required would be somewhat more, perhaps the *ca.* 10 kcal required of methylcyclohexane,[15] although the *gem*-diphenyl function could alter this somewhat. Nonetheless, the decreased strain present in the Ar$_1$[2.2.2] intermediate relative to all the others (Table I) makes rearrangement appear possible here as well. Clearly, the situa-

(9) *A priori*, Ar$_2$[*x′.y′.z′*] intermediates are conceivable for the processes also. Indeed, Ar$_2$-6 intermediacy has been noted before in certain radical rearrangements.[4,10] Normally, however, such Ar$_2$-*m* intermediates lead to cyclized products *via* aromatization by hydrogen atom donation to some acceptor species. As no such products implicating this route were detected, we believe that Ar$_1$ involvement is more probable in the present examples.

(10) U. K. Pandit and I. P. Dirk, *Tetrahedron Lett.*, 891 (1963).

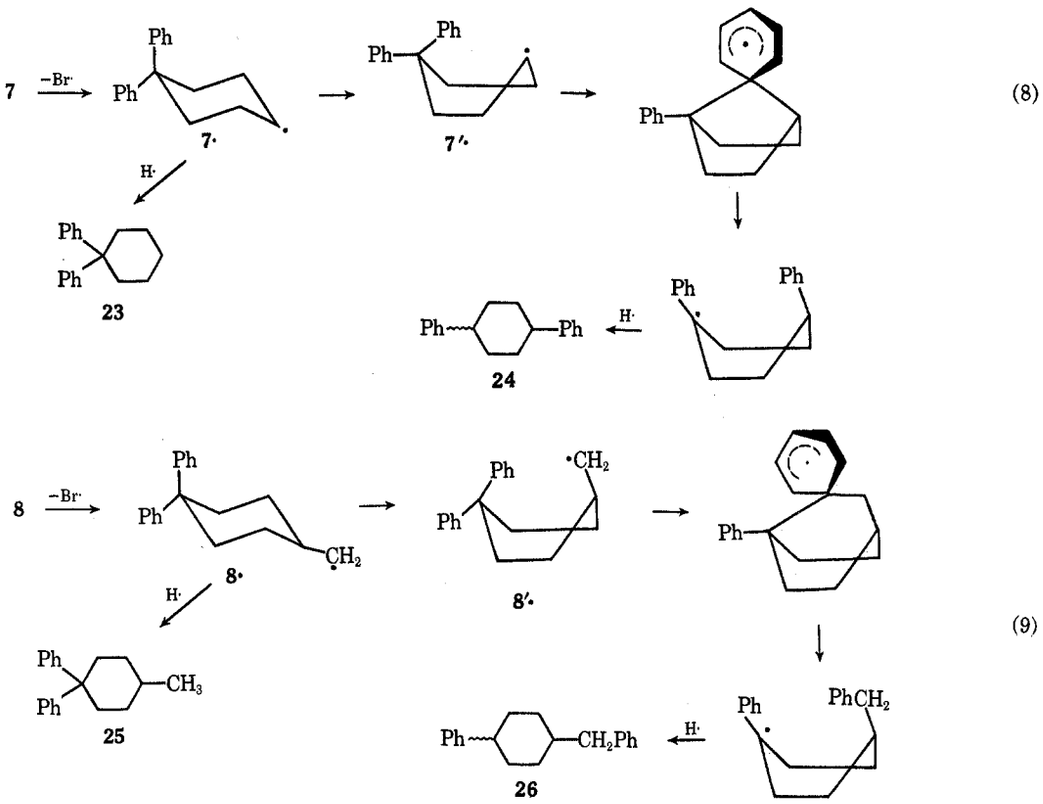
(11) The Ar$_1$[2.2.1] intermediate has previously been invoked to explain transannular phenyl migration: (a) H. Pines, W. F. Fry, N. C. Sih, and C. T. Goetschel, *J. Org. Chem.*, **31**, 4094 (1966), obtained *p*-terphenyl from 1,1-diphenylcyclohexane over nonacidic chromia–alumina B at 390–497°, a process they suggested involved the same radical rearrangement sought here. Incidentally, no rearrangement attended passage of 1,1-diphenylcyclohexane over glass beads at these temperatures. (b) In an elimination reaction of **19** with sodium *tert*-butoxide, the 1,4 phenyl shift observed by A. R. Abdun-Nur and F. G. Bordwell, *J. Amer. Chem. Soc.*, **86**, 5695 (1964), was rationalized by an ionic analog of the [2.2.1] intermediate. In this brief communication, the radical possibility was termed "unlikely."

