column to yield 12 g. of forerun, b.p. 75–110° (2 mm.), and 70 g. (72%) of V: b.p. 110–111° (2 mm.); $n^{25}\mathrm{D}$ 1.4590, $d^{25}{}_4$ 0.9951; MR 66.52 (calcd. 67.27); and $\lambda_{\max}$ 2.80, 3.90, 6.83, 7.27, 7.60–7.70, 8.62, 9.15, 9.65, 10.27, 10.55, 10.72, and 11.42 μ.

Anal. Calcd. for $C_{14}H_{26}O_3$: C, 69.38; H, 10.81. Found: C, 69.65; H, 10.50.

Dihydrojasmone (VI).—To 38 g. (0.157 mole) of 2-*n*-amyl-3-methylcyclopentan-2-ol-1-one propylene ketal (V) was added 100 ml. of 25% sulfuric acid solution, the resulting suspension was stirred and refluxed for 2 hr., and then the reaction mixture was steam distilled. The organic layer was separated and the water layer was saturated with sodium chloride before extraction with 200 ml. of ether. The combined organic layers were dried over anhydrous magnesium sulfate, the ether was removed, and the residue was distilled to give 22 g. (84%) of dihydrojasmone: b.p. 87–88° (2 mm.); $n^{25}\mathrm{D}$ 1.4771; $d^{25}{}_4$ 0.9157; MR 51.31 (calcd.[37] 50.34) [lit.[2] b.p. 101–102° (5 mm.); $n^{15}\mathrm{D}$ 1.48107, d^{15} 0.9201; lit.[9] b.p. 117° (9 mm.); $n^{18}\mathrm{D}$ 1.4810, $d^{18}{}_4$ 0.9165]; $\lambda_{\max}^{\mathrm{EtOH}}$ 236 mμ (ϵ 12,000); and $\lambda_{\max}$ 3.43, 5.85, 6.05, 6.93, 7.09, 7.23, 7.40, 7.48, 7.72, 7.90, 8.50, 9.33, 9.84, 10.05, 10.62, 10.80, 12.20, and 13.75 μ. The product was shown to be 97% pure by vapor phase chromatographic analysis.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.61; H, 11.38.

3-Methyl-1,2-cyclopentanedione 1,1-propylene ketal (IV) may be converted into VI directly, thus avoiding the isolation of V, and with profit in yield. From the reaction between 61 g. of IV and *n*-amylmagnesium chloride (prepared from 69 g. of *n*-amyl chloride and 13.6 g. of magnesium), a residue was obtained as described in the preparation of V, which, without further purification, was stirred with 120 ml. of 25% sulfuric acid and then steam distilled. This distillate was worked up and gave 39 g. (65%) of VI, b.p. 86–89° (2 mm.). Refractionation of the odorous material through a packed column gave a product which boiled at 86.5–88° (2 mm.), $n^{25}\mathrm{D}$ 1.4771, and was identified as VI by its infrared spectrum.

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[37] Uncorrected for exaltation.

Ring-Size Effects in the Neophyl Rearrangement. V. The Carbenoid Decomposition of 1-Phenylcycloalkanecarboxaldehyde Tosylhydrazones

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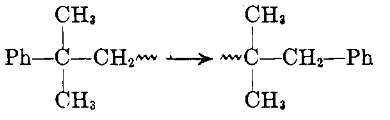
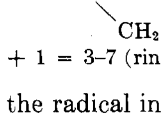
1-Phenylcycloalkylcarbenes (**5**) have been prepared *in situ* by the decomposition of 1-phenylcycloalkanecarboxaldehyde tosylhydrazones with sodium methoxide in N-methyl-2-pyrrolidone at 180° (the aprotic Bamford–Stevens reaction). The ring sizes studied were the three- through six-membered. These reactive intermediates (**5**) rearrange to mixtures of hydrocarbons in good yield, with varying degrees of phenyl migration and alkyl migration (ring expansion). The percentage of phedyl migration (the neophyl rearrangement) was found to increase with increasing ring size, from none in the cyclopropane case to 41% in the cyclohexane case. No evidence of insertion products was found in the hydrocarbon mixtures, although they conceivably could have formed and then rearranged under reaction conditions. The synthesis and properties of the starting aldehydes and tosylhydrazones are discussed, as well as attempted syntheses of possible insertion products. Comparisons are made between the results obtained here and those of related carbenoid systems in the literature.

The neophyl rearrangement is that shown below.



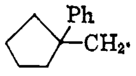
$$\mathrm{Ph{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2}\!\sim\ \longrightarrow\ \sim\!\mathrm{\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}Ph}$$

There exist examples of this rearrangement in radical, carbonium ion, and carbene processes. We have been studying the effect of pinning back the *gem*-dimethyl group into rings of various sizes to ascertain the effect such rings have on the ability of phenyl to migrate in all three types of intermediates. These studies show that there are definite differences in the ability of phenyl to migrate in such 1-phenylcycloalkylcarbinyl systems. The past work has involved ring sizes three through seven in the carbonium ion intermediates **1**[2] and ring sizes five and six in the radical intermediates **2** and **3**.[3] The ring-size effect in the fused system **2′** (related to **2**) has also been determined.[4] Work has been completed[5] on the radicals shown (**4**) and this will be reported separately at a later date. The present paper presents the results of such ring-size effects in the neophyl carbene rearrangement.[6] Carbene intermediates of structure **5** have been produced and their rearrangement has been studied. The results obtained for ring sizes five and six in this work substantiate the earlier observations concerning the effect of these rings in neophyl re-



$$(\mathrm{CH_2})_n\mathrm{C}\begin{matrix}\diagup\mathrm{Ph}\\ \diagdown\mathrm{CH_2^+}\end{matrix}$$

1, $n + 1 = 3\text{–}7$ (ring size)



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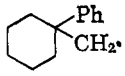

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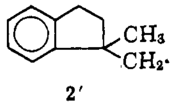
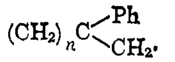
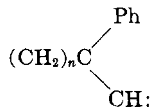


2′



$$(\mathrm{CH_2})_n\mathrm{C}\begin{matrix}\diagup\mathrm{Ph}\\ \diagdown\mathrm{CH_2}\cdot\end{matrix}$$

4, $n + 1 = 3$, 4, and 7 (ring size)



$$(\mathrm{CH_2})_n\mathrm{C}\begin{matrix}\diagup\mathrm{Ph}\\ \diagdown\mathrm{CH}:\end{matrix}$$

5, $n + 1 = 3\text{–}6$ (ring size)

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[1] Taken from the M.S. Thesis of J. M. K., June 1962, and the Ph.D. Dissertation of R. C. O., Feb. 1965, Loyola University, Chicago, Ill.

[2] J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, **27**, 3430, 3434 (1962).

[3] J. W. Wilt and H. Philip, *ibid.*, **25**, 891 (1960).

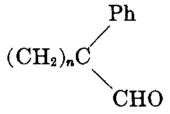
[4] J. W. Wilt and C. A. Schneider, *ibid.*, **26**, 4196 (1961).

[5] J. W. Wilt, J. F. Zawadzki, and L. A. Maravetz, to be published.

[6] Neophyl carbene itself has been studied by H. Philip and J. Keating [*Tetrahedron Letters*, 523 (1961)].

TABLE I

1-PHENYLCYCLOALKANECARBOXALDEHYDES AND DERIVATIVES

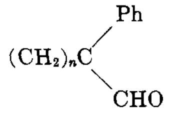

$$(CH_2)_nC(Ph)CHO$$

$n + 1$ (ring size)	Yield, %	B.p., °C. (mm.)	2,4-DNP m.p., °C.	Tosylhydrazone m.p., °C.
3	73	87–89 (2)[a]	189.5–191.5[b]	134.5–135[c]
4[d]	70	95–97 (1)[e]	154.5–155.5[f]	118–119[g]
5	46	81–83 (1)[h]	167–168[i]	136[j]
6	63	98–99 (1)[k]	201–202[l]	175–176[m]

[a] D. I. Schuster and J. D. Roberts [*J. Org. Chem.*, **27,** 52 (1962)] gave b.p. 65–71° (1 mm.). [b] Lit.[a] m.p. 190.4–191.8°. [c] In 77% yield from the aldehyde. *Anal.* Calcd. for $C_{17}H_{18}N_2O_2S$: C, 64.94; H, 5.78. Found: C, 64.99; H, 5.82. [d] *Anal.* Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.24; H, 7.60. [e] $n^{11}D$ 1.5407. [f] *Anal.* Calcd. for $C_{17}H_{16}N_4O_4$: N, 16.46. Found: N, 16.26. [g] In 83% yield from the aldehyde. *Anal.* Calcd. for $C_{18}H_{20}N_2O_2S$: C, 65.82; H, 6.14. Found: C, 65.96; H, 6.28. [h] $n^{20}D$ 1.5392, d^{20}_4 0.987; M. Tiffeneau [*Bull. soc. chim. France*, **49,** 1595 (1931)] gave b.p. 134° (15 mm.). [i] *Anal.* Calcd. for $C_{18}H_{18}N_4O_4$: N, 15.81. Found: N, 15.69. Semicarbazone m.p. 193–194°, lit.[h] m.p. 196.5°. [j] In 92% yield from the aldehyde. *Anal.* Calcd. for $C_{19}H_{22}N_2O_2S$: C, 66.63; H, 6.48. Found: C, 66.53; H, 6.58. [k] $n^{20}D$ 1.5389, d^{20}_4 0.996; M. Tiffeneau, P. Weill, J. Gutman, and B. Tchoubar [*Compt. Rend.*, **201,** 277 (1935)] gave b.p. 144–145° (19 mm.). [l] *Anal.* Calcd. for $C_{19}H_{20}N_4O_4$: N, 15.21. Found: N, 15.09. Semicarbazone m.p. 209–210°, lit.[k] m.p. 219°. [m] In 98% yield from the aldehyde. *Anal.* Calcd. for $C_{20}H_{24}N_2O_2S$: C, 67.38; H, 6.79. Found: C, 67.09; H, 6.54.

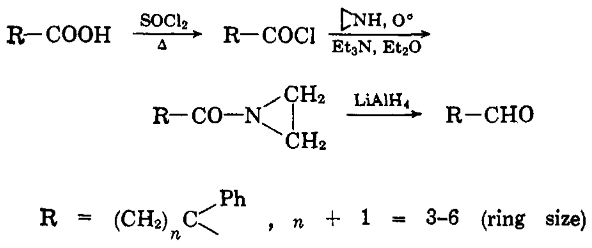
arrangements of the ions and radicals and extend the previously put forward explanation of them to the neophyl carbene rearrangement as well.

The series of 1-phenylcycloalkanecarboxaldehydes (6) was prepared and individual members, where new, were characterized (Table I). Their preparation was


$$(CH_2)_nC(Ph)CHO$$

6, $n + 1 = 3\text{–}6$ (ring size)

best effected by us from the corresponding acids *via* the N-acylaziridines, as shown (eq. 1). Other methods