(12) *I.e.*, the influence of the additional phenyl and cyclohexadienyl moieties on these bicyclic strain energies is unknown. Moreover, the *transition states* may not be symmetrical with regard to bonding of the migrator between the origin and terminus sites, thus changing the geometry of the aliphatic portion of the bicycle to some degree, relative to these *intermediates*.

(13) As a model for radical **7** one might choose ketone **12**. This ketone possesses a chair cyclohexane ring flattened near the carbonyl group with the phenyl rings at C-4 nearly perpendicular to one another: J. B. Lambert, R. E. Carhart, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **91**, 3567 (1969).

(14) The energy barrier for the conformational change chair → boat is apparently unknown for cyclohexanone, although an upper limit of 6 kcal mol^{-1} has been suggested by E. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison in "Conformational Analysis," Interscience, New York, N. Y., 1965, p 186. Just what effect the 4,4-diphenyl function would have on this barrier is also unknown.

(15) Reference 14, p 185.



(8)

(9)

tion for such rearrangement grows bleaker in the smaller rings.

These naive expectations based upon such strain considerations were fulfilled. *Transannular neophyl rearrangement indeed occurred with* **7** *and* **8**, whereas none at all was found for **4–6**. Frankly, the fact that rearrangement occurred at all for **7** and **8** is surprising. In order to have rearrangement, energy-rich conformers of short-lived radicals are required and the competitive chain transfer reaction to produce unrearranged hydrocarbon is quite fast ($k_t = 10^6\ M^{-1}\ \text{sec}^{-1}$ at 25° [16]). Although the results obtained are inadequate for an accurate determination, the activation energy for the rearrangements in these systems is obviously low.[17] The results of the studies on **7** and **8** are shown in Table II. The rearranged product, in

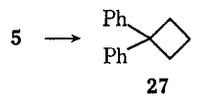
TABLE II

Bromide	M^a	Temp, °C (bath)	% rearrangement[b]
7	0.318	145	1.0[c,d]
	0.306	155	2.6[d]
	0.102	150	3.2[d]
8	0.304	145	Trace[c,e]
	0.030	145	0.7[e]
	0.015	145	1.1[e]

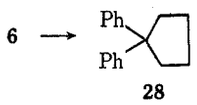
[a] In dry, thiophene-free benzene with 1.1 equiv of tri-*n*-butyltin hydride present. [b] Yields of hydrocarbon product were over 90%. Duplicate runs agreed within 5%. [c] No rearranged product at 78°. [d] Rearranged product isolated by column chromatography. [e] By gas–liquid partition chromatography.

one case hydrocarbon **24** and in the other **26**, was resolvable chromatographically from the related unrearranged product **23** or **25**. Comparison with an authentic sample established the structure for each.

The results with bromides **5** and **6** were unexciting. Each afforded the *gem*-diphenylcycloalkane, as indicated in eq 10 and 11.

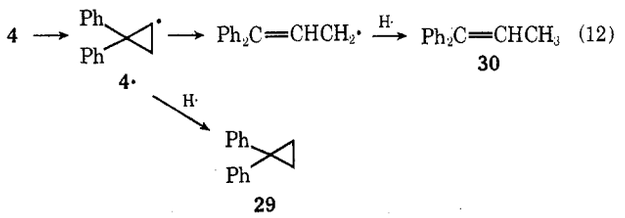


(10)



(11)

Bromide **4**, however, led to ring-opened product **30** along with the expected *gem*-diphenyl product **29** (eq 12).



(12)

Ring opening, an uncommon reaction of cyclopropyl radicals in spite of the *ca.* 30 kcal mol^{-1} release of strain energy,[18] became more pronounced with increased temperature and/or lowered tin hydride concentrations. The data is given in Table III. This ring opening of **4**· is undoubtedly assisted by the ability of the phenyl groups to stabilize the opened radical.[19,20]

(16) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

(17) Approximate calculations yielded a value of about 15 kcal mol^{-1} for the activation energy associated with **7** → **24**.[1a]

(18) J. D. Roberts and D. Schuster, *J. Org. Chem.*, **27**, 51 (1962).