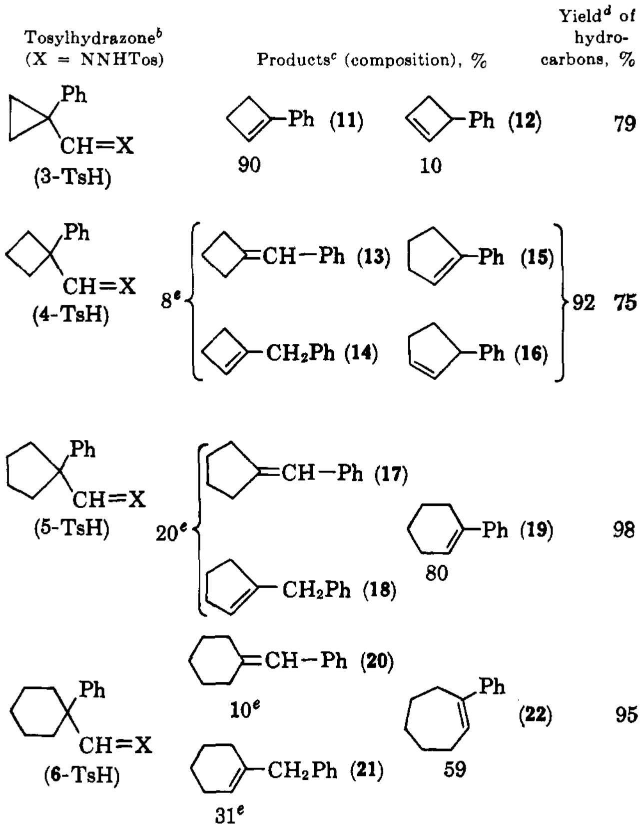


(1)

were also used and these are briefly described in the Experimental section. The aprotic Bamford–Stevens reaction[7] was then carried out on the tosylhydrazones (see Table I) under the conditions described by Friedman and Schechter.[8] The reactions proceeded quite well and afforded hydrocarbon products in good yields. The products obtained as well as other reaction data are contained in Table II.

TABLE II

PRODUCTS FROM TOSYLHYDRAZONE DECOMPOSITIONS[a]



[a] Performed in N-methyl-2-pyrrolidone solvent at 180°, using sodium methoxide as the base. The nitrogen evolution was essentially quantitative in all cases. [b] For properties, see Table I. [c] Hydrocarbons only, established *via* infrared and n.m.r. spectroscopy, gas chromatography, and comparison with knowns. The compositions given are those for short reaction times (5–10 min.). With further heating, particularly in the phenylcyclobutene products, isomerization occurred (see Discussion and Experimental). [d] All yield and composition data are from at least three runs and are averaged. The agreement among runs was ±3%. Products that were not volatile in gas chromatography were not investigated. [e] Extent of neophyl rearrangement.

Carbenes are postulated intermediates in a number of reactions.[9] An unequivocal demonstration of their formation in the Bamford–Stevens reaction has not appeared, however, and the entire body of data found in this paper could conceivably be explained without their intermediacy. For instance, carbonium ions, formed in the aprotic solvent (N-methyl-2-pyrrolidone, NMP) used, at the high temperature employed (180°), could be the true precursors of the products observed,[10] but carbenes are generally cited as the intermediates in such

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(7) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952). The original work was done in a protic solvent. For aprotic modifications of the reaction, *cf.* J. W. Wilt and W. J. Wagner, *J. Org. Chem.*, **29**, 2788 (1964), and the references therein.

(8) (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (b) *ibid.*, **82**, 1002 (1960); (c) *ibid.*, **83**, 3159 (1961).

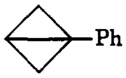
(9) *Cf.* J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964.

(10) The situation is confused because carbenes and highly energetic ("hot") carbonium ions show similar reaction behavior (*viz.*, alkyl/aryl migration, hydride shifts, and even insertion). The addition of carbenes to double bonds to form cyclopropanes is probably is the best method of differentiation, but such additions have been rarely sought in reactions of the type described and found but once. R. J. Crawford and R. Raap [*Proc. Chem. Soc.*, 370 (1963)] trapped phenylmethoxycarbene with 1-decene to give a cyclopropyl derivative in 3% yield under aprotic Bamford–Stevens conditions. Several other carbenes were not so captured in their study.

reactions,[11] and the present results will be discussed in these terms so as to relate the present results to others in the literature.

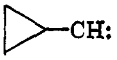
As a general statement of the results, one sees from Table II that phenyl and/or alkyl migration comprised the reaction pathway found. *No detectable insertion products were observed* (see later). The ring size present affected the relative amount of phenyl migration (*i.e.*, the neophyl rearrangement), from none in the cyclopropyl compound to some 41% in the cyclohexyl case with a gradual increase in each succeeding ring size. A complete summary of the effect of ring size on the neophyl rearrangement will be presented later when the further results of the radical study are published.[5]

1-Phenylcyclopropanecarboxaldehyde tosylhydrazone (3-TsH) yielded seemingly only ring-expanded products though very minor products (<1%) apparent in gas chromatography were not extensively investigated. Even the results obtained were dependent upon the presence of diphenylamine in the reaction. Otherwise, only polymer (probably polymerized **11**) resulted. No substance with properties expected for **7** (a possible insertion product) was found.



7

It would be unlikely, however, for a substance of this structure to survive the reaction conditions employed (180°) and whether **7** was formed cannot be certainly answered.[12] Also, the reported fragmentations of α-cyclopropylcarbenes such as **8**[8b] and **9**[13] to unsaturated products (ethylene and acetylene from **8** and **10** from **9**) was not observed in the present instance.



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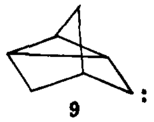

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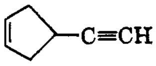
The likely products from such a fragmentation, would be ethylene and phenylacetylene as shown by eq. 2.



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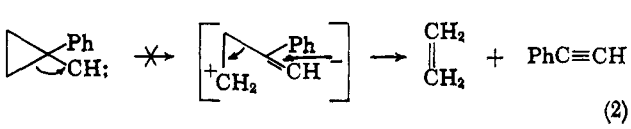

Neither product was observed and phenylacetylene was found absent in the hydrocarbon product through comparison with an authentic sample. The ring expansion actually observed with the present system parallels the behavior of the analogous carbonium ion[2] and probably reflects the driving force associated with the relief of considerable ring strain. Control experiments (Table III) proved that the major product **11** was isomerized to **12** (eq. 3) under longer heating times (together with polymer formation, however, which accounts for the lower yields with increased heating times), so that **12** is not considered a direct reaction product.[14]

11 **12** (3)

In accord with this is the finding that a separately prepared mixture of **11** and **12** (11-fold richer in **11**) gave an isomerized mixture only 1.5-fold richer in **11** after heating in N-methyl-2-pyrrolidone (diphenylamine present) for 10 min. This isomerization can perhaps be rationalized from the examination of scale drawings of **11** and **12**.[15] In **11** there is considerable crowding between the ortho phenyl hydrogen and the vinyl hydrogen when the rings are coplanar. Presumably this steric effect twists the molecule somewhat and destabilizes the system, allowing the less strained **12** to form in a base-catalyzed isomerization (possibly *via* the allylic anion of **11**).

TABLE III

EFFECT OF TIME ON THE DECOMPOSITION OF 1-PHENYLCYCLOPROPANECARBOXALDEHYDE TOSYLHYDRAZONE

Reaction time, min.	Ratio, 11:12	Yield, %
5	9.5	79
10	2.5	58
20	0.65	55
30	0.33	33

1-Phenylcyclobutanecarboxaldehyde tosylhydrazone (4-TsH) gave primarily ring-expanded olefinic products, but the neophyl rearrangements did occur to a slight extent. As with 3-TsH, no insertion products were detected.[16] The identification of **13** in the reaction product was indirect. Authentic **13** and **15** are chromatographically indistinguishable and even their various spectra are difficult to tell apart, but catalytic hydrogenation of the reaction products yielded both

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(11) For some recent studies, *cf.* D. M. Lemal and A. J. Fry, *J. Org. Chem.*, **29**, 1673 (1964); D. G. Farnum, *ibid.*, **28**, 870 (1963); and further pertinent references given elsewhere in this paper. The review by E. Chinoporos [*Chem. Rev.*, **63**, 235 (1963)] has been updated further in *Chim. Chronika* (Athens, Greece), **28A**, 168 (1963).

(12) Some question exists as to whether the aprotic Bamford–Stevens reaction of cyclopropanecarboxaldehyde tosylhydrazone itself yields insertion products. Friedman and Shechter[8b] report cyclobutene as the major product (over 60%) with no specific mention being made about insertion products. However, H. M. Frey and I. D. R. Stevens [*Proc. Chem. Soc.*, 144 (1964)] claim to obtain principally bicyclobutane, the predicted insertion product, with only some 20% cyclobutene. The confusion does not end here, for the properties of bicyclobutane seem to vary with the mode of preparation. It has been reported by D. M. Lemal, F. Menger and G. W. Clark [*J. Am. Chem. Soc.*, **85**, 2529 (1963)] to be prone to autoxidation and radical polymerization below 0° and to isomerize thermally to butadiene within 4 min. at 150°. But Frey and Stevens (*op. cit.*) assert the bicyclic hydrocarbon is stable at 180°! The hydrocarbon has also been made by K. B. Wiberg and G. M. Lampman [*Tetrahedron Letters*, 2173 (1963)] and by R. Srinivasan [*J. Am. Chem. Soc.*, **85**, 4045 (1963)]. The former report the substance is stable at room temperature while the latter agrees with Lemal's finding that isomerization to butadiene occurs at a "relatively low temperature." Be all this as it may, the thermal isomerization of **7** to phenylcyclobutene (**11**) would be expected to be relatively easy, since conjugation with the phenyl group would be developed in the transition state.

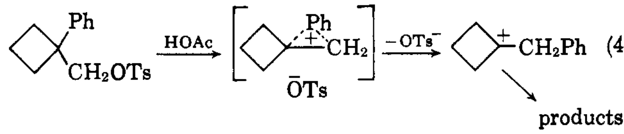
(13) S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963).

(14) Inspection of the data in Table III indicates that the ratio of **11**:**12** drops too fast, when compared with the yields obtained, for **11** to be lost solely through polymer formation.

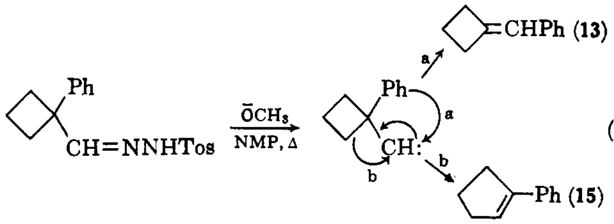
(15) Bond angles and distances were obtained from E. Goldish, K. Hedberg, and V. Schomaker, *J. Am. Chem. Soc.*, **78**, 2714 (1956); R. C. Lord and D. G. Rea, *ibid.*, **79**, 2401 (1957); J. R. Nielsen, M. Z. El-Sabban, and N. Alpert, *J. Chem. Phys.*, **23**, 324 (1955); and L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, 2nd Ed., 1960, p. 260.

(16) The expected insertion product would be 1-phenylbicyclo[2.1.0]-pentane. The parent bicyclopentane has been prepared and is stable to thermal isomerization at 230° for 36 hr. At 330° cyclopentene is formed. *Cf.* R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957). Again it is probable that a 1-phenyl substituent would lower the temperature needed for isomerization.

phenylcyclopentane and benzylcyclobutane and the sequence of gas chromatographic (g.c.) peaks suggested (by analogy with the other ring studies) the presence of **14** as well as **13** to account for the benzylcyclobutane. Synthetic mixtures of the saturated hydrocarbons were prepared for comparison until the g.c. and n.m.r. evidence indicated a match with the hydrogenated product, *viz.*, the 92:8 of Table II. The formation of principally **15** and **16** represents a decided difference between this study and that of the carbonium ion,[2] where the neophyl rearrangement was the sole reaction pathway. The difference probably lies in the fact that the acetolysis studied earlier involved phenyl rate participation as shown by eq. 4, with the 1-phenylcyclobutylcarbinyl cation actually never intervening, while the present study involved the *preformed* carbene, which by suitable electron shifts isomerized to more stable products (eq. 5). Thus, the highly reactive carbene, could be stabilized by processes a and b to yield **13** and **15**, respectively. This difference in product type (eq. 4 *vs.* eq. 5) appears to be another example of a solvolytic rearrangement which differs from one involving a more energetic intermediate.[17] The more energetic the intermediate, the more random the rearrangement process becomes. It is noteworthy in this regard, however, that phenyl migration to **13** (and **14**) still occurred, even though the strained cyclobutane ring is retained by such a change. Phenyl migration in carbenes still apparently possesses some of the advantages it has in solvolyses.[18] Indeed, when various steric restrictions (ring strain or conformational restriction) disappear—as in 6-TsH—phenyl migration becomes a major process (see later). Further experiments indicated that increased heating did not increase the per cent of **16**, unlike the results mentioned above with 3-TsH. While some *direct* formation of **16** may occur, thermal isomerization is its probable source. Conceivably, further heating led to no change because of less favorable thermodynamics here than in the case of **11** and **12**; *i.e.*, there is in **15** little of the steric hindrance associated with **11**.