(19) Approximate calculations yielded a value of *ca.* 11 kcal mol^{-1} for the ring opening in **4**.[1a]

(20) For another instance of such phenyl assistance, *cf.* H. M. Walborsky and J.-C. Chen, *J. Amer. Chem. Soc.*, **92**, 7573 (1970).

TABLE III

4, M^a	Bu_3SnH, M	Temp, °C	% 30[b]
0.320	0.330	78	13
0.105	0.110	78	38
0.320	0.330	150[c]	76
0.105	0.110	150[c]	91

[a] In benzene. Reaction time 24 hr. [b] *Via* glpc. [c] Bath temperature.

The neophyl rearrangement, with its surprising reach, thus appears to be one of the more adaptable radical rearrangements known. This study, together with an earlier one,[21] also illustrates the utility of the tin hydride reduction method for uncovering seemingly unpropitious rearrangements.

Experimental Section

Melting points were taken on a calibrated Fisher-Johns block. Boiling points are not corrected for stem exposure. Combustion analyses were by Micro-Tech Laboratories, Skokie, Ill., or by the analytical laboratories of G. D. Searle and Co., Skokie, Ill. Gas–liquid partition chromatography (glpc) was carried out on Varian Aerograph A-90P and Hewlett–Packard Model 5750 instruments with disc and electronic integration, respectively. Infrared, nmr, and mass spectra were determined on Beckman IR-5A, Varian A-60A, and Perkin-Elmer Model 270 instruments, respectively.

Preparation of Bromides. 2-Bromo-1,1-diphenylcyclopropane (4).—2,2-Dibromo-1,1-diphenylcyclopropane[22] [20, mp 149.5–151°, δ (CCl_4) 7.35 m (Ar H) and 1.03 s (CH_2) (lit.[22] mp 150–151°), 14.83 g, 0.042 mol] in benzene (100 ml) was stirred at 45° under nitrogen as tri-*n*-butyltin hydride[23] (12.13 g, 0.042 mol) in benzene (50 ml) was added dropwise over 20 min. The mixture was allowed to stir for an additional 90 min. Removal of solvent left an oil which was taken up in 95% ethanol (75 ml) and refrigerated. White needles of **4** were collected (8.44 g, 74%, mp 76–78°). Recrystallization from 95% ethanol gave an analytical sample: mp 81–82.5°; δ (CCl_4) 7.3 m (Ar H), 3.60 t (CHBr, J = 6 Hz), 1.78 d (CH_2). The deceptive A_2X system became ABX in benzene, δ 3.48 dd (CHBr, J = 5 and 8 Hz), 1.50 m (CH_2).

Anal. Calcd for $C_{15}H_{13}Br$: C, 65.96; H, 4.79. Found: C, 66.11; H, 4.50.

3-Bromo-1,1-diphenylcyclobutane (5).—3,3-Diphenylcyclobutanone (**9**) was reduced with lithium aluminum hydride and the alcohol **10** so obtained (95%) was converted to the tosylate **11** (87%, mp 116–117°).[24] A solution of tosylate **11** (0.5 g, 1.4 mmol) and lithium bromide (0.4 g, 46 mmol) in dry diglyme (20 ml) was heated at 120° for 20 hr. The orange solution was cooled, poured into ice water, and extracted with chloroform. The chloroform extracts were dried ($MgSO_4$) and carefully evaporated. The solid residue was chromatographed over silica gel with hexane as the eluting solvent to give bromide **5** (0.34 g, 85%). Recrystallization from hexane afforded an analytical sample: mp 93–94°; δ (CCl_4) 7.25 m (Ar H), 4.55 pentuplet with further splitting (CHBr), 3.35 m (CH_2).

Anal. Calcd for $C_{16}H_{15}Br$: C, 66.91; H, 5.26. Found: C, 66.84; H, 5.23.

3-Bromo-1,1-diphenylcyclopentane (6).—4,4-Diphenylcyclohexanone (**12**) was converted to 3,3-diphenylcyclopentanecarboxylic acid (**13**) as reported.[25] Acid **13** (4.0 g, 14 mmol) in ether was stirred at 25° while excess ethereal methyllithium was added dropwise over 5 min. Ten minutes after the addition was completed, the reaction was quenched at 0° with saturated ammonium chloride. The ether layer was separated, washed with 10% sodium carbonate solution, water, and brine, and then dried (Na_2SO_4). Distillation gave **methyl 3,3-diphenylcyclopentyl ketone** [**14**, 2.9 g, 77%, bp 190–197° (0.2 mm)]. About 5% (3,3-diphenylcyclopentyl)dimethylcarbinol was also present in this material. Ketone **14** was purified *via* regeneration from its semicarbazone as a colorless oil: bp 167–169° (0.1 mm); λ (neat) 5.90 (C=O), 7.40 (CH_3); δ (CCl_4) 7.25 m (Ar H), 3.20–2.65 m (CH), 2.62–1.50 m (CH_2), 2.00 s (CH_3).

Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.54; H, 7.38.

The orange **2,4-dinitrophenylhydrazone** was readily prepared, mp 152.5–153.5° dec from ethyl acetate.

Anal. Calcd for $C_{25}H_{24}O_4N_4$: N, 12.61. Found: N, 12.59.

In an ice bath, crude ketone **14** (2.63 g, 10 mmol) in methylene chloride (40 ml) containing suspended disodium hydrogen phosphate (9.2 g) was treated dropwise with trifluoroperacetic acid (from the reaction of trifluoroacetic anhydride, 7.3 g, 34 mmol, and hydrogen peroxide, 90%, 3 ml, in methylene chloride, 25 ml) over a 20-min period with efficient stirring. A slow rate of addition and the ice bath helped to control the exothermic reaction. After the addition the reaction material was stirred for an additional 1.75 hr. The salts present were filtered off and the methylene chloride solution was washed well with water, 10% sodium carbonate solution, water, and brine until neutral. Removal of solvent left crude **3,3-diphenylcyclopentyl acetate** (**15**, 2.42 g, 85%). A portion was chromatographed on alumina using 1:1 ether–hexane as the eluting solvent and then distilled in a micro-Hickman still. Ester **15** was a colorless oil with a floral odor: λ (neat) 5.82 (C=O), 7.31 (CH_3), 8.10 (acetate CO); δ (CCl_4) 7.00 m (Ar H), 4.90 m (CHOAc), 3.08 m (one H of the 2-CH_2, AB portion of ABX pattern), 2.60–2.00 m (all other ring H's), 1.90 s (-$OCOCH_3$).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.42; H, 7.31.

Ester **15** (crude product from the above preparation on a threefold larger scale) was added to methylmagnesium iodide (100 mmol) in ether. After 30 min the cooled solution was hydrolyzed with dilute sulfuric acid and the ether layer was separated and washed with 10% sodium bisulfite solution, water, and brine. Evaporation of the dried (Na_2SO_4) ether solution left an oily solid, **3,3-diphenylcyclopentanol** (**16**, 3.4 g, 50.5%). An analytical sample was obtained by three distillations in a micro-Hickman still as a colorless oil that slowly solidified: lit.[26] mp 55–57°; λ (neat) 2.95 (OH), 9.38 (CO); δ (CCl_4) 7.20 m (Ar H), 4.37 m (CHOH), 2.80 dd (one H of the 2-CH_2, J_{gem} = 15, J_{vic} = 7 Hz), 2.50–1.53 m (OH and all other ring H's).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.71; H, 7.81.

Conversion of alcohol **16** to its **tosylate 17** was achieved in 58% yield by the usual pyridine–tosyl chloride method.[27] An analytical sample of **17** was obtained from ether–petroleum ether (bp 30–60°), mp 80–81.5°.

Anal. Calcd for $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16. Found: C, 73.51; H, 6.18.

A solution of tosylate **17** (1.0 g, 2.5 mmol) and lithium bromide (1.0 g, 11.5 mmol) in acetone (freshly distilled from potassium permanganate, 25 ml) was refluxed (drying tube attached) for 20 hr. The acetone was removed and the residue was treated with water to a volume of 50 ml. Ether extraction followed. The dried (Na_2SO_4) extracts were concentrated to produce bromide **6** (0.73 g, 97%). An analytical sample was obtained from hexane: mp 64–65.5°; δ (CCl_4) 7.2 s (Ar H), 4.30 m (CHBr), 3.15 dd, 2.65 dd (2-CH_2), AB portion of ABX pattern, J_{gem} = 14, J_{vic} = 7 and 9 Hz), 2.6–2.1 m (other ring H's).

Anal. Calcd for $C_{17}H_{17}Br$: C, 67.79; H, 5.69. Found: C, 67.76; H, 5.75.

4-Bromo-1,1-diphenylcyclohexane (7).—Reduction of ketone **12** with lithium aluminum hydride produced **4,4-diphenylcyclohexanol** (**18**, 98%, mp 139.5–140.5°) from benzene–petroleum ether).[11b] The alcohol was converted to the tosylate **19** in standard fashion[27] (86%, mp 123.5–125° from benzene–ether).