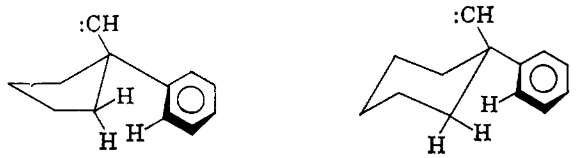


(4)



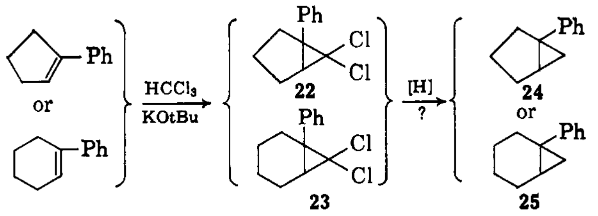
(5)

1-Phenylcyclopentane- and 1-phenylcyclohexanecarboxaldehyde tosylhydrazones (5-TsH and 6-TsH) demonstrated in their product compositions the difference between these two ring sizes previously found in both the corresponding carbonium ions[2] and radicals.[3] The neophyl rearrangement was favored considerably in the six-membered ring analog in all cases. We suggested earlier[3] a conformational difference that would be shown as follows in the present instance. Models indicate a restricted rotation of the phenyl ring in i caused by the adjacent cyclopentane ring hydrogens interfering with the passage of the ortho ring hydrogens. Probably the transition state requirements for the neophyl rearrangement in i are those associated with the carbonium ion and radical, and this restricted rotation accounts for the decreased ability of phenyl to migrate in such intermediates. The situation is normal in ii and the neophyl rearrangement to **20** and **21** occurs readily. The statistical distribution of phenyl-migrated product(s) is 33% and the 41% observed indicated a slight preference for phenyl migration over ring expansion in this system.[18]

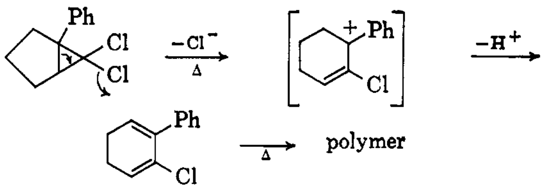


i ii

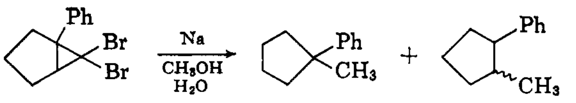
We thought the possible insertion products **24** and **25** might be synthesized in these two ring sizes, since the parent bicycloalkanes are known. If these 1-phenylbicycloalkanes could be made, tests could be carried out to see if they survive reaction conditions such as were used in this work. The route tried is shown by eq. 6. Dichlorocarbene addition apparently proceeded acceptably in both cases, but **22** proved quite unstable, polymerizing readily upon attempted vacuum distillation with liberation of hydrogen chloride. Possibly the diene shown was the cause of this undesired side reaction (eq. 7). The preparation of the dibromo analog of **22** was similarly effected and the crude, undistilled product was reduced with sodium in wet methanol. Ring cleavage resulted (eq. 8), however, and no evidence for **24** was found. The instability of **22** and the formation of phenylmethylcyclopentanes and no phenylcyclohexane in the above reduction are perhaps ex-



(6)



(7)



(8)

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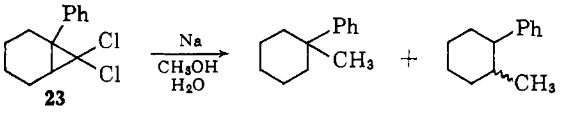
[17] *Cf.* J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 205 ff, for references and discussion of this point.

[18] Philip and Keating (ref. 6) give the phenyl/methyl "migration aptitude" in neophyl carbene itself as *ca.* 10:1. The same ratio in the solvolysis of neophyl systems is, however, about 100 times greater.

pected.[19a,b] Likewise, the attempt to prepare **25** from **23** (which was distillable[19a]) led to ring opening (eq. 9). Since no phenylcyclohexane was formed in the



(9)

reduction of the dibromo analog of **22**, no phenylcycloheptane was believed to be produced here. The evidence, however, is by analogy since this latter hydrocarbon was gas chromatographically indistinguishable from the ring-opened products. The observation that **23** was thermally stable while **22** was not lends credence to the mode of decomposition cited above (eq. 7), since the less likely expansion to a seven-membered ring would be required of **23**.[19a]

Lastly, the formation of isomerized phenyl-migration products (**18** and **21**) again represents probable thermal isomerization under reaction conditions, as previously observed.[2] As **17** and **19** were not separable gas chromatographically under all conditions tried, the exact amount of **17** is unknown. The infrared spectrum of the collected product (mostly **19**) indicated very little **17**, however, and most of the neophyl rearrangement in this ring size showed up as **18**.

During the course of this work a study appeared[20] on the effect of ring size on the reactions of cycloalkylcarbenes formed by the action of sodium metal on cycloalkylcarbinyl chlorides. The results indicated that insertion products were generally minor (though found at times) and that ring expansion was competitive in the small rings—results with which our own are in general agreement.