Anal. Calcd for $C_{25}H_{26}O_3S$: C, 74.04; H, 6.21. Found: C, 73.97; H, 6.46.

(21) J. W. Wilt, S. N. Massie, and R. A. Dabek, *J. Org. Chem.*, **35**, 2803 (1970).

(22) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956).

(23) H. G. Kuivila and O. F. Beumel, Jr., *ibid.*, **83**, 1246 (1961).

(24) We are indebted to Dr. C. J. Michejda and Mr. R. Comnick, Department of Chemistry, University of Nebraska, for the details of their preparation of **9**, **10**, and **11** (March 12, 1969).

(25) F. G. Bordwell, R. R. Frame, R. G. Scamehorn, J. G. Strong, and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 6704 (1967).

(26) During the course of this work, A. Warshsawsky and B. Fuchs, *Tetrahedron*, **25**, 2633 (1969), reported the preparation of alcohol **16** by another path. The nmr spectrum of **16** illustrated in their paper matched that of our sample.

(27) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

In the manner described above for bromide **6**, tosylate **19** (2.58 g, 6.3 mmol) and lithium bromide (1.54 g, 17 mmol) in refluxing acetone (60 ml) for 115 hr[28] afforded bromide **7** (1.65 g, 83%, mp 95–99°). Colored acetone-derived aldol contaminants were easily removed with a cold petroleum ether wash. An analytical sample of **7** was obtained by chromatography on alumina with hexane as the eluting solvent: mp 100.5–102°; δ ($CDCl_3$) 7.20 m (Ar H), 4.34 m (CHBr), 2.85–1.95 m (CH_2's).

Anal. Calcd for $C_{18}H_{19}Br$: C, 68.58; H, 6.07. Found: C, 68.57; H, 6.16.

4-Bromomethyl-1,1-diphenylcyclohexane (8).—Under nitrogen, *n*-butyllithium in hexane (0.1 mol) mixed with dry ether (250 ml) was treated with methyltriphenylphosphonium bromide (28.5 g, 0.08 mol) suspended in more ether (250 ml). The orange solution of the ylide was stirred at 25° for 1 hr. Ketone **12** (20.0 g, 0.08 mol) in a slurry with ether (500 ml) was then added and the yellow mixture was refluxed for 80 min, after which time thin layer chromatography (tlc) indicated that the reaction was complete. The cooled solution was filtered and washed well with water. After being dried (Na_2SO_4), the solution was evaporated and the residual oil was taken up in benzene. After the material had been passed through a column of silica gel, it was distilled to afford **1-methylene-4,4-diphenylcyclohexane (21)**: 12 g, 55.5%; bp 114–118° (0.04 mm); mp 48–49°; λ ($CHCl_3$) 3.28, 3.33, 6.06, 11.22 (C=CH_2); δ ($CDCl_3$) 7.26 m (Ar H), 4.62 s (C=CH_2), 2.32 sharp m (ring CH_2's).

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 92.05; H, 8.17.

With slight warming, benzoyl peroxide (0.29 g) was dissolved in mixed hexanes solvent (Skellysolve B, bp 56–71°, 120 ml) containing olefin **21** (2.98 g, 12 mmol). At 32° a slow stream of anhydrous hydrogen bromide was introduced over 2 hr, at which time tlc analysis showed complete reaction. The solution was washed with water, 10% ferrous sulfate solution, and water and then dried (Na_2SO_4). Removal of solvent left bromide **8** as an oil which solidified when triturated with a little ether. Further purification by low-temperature crystallization from ether gave pure **8** as a colorless solid: 2.37 g, 60%; mp 69–71°; δ ($CDCl_3$) 7.50–7.00 m (Ar H), 3.19 d (CH_2Br, J = 6 Hz), 3.00–0.99 m (other ring H's).

Anal. Calcd for $C_{19}H_{21}Br$: C, 69.30; H, 6.47; Br, 24.24. Found: C, 69.64; H, 6.65; Br, 24.31.

Interestingly, the above reaction carried out at 0° gave a 77.4% yield of **4-bromo-4-methyl-1,1-diphenylcyclohexane (22)**: mp 93–94° from ether; λ ($CHCl_3$) 7.23 (CH_3); δ ($CDCl_3$), 1.77 s (CH_3).