Experimental

Melting points were taken on a calibrated Fisher-Johns block. Neither melting points nor boiling points are corrected for stem exposure. Infrared data was obtained on a Perkin-Elmer Model 21 spectrophotometer using sodium chloride optics. Only significant absorptions are listed when the spectra are given. Gas chromatography was performed using helium as the carrier gas on an Aerograph A-90-P (Wilkens) instrument for 3- and 4-TsH (flow rate *ca.* 60 ml./min.) and on a Model 154-C (Perkin-Elmer) for 5- and 6-TsH (5-lb. pressure). The composition and yield of products was usually calculated from g.c. peak areas, using calibration data obtained for individual hydrocarbons to correct for differences in thermal conductivity responses. N.m.r. data was obtained through the courtesy of the Analytical Division of G. D. Searle and Co., Skokie, Ill., and the courtesy of Drs. R. C. Miller and C. G. Miller, De Paul University, Chicago, Ill. Analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparation of 1-Phenylcycloalkanecarboxaldehydes (6).—These compounds were best prepared by the reaction of the appriate 1-phenylcycloalkanecarboxylic acid chloride[21] and ethylenimine followed by reduction with lithium aluminum hydride. The procedure used was that of Brown and Tsukamoto.[22] The infrared spectra of all the aldehydes were compatible with their structures. Further data on these aldehydes are given in Table I. **1-Phenylcyclopentane- and 1-phenylcyclohexanecarboxaldehydes** were also prepared (11 and 18%, respectively) by the oxidation of the carbinols[2] with chromium trioxide in *t*-butyl alcohol and by the reduction of the carbonitriles[21] with lithium triethoxyaluminohydride[23] (32 and 25%, respectively). 1-Phenylcyclohexanecarboxaldehyde was synthesized in addition, in very poor yield, by the interaction of phenyl Grignard reagent and 1-bromocyclohexanecarboxaldehyde,[24] as reported.[25]

1-Phenylcycloalkanecarboxaldehyde Tosylhydrazones (3-TsH through 6-TsH).—These were prepared as described below for a representative case. A mixture of 1-phenylcyclopentanecarboxaldehyde (2 g., 12 mmoles), tosylhydrazine (2.2 g., 12 mmoles), and glacial acetic acid (3 drops) was heated at reflux in ethanol (40 ml.) for 30 min. After cooling the solution in ice, the precipitated tosylhydrazone was filtered and recrystallized from ethanol. Further data on these compounds may be found in Table I.

Decomposition of Tosylhydrazones.—All decompositions were carried out as follows. The tosylhydrazone was dissolved in N-methyl-2-pyrrolidone (the generous gift of Antara Chemicals), using 20 ml. of solvent per gram of tosylhydrazone. Freshly prepared sodium methoxide (1.2 equiv.) was added[26] and the mixture was stirred briefly and then immersed in a bath at 180° for 5 min. In the case of 3-TsH only, diphenylamine (0.25 equiv.) was added with the methoxide. Nitrogen was evolved quickly and essentially quantitatively and was collected over water after passage through cold traps. The reaction material was cooled and water was added. Emulsions at this point were dispersed with solid ammonium chloride. The hydrocarbon products were extracted with either pentane or hexane. Gas chromatography was then done on the extracts and the collected hydrocarbons were identified by instrumental methods (see later). The scale of the decompositions ranged from *ca.* 0.1- to 10-g. samples of the tosylhydrazones. Further information is contained in Table II.

Identification of Products.—The products of these reactions were identified through comparison with known samples, principally *via* infrared and n.m.r. spectroscopy and g.c. retention times. The preparation of the authentic hydrocarbons is described below. N-Methyl-2-pyrrolidone was frequently found with the hydrocarbon fraction, but g.c. separation or more efficient extraction procedures removed it. Also, very minor peaks (<1% of the total peak area of hydrocarbons) were unidentified from 3-TsH. They were not, however, either styrene or phenylacetylene, both of which were eliminated through comparison with knowns.

Preparation of Authentic Hydrocarbons.—**1-Phenylcyclobutene** (**11**) was prepared as described.[2] The ultraviolet and infrared spectra[2] of this material matched that of the material isolated from the decomposition of 3-TsH, as did their retention times (7 min.) on a column of Carbowax 20M (20%) on firebrick (5 ft. × 0.25 in.) at 150°. N.m.r.[27] (A-60, TMS standard, in CCl_4, in δ, p.p.m.) had a multiplet (2H) at 2.52 (4-CH_2), multiplet (2H) at 2.8 (3-CH_2), triplet (1H) at 6.21 (—CH=C<, $J \sim 1$ c.p.s.[28]), and the aromatics (5H) at 7.2 (C_6H_5). **3-Phenylcyclobutene** (**12**, retention time under above conditions 3.4 min.) was not otherwise prepared for comparison. Rather, the mixture of hydrocarbons from 3-TsH was hydrogenated over Adams catalyst at 20 p.s.i.g. to give only phenylcyclobutane (*q.v.*). From this result and from the isomerization of **11** to a substance with a retention time of 3.4 min., the latter material was assumed to be **12**. **Phenylcyclobutane** was prepared by the reductive cleavage of 1-phenylcyclobutyl methyl ether with sodium–potassium alloy[5] and its retention time under the above conditions,

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(19) (a) Others have noted the instability of the dihalocarbene–cyclopentene adduct (and the stability of the corresponding cyclohexene adduct): *cf.* E. Bergman, *J. Org. Chem.*, **28**, 2210 (1963). The phenyl substituent should accentuate this behavior. (b) Whereas Criegee and Rimmelin[16] obtained only cyclopentane from bicyclo[2.1.0]pentane by catalytic hydrogenation, W. von E. Doering and A. K. Hoffmann [*J. Am. Chem. Soc.*, **76**, 6162 (1954)] obtained methylcyclohexane and not cycloheptane by Raney nickel reduction of 7,7-dichloronorcarane. While the latter result is more nearly apropos to ours, reduction with sodium in wet methanol usually does not open the cyclopropane ring. One is again tempted to ascribe the difference observed in the present case to the phenyl substituent.

(20) H. G. Richey, Jr., and E. A. Hill, *J. Org. Chem.*, **29**, 421 (1964).

(21) *Cf.* ref. 2 and also J. W. Wilt and H. Philip, *ibid.*, **24**, 616 (1959).