Anal. Calcd for $C_{19}H_{21}Br$: C, 69.30; H, 6.47; Br, 24.24. Found: C, 69.52; H, 6.44; Br, 23.95.

Presumably chain initiation at this temperature was inefficient relative to the competing ionic addition.

Preparation of Reference Hydrocarbons. 1,1-Diphenylcyclohexane (23).—Reduction of 2,2-diphenylcyclohexanone[29] by the Huang-Minlon method as described[30] gave **23** as colorless platelets: 30%; mp 42–44° from ethanol (lit.[30] mp 42–44°); δ (CCl_4) 7.23 s (Ar H), 2.25 m (2, 6-CH_2's), 1.50 m (other CH_2's).

***cis*- and *trans*-1,4-Diphenylcyclohexane (24).**—The hydrocarbon was prepared by catalytic hydrogenation (2.5 atm, Pd/C catalyst, 25°, 17 hr) of 1,4-diphenylcyclohexene in acetic acid, largely as described.[11a] The product formed white platelets: mp 158–168° from benzene–hexane (lit.[11a] mp 159–173°); δ ($CDCl_3$) 7.35 s (Ar H), 2.67 broad m (1, 4-CH), 2.16–1.38 m (remaining H's); mass spectrum[31] (70 eV) base peak 91 (tropylium ion), other peaks greater than 50% of the base peak, 236 (parent), 158, 117, 104 amu. The melting point range of this product was identical with that of the product from the reduction of **7** (*vide infra*). From this range, each product is undoubtedly a cis–trans mixture. No investigation of the composition of the mixture was made, however.

4-Methyl-1,1-diphenylcyclohexane (25).—Olefin **21** (590 mg) was reduced in absolute ethanol (4 ml) and benzene (2 ml) with hydrogen gas (52 psig) over a Pd/C catalyst (5%) for 2.5 hr. Removal of the catalyst and solvent left **25** as a colorless solid: 390 mg, 66.2%; mp 41–43°; λ ($CHCl_3$) 7.24 (CH_3); δ (CCl_4) 7.5–7.0 m (Ar H), 2.90–0.70 m (ring H's), 0.81 distorted d (CH_3, J = *ca.* 5 Hz).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.27; H, 8.83.

***cis*- and *trans*-1-Benzyl-4-phenylcyclohexane (26).**—4-Phenylcyclohexanone[32] (7.31 g, 42 mmol) was treated with benzylmagnesium chloride (51 mmol) in ether under nitrogen at reflux for 90 min. The reaction material was poured into ice water containing hydrochloric acid (30 ml of acid). The separated ether layer, together with ether extracts of the aqueous phase, were washed with water until neutral, dried (Na_2SO_4), and evaporated. The resulting oil crystallized upon addition of Skellysolve B and subsequent chilling. **1-Benzyl-4-phenylcyclohexanol** formed white crystals: 5.55 g, 50%; mp 87–88°; λ ($CHCl_3$), 2.78 (OH), 8.76 (CO); δ ($CDCl_3$) 7.20 d (Ar H), 2.78 s (CH_2Ph), 1.90–1.40 m (ring H's), 1.20 s (OH, exchanges).

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.33; O, 6.01. Found: C, 86.03; H, 8.35; O, 5.95.

This alcohol (3.15 g, 11.4 mmol), together with potassium bisulfate (1.57 g, 11.4 mmol), was refluxed in chlorobenzene (50 ml) for 50 min. After being washed with water until neutral, the chlorobenzene solution was dried (Na_2SO_4) and evaporated. The residual oil was distilled to give **1-benzyl-4-phenylcyclohexene**, 2.0 g, 71.8%, bp 136–137° (0.2 mm), containing about 17% **4-phenyl-1-benzylidenecyclohexane**: δ ($CDCl_3$) 7.23 s (Ar H), 6.30 m (=CHPh), 5.55 m (CH=C<), 3.30 m (-CH_2Ph), 3.0–1.3 m (other ring H's).

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.82; H, 8.17.