(22) H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 4549 (1961).

(23) H. C. Brown, C. J. Schoaf, and C. P. Garg, *Tetrahedron Letters*, 9 (1959).

(24) I. Heilbron, E. R. H. Jones, R. W. Richardson, and F. Sondheimer, *J. Chem. Soc.*, 737 (1949).

(25) B. Tchoubar and O. Sackur, *Compt. Rend.*, **207**, 1105 (1938).

(26) A purple color often developed at this point owing to some still unexplained reaction between the methoxide and N-methyl-2-pyrrolidone.

(27) Unless the actual range is given, the δ positions of multiplets are their centers. The solvent unless stated otherwise was deuteriochloroform.

(28) G. V. Smith and H. Kriloff [*J. Am. Chem. Soc.*, **85**, 2016 (1963)] give the coupling constant between the vinyl and methylene protons in cyclobutene as 1.5 and in cyclopentene as 2.1 c.p.s.

4.4 min., and infrared and n.m.r. spectra matched those of the material isolated from the hydrogenation of the 3-TsH products. The infrared spectrum (neat liquid) had absorptions at 6.2, 6.66, 6.88, 8.04, 9.67, 11.1, 12.75, 13.35, 13.7, and 14.37 μ. N.m.r. had a multiplet (6H), δ 1.6–2.5 (ring CH_2); quintet (but split further, 1H), 3.4 (–CH<); and the aromatics (5H), at 7.1 (C_6H_5).

1-Phenylcyclopentene (**15**) was prepared by the method of Tallent.[29] Its g.c. retention time on Carbowax 20M at 175° (7.3 min.) and infrared and n.m.r. spectra were the same (with the exception noted below) as those of the material isolated from 4-TsH. It absorbed in the infrared (neat liquid) at 3.25, 3.35, 3.48, 6.13, 6.23, 6.33, 6.67, 6.89, 7.45, 7.53, 7.72, 9.32, 9.64, 10.45, 11.03, 12.32, 13.34, and 14.5 μ. N.m.r. spectrum had a quintet (with further splitting, 2H), δ 1.7–2.3 (4-CH_2); multiplet (4H), 2.3–3.0 (3- and 5-CH_2); triplet (further split, 1H), 6.2 (—CH=C<, $J \sim 2$ c.p.s.[28]); and the aromatics (5H), 7.1–7.6 (C_6H_5). The infrared spectrum of **15** collected from 4-TsH has a split peak at 11.67 μ due to benzalcyclobutane (**13** *q.v.*) which had the same retention time as **15**. **3-Phenylcyclopentene** (**16**) was also prepared by the method of Tallent.[29] Its retention time on Carbowax 20M (175°) was 3.8 min. Throughout this work it was noticed that the unconjugated olefins (*e.g.*, **12** and **16**) eluted prior to their conjugated isomers. The presence of **16** in the products from 4-TsH was deduced from the retention time and from its catalytic reduction to phenylcyclopentane (*q.v.*). **Benzalcyclobutane** (**13**) and **1-benzylcyclobutene** (**14**) were believed produced from 4-TsH from the following facts: the infrared spectrum of **15** from this reaction showed the presence of **13** (*vide supra*) and the first-eluted material (Carbowax 20M, 175°, retention time 3 min.) was neither **15** nor **16**, and was reducible to benzylcyclobutane (*q.v.*). This material was therefore assigned structure **14**. Preparation of **13** and **14** as before[2] confirmed these g.c. assignments. To obtain the composition of the product, the hydrocarbons from 4-TsH were collected gas chromatographically and catalytically hydrogenated over Pd–C (5%) in methanol (50 p.s.i.g.). This reaction product was isolated and its infrared, n.m.r., and g.c. behavior matched that of a synthetic mixture of 92% phenylcyclopentane and 8% benzylcyclobutane. **Phenylcyclopentane** was prepared by the hydrogenation of authentic **15** (Pd–C, methanol, 40 p.s.i.g. of H_2, 80% yield, b.p. 70–71° at 1 mm., $n^{22.5}D$ 1.5270). It was identical with the major product obtained by the hydrogenation of the products from 4-TsH: retention time (Carbowax 20M, 175°) 6.2 min.; n.m.r. multiplet (8H), δ 1.3–2.3 (ring CH_2); multiplet (1H), 2.8–3.2 (ring —CH<); and aromatics (5H), 7.25 (C_6H_5). Benzylcyclobutane was prepared by the Huang-Minlon reduction of phenyl cyclobutyl ketone.[30] It was identical with the minor product isolated from the reduction of the 4-TsH products: retention time (Carbowax 20M, 175°) 4.6 min.; n.m.r. multiplet (6H), δ 1.5–2.3 (ring CH_2); a sharper multiplet (3H), 2.6–2.82 (ring -CH< superimposed on the benzylic CH_2); and the aromatics (5H), 7.2 (C_6H_5).

Benzalcyclopentane (**17**) and **1-benzylcyclopentane** (**18**) were obtained as a mixture by the dehydration of 1-benzylcyclopentanol.[2] Their retention times (Hercoflex,[31] 20% on Celite, column 8 ft. × 0.25 in., 190°) were 37 and 20 min., respectively. The benzyl isomer **18** was the major product from the dehydration and its infrared spectrum matched that of the first-eluting hydrocarbon (20 min.) isolated from the decomposition of 5-TsH: λ^{Nujol} 6.03, 6.21, 6.67, 7.71, 8.22, 9.3, 9.63–9.7 (doublet), 10.36, 12.08, 12.75, 13.25, and 14.33 μ. The presence of **17** in the reaction product was not definitely established. Its retention time under the conditions employed was the same as that of 1-phenylcyclohexene (**19**, *q.v.*) and a small amount may have been present in the collected **19**. However, the characteristic infrared absorptions (9.85, 10.48, and 11.62 μ) were weak in the infrared spectrum of collected **19**. **1-Phenylcyclohexene** (**19**), b.p. 91–95° (3–3.5 mm.), 46%, was prepared by the dehydration of 1-phenylcyclohexanol with *p*-toluenesulfonic acid. Its retention time of 35.5 min. (Hercoflex, 190°) matched that of the second-eluting hydrocarbon in the 5-TsH decomposition products and their infrared spectra were identical: λ^{Nujol} 6.06, 6.22, 6.67, 7.41, 8.80, 9.30, 9.46, 9.66, 9.93, 10.88, 11.08, 11.62 (weak but present in **19** from 5-TsH), 11.82, 12.47, 13.2, 13.5, and 14.45 μ.