This mixture of olefins (500 mg) was hydrogenated for 3 hr over Pd/C (5%, 100 mg) in 1:1 benzene–ethanol (100 ml). After separation of the catalyst and evaporation of the solvent, hydrocarbon **26** was obtained as an oil: 500 mg, quantitative yield; δ ($CDCl_3$) 7.20 m (Ar H), 2.80 m (>CHPh), 2.62 broad d (-CH_2Ph of trans isomer, J = 7 Hz), 2.55 broad d (-CH_2Ph of cis isomer, J = 7 Hz), 2.1–1.0 m (other ring H's). Integration data indicated an approximate 1:1 ratio of cis and trans isomers. The mixture was not resolved on any of several glpc columns. It was essentially identical with the mixture obtained by the reduction of bromide **8** (*vide infra*).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.40; H, 8.72.

1,1-Diphenylcyclobutane (27).—Reduction of tosylate **11** (0.6 g, 1.6 mmol) with lithium aluminum hydride (0.8 g, 23.5 mmol) in tetrahydrofuran (50 ml) was achieved under reflux for 16 hr. The cooled solution was hydrolyzed with water (100 ml) containing hydrochloric acid (6 *N*, 10 ml). The solution was extracted with ether. The ether extracts were washed with water and brine until neutral, dried (Na_2SO_4), and evaporated. The residual oil was chromatographed on alumina using hexane as the eluting solvent. Distillation of the purified oil in a micro-Hickman still gave **27** as a colorless oil: 150 mg, 45%; δ (CCl_4) 7.03 m (Ar H), 2.60 t (2, 4-CH_2, J = 7 Hz), 1.83 pentuplet with further splitting (3-CH_2).

Anal. Calcd for $C_{16}H_{16}$: C, 92.25; H, 7.75. Found: C, 91.96; H, 7.77.

1,1-Diphenylcyclopentane (28).—In similar fashion, tosylate **17** was reduced with lithium aluminum hydride in ether under reflux for 90 min. Hydrocarbon **28** was obtained as white needles from 95% ethanol: mp 72–72.5°; δ (CCl_4) 7.20 m (Ar H), 2.30 m (2, 5-CH_2), 1.73 m (3, 4-CH_2).

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.95; H, 8.29.

1,1-Diphenylcyclopropane (29).—Spectral identification of material isolated in these studies (*vide infra*) was made by comparison with that previously reported:[33] δ (CCl_4) 7.15 s (Ar H), 1.24 s (CH_2).

1,1-Diphenylpropene (30).—Preparation was achieved as reported:[34] 65%, mp 46–47° from 95% ethanol; δ (CCl_4) 7.20 m (Ar H), 6.12 q (>C=CH, J = 7 Hz), 1.74 d (CH_3, J = 7 Hz).

Reduction of Bromides with Tri-*n*-butyltin Hydride. Bromide

(28) The increased reaction time reflects the decreased S_N2 reactivity in this system compared to the cyclopentyl case.

(29) Prepared by the method of A. Burger and W. B. Bennett, *J. Amer. Chem. Soc.*, **72**, 5414 (1950).

(30) F. J. Bojer and H. W. Post, *J. Org. Chem.*, **27**, 1422 (1962).

(31) We deeply thank Dr. Henry F. Dabek, Jr., for the mass spectral determinations.

(32) We thank Dr. L. Chinn of G. D. Searle and Co. for a generous supply of this ketone.

(33) C. Walling and L. Bollyky, *J. Org. Chem.*, **28**, 256 (1963).

(34) A. Klages, *Ber.*, **35**, 2646 (1902).

7.—Amounts of the bromide (1.1–4.84 g) were dissolved in thiophene-free, dry benzene to make solutions of molarities given in Table II. Freshly distilled tri-*n*-butyltin hydride (1.1 equiv relative to the amount of **7** used) was then added and the solutions were sealed in pressure bottles under nitrogen. The reaction mixtures were placed in sand baths for 42 hr at 145° and 24 hr at 155 and 150°. The vessels were cooled and opened and the contents were reduced in volume to about 5 ml by distillation of the benzene solvent. In each case the material was then chromatographed on alumina using hexane as the eluting solvent. Hydrocarbon **23** eluted first with the rearranged product **24** afterward. On occasion the elutions were speeded by use of 25–50% benzene–hexane mixtures as the eluting agent. Identification of products was by mixture melting point and spectral (ir, nmr, and mass) comparison with authentic material. Yields were calculated from the weights of isolated product.

Bromide 8.—The procedure here was similar to the above, except that all reactions were conducted at 145° for 44 hr and all the benzene was removed after the heating period. The chromatographic eluting agents employed were Skellysolve B, followed by a 1:1 mixture of Skellysolve B with benzene. Gas–liquid partition chromatography (4 ft SE-30 column at 170°) was then used on this column-chromatographed material to separate products **25** (retention time 5.79 min) and **26** (retention time 9.27 min). Identification of products was by coinjection of and spectral comparison with knowns. Compositions were calculated by electronic integration of the glpc peaks and yields by weight of column chromatographed product.