Benzalcyclohexane (**20**) and **1-benzylcyclohexene** (**21**) were synthesized by the dehydration of 1-benzylcyclohexanol.[2] Their retention times were 30.2 and 26 min., respectively (Hercoflex, 190°) and these times were matched by the first- and second-eluting hydrocarbons from the decomposition of 6-TsH. The infrared spectra confirmed the g.c. identifications: λ (of the neat liquid mixture of **20** and **21**, 81% of the latter, from the dehydration) 6.05, 6.67, 9.15, 9.6, 10.4, 10.77, 11.8, 12.6, 13.5, and 14.25 μ. The mixture of **20** and **21** isolated together as the first two eluting fractions from the decomposition of 6-TsH gave essentially the same spectrum, confirming the composition as assigned by g.c., *viz.*, 75.5% **21** and 24.5% **20**. **1-Phenylcycloheptene** (**22**) was prepared by dehydration of 1-phenylcycloheptanol[32] and eluted in 36.5 min. (Hercoflex, 190°): λ^{Nujol} 6.05, 6.22, 9.3, 9.75, 10.4, 11.75, 11.83, 13.3, and 14.35 μ. The final eluting hydrocarbon from the decomposition of 6-TsH was identical with it in g.c. retention time and infrared spectrum.

Isomerization of Phenylcyclobutenes (11 and 12).—In addition to the 5-min. heating period usually used, the decomposition of 3-TsH (with diphenylamine present) was also carried out for longer periods (see Table III). The yields of hydrocarbon and the ratio of **11** to **12** were determined gas chromatographically.

Attempted Synthesis of 1-Phenylbicyclo[3.1.0]hexane (24) and 1-Phenylbicyclo[4.1.0]heptane (25).—1-Phenylcyclopentene was treated with potassium *t*-butoxide in hexane and chloroform was added dropwise at 0°.[33] The customary processing of the reaction led to extensive decomposition during the vacuum distillation of the product. Much hydrogen chloride was identified in the vapor, while the dark residue showed strong absorption at 6.1, 6.23, and 6.33 μ, indicating a phenyl-conjugated olefin—probably a phenyl x-chloro-1,3-cyclohexadiene. Similarly, the addition of bromoform was performed and the crude product (presumably 6,6-dibromo-1-phenylbicyclo[3.1.0]hexane) was immediately reduced with sodium in wet methanol. The isolated hydrocarbons (b.p. 47–49° at 1 mm., $d^{20}{}_4$ 0.880, $n^{20}D$ 1.5191) were a mixture, giving two g.c. peaks. Comparison with a known showed that neither peak represented phenylcyclohexane. The presence of C-methyl groups in the reduced product was indicated by infrared absorption at 7.25 μ, and the combustion analysis confirmed that reduction to phenylcycloalkanes had occurred.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.92, 89.73; H, 9.94, 10.07.

Because the first-eluting hydrocarbon possessed its aromatic C–H out-of-plane deformation at *ca.* 13.5 μ, while the the second had this absorption at *ca.* 13.3 μ, the former was very probably 1-phenyl-2-methylcyclopentane (stereochemistry unknown) and the latter was 1-phenyl-1-methylcyclopentane.[3]

1-Phenylcyclohexene was treated analogously with dichlorocarbene. 7,7-Dichloro-1-phenylbicyclo[4.1.0]heptane (28%, b.p. 99–100° at 0.7 mm., no reaction with $KMnO_4$ in acetone) was isolated. It appeared to be relatively stable thermally.

Anal. Calcd. for $C_{13}H_{14}Cl_2$: C, 64.74; H, 5.85. Found: C, 66.09; H, 6.27.

The infrared spectrum was exceedingly rich: 3.28, 3.32, 3.43, 3.52, 6.23, 6.70, 6.83, 6.93, 7.22, 7.49, 7.54, 8.08, 8.50, 8.80, 9.33, 9.54, 9.63, 9.73, 9.97, 10.23, 11.28, 11.50, 11.63, 11.85, 12.40, 12.75, 13.20, and 14.3 μ.

Reduction of this halide (6.5 g.) in dry ether (75 ml.) with sodium (12.6 g.) in methanol (66 ml.) containing water (4 ml.) yielded a hydrocarbon (b.p. 67–67.5° at 1.2 mm., $n^{20}D$ 1.5298, $d^{20}{}_4$ 0.924), homogeneous upon g.c. analysis.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.90, 89.84; H, 10.24, 10.08.

The infrared spectrum of the neat liquid showed λ 7.25, 13.2, and 13.55 μ. The available data suggest that in this case the products were again phenylcycloalkanes, presumably a mixture of 1-phenyl-1-methylcyclohexane and 1-phenyl-2-methylcyclohexane (stereochemistry unknown).

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[29] W. H. Tallent, *J. Org. Chem.*, **21**, 862 (1956).

[30] We thank Mr. L. Maravetz for this preparation. The ketone was a gift from Dr. R. P. Mariella (*cf.* R. P. Mariella and R. Raube, *J. Am. Chem. Soc.*, **74**, 521 (1952).

[31] An ester made from pentaerythritol and mixed C_{12} acids by the Hercules Powder Co., Wilmington, Del.

[32] This olefin was a sample prepared by J. W. Hill from alcohol prepared as given in J. W. Wilt and J. W. Hill, *J. Org. Chem.*, **26**, 3523 (1961).

[33] W. von E. Doering and A. K. Hoffmann, *cf.* ref. 19b.