Bromides 5 and 6.—Approximately 0.1 *M* solutions of these bromides (0.4 g scale) in benzene were reduced with tri-*n*-butyltin hydride as described for **7** at 150° for 20–24 hr. Chromatography on alumina afforded only unrearranged product. Runs conducted at 78° (refluxing benzene) gave identical results.[35]

Bromide 4.—Amounts of **4** (0.27–1.00 g) were dissolved in benzene to give the molarities shown in Table III. Reduction with tri-*n*-butyltin hydride was carried out in sealed ampoules under nitrogen and the reaction material was chromatographed on alumina as described above for **7**. Analysis by glpc (4 ft polypropylene glycol succinate column at 190°) gave the composition data. Yields were obtained from the weight of the column chromatographed product. Identification of **29** and **30** was by coninjection of and spectral comparison with known samples. No evidence was found for the known[36] rearrangement possibility, 1,2-diphenylcyclopropane.

Registry No.—**4**, 32812-52-5; **5**, 32812-53-6; **6**, 32812-54-7; **7**, 32812-55-8; **8**, 32812-56-9; **14**, 32812-57-0; **14** 2,4-DNP, 32812-58-1; **15**, 32812-59-2; **16**, 24771-20-8; **17**, 32812-61-6; **19**, 807-24-9; **21**, 32812-63-8; **22**, 32812-64-9; **25**, 32812-65-0; *cis*-**26**, 32819-58-2; *trans*-**26**, 32819-59-3; **27**, 32812-66-1; **28**, 32812-67-2; **30**, 778-66-5; 1-benzyl-4-phenylcyclohexanol, 32812-69-4; 1-benzyl-4-phenylcyclohexene, 32812-70-7; 4-phenyl-1-benzylidenecyclohexane, 32812-71-8.

(35) A referee has objected that rearrangement in these cases is not precluded because no comparison was made of these reduction products with the appropriate 1,3-diphenylcycloalkane. While no such comparison was made, detailed examination by spectral and chromatographic methods of the reduction products (the interested reader may see ref 1a) showed *only* unrearranged product. Within the certainty that such results possess we claim that no rearrangement occurred under the conditions studied.

(36) C. G. Overberger, R. E. Zangaro, and J.-P. Anselme, *J. Org. Chem.*, **31**, 2046 (1966), and references therein.

Mass Spectra of Trimethylsilyl Derivatives of Pyrimidine and Purine Bases

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Trimethylsilyl derivatives of pyrimidine and purine bases were prepared by reaction with *N,O*-bis(trimethylsilyl)acetamide or *N,O*-bis(trimethylsilyl)trifluoroacetamide, and their mass spectra studied in detail using high-resolution and deuterium-labeling techniques. The position of thiation or methylation (C-5 *vs.* C-6) in pyrimidines can be established from a major ion species composed of C-4,5 and their attached groups, which is derived from the abundant M − Me ion. A similar process is followed in the decomposition of O^2,N^4-bis(trimethylsilyl)-cytosine following migration of trimethylsilyl to N^4 to produce *m/e* 170. Bases containing methylated amino functions characteristically eliminate methylene imine in parallel to the behavior of free bases and nucleosides. Mass spectra of bases which bear more than one trimethylsilyl group often exhibit intense peaks associated with the doubly charged species $(M - 2Me)^{2+}$, which was found by deuterium labeling to have different mechanistic origins in different bases.

Basic electron impact induced fragmentation reactions of the common pyrimidine and purine bases from ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) have been studied in some detail[1] and are clearly useful for the characterization of such compounds.[2] However, since the isolation of small quantities of biologically modified bases as single components from RNA or DNA hydrolysates for mass spectrometry is often not feasible, we have examined the mass spectra of the more volatile trimethylsilyl derivatives, which are suitable for gas chromatography–mass spectrometry. Although these derivatives[3] have been used for a number of years in synthetic procedures, the work of Sasaki and Hashizume[4] first drew our attention to their gas chromatographic properties.[5]

The present report is based on a detailed study of the mass spectra of trimethylsilyl derivatives of 33 bases, with emphasis on those compounds which are derived from RNA and DNA.[6]

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