Ring-Size Effects in the Neophyl Rearrangement. VI.[1] The 1-Phenylcycloheptylcarbinyl System

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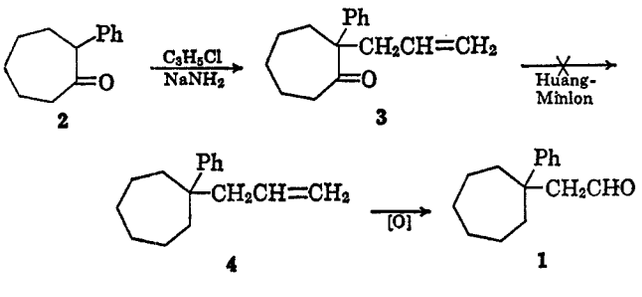
Several different methods of synthesis of 1-phenylcycloheptylcarbinyl derivatives are reported. Among the compounds synthesized are (1-phenylcycloheptyl)acetaldehyde (**1**), 1-phenylcycloheptylcarbinyl tosylate (**20**), and 1-phenylcycloheptanecarboxaldehyde tosylhydrazone (**23**). These three compounds were investigated as neophyl-like substrates in radical, cationic, and carbenic rearrangements, respectively. The rearrangement data show a close correspondence between the 1-phenylcycloheptylcarbinyl system and its cyclohexyl analog. With the pure compound in hand, the data reported earlier for the acetolysis of crude **20** has been corrected. All the data collected in this study of the neophyl rearrangements support the contention that conformational effects primarily determine the migration ability of the phenyl group, with little influence being ascribed to the electronic nature of the migration terminus.

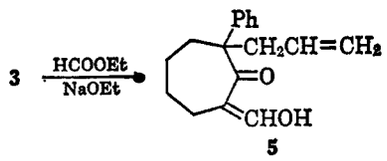
For some time investigations in this laboratory have dwelled on ring-size effects in the neophyl rearrangement. Much of the planned program has been achieved and published. An earlier report[3] on the carbonium ion rearrangement, however, mentioned the difficulty encountered in the synthesis of 1-phenylcycloheptylcarbinol and the attendant doubts that followed in the acetolysis of its tosylate and brosylate. A goal was therefore set to find a better synthesis of 1-phenylcycloheptylcarbinyl compounds and to establish more precisely the ring-size effect in this system. This paper reports the synthesis of such compounds and their behavior in the cationic, carbenic, and radical neophyl rearrangements. The data on the cationic rearrangement represent, in a sense, a reinvestigation of the earlier work,[3] while the latter two rearrangements in this system are discussed here for the first time.

Chronologically, the radical rearrangement was the first investigated. (1-Phenylcycloheptyl)acetaldehyde (**1**) was required as the substrate for rearrangement and its synthesis proved laborious. In fact, a number of the synthetic sequences investigated will not even be mentioned here. Initially it was felt that the route (Chart I) used for the synthesis of its lower ring homologs[4] would also suffice for **1**. Indeed, formation of 2-

CHART I

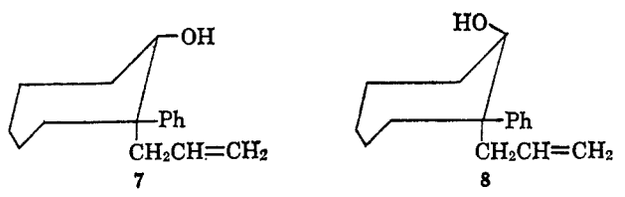


allyl-2-phenylcycloheptanone (**3**) was easily achieved. That allylation has occurred as shown was proved by the formation from **3** of a 7-hydroxymethylene derivative (**5**), characterized as its 2,4-DNP (2,4-dinitrophenylhydrazone) derivative (**6**). Repeated and varied



attempts to convert **3** to 1-allyl-1-phenylcycloheptane (**4**) were without success, however. The Clemmenson, Huang-Minlon, and mercaptal reductions were failures. The first left **3** untouched, a tribute to the steric hindrance of the carbonyl group; the second process also was without effect on **3** usually, though certain modifications of the reduction led to isomerization of the allyl function and formation of an unknown basic substance; and use of the mercaptal method was precluded by the failure of **3** to react with ethanedithiol.

As **3** was easily available, an attempt to effect reduction in steps was next tried. Reduction of **3** with a combination of aluminum chloride and lithium aluminum hydride[5] led to an epimeric pair of alcohols (**7**, **8**), one being formed in much greater percentage. It might be surmised that under the conditions used the more stable isomer would predominate,[6] though this was not proved. Because **7** has both the phenyl and hydroxyl groups equatorial, it may be the more stable. In any event, reduction of the tosylate(s) of this alcohol mixture with lithium aluminum hydride to **4** was unpromising and further investigation of methods to convert **3** to **1** was abandoned.



Attention was next given to a synthetic route (Chart II) that also placed a three-carbon substituent on the cycloheptane ring that was amenable to subsequent conversion to **1**, namely, one involving cyanoethylation. The sequence proved successful, affording **1** in an overall yield of 22.3% from 2-phenylcycloheptanone (**2**). All of the reactions were straightforward and require

(1) Paper V: J. W. Wilt, J. M. Kosturik, and R. C. Orlowski, *J. Org. Chem.*, **30**, 1052 (1965).

(2) Taken in part from the Dissertation of J. F. Z., Loyola University, 1962, and the M.S. Thesis of D. G. S., S. J., 1965.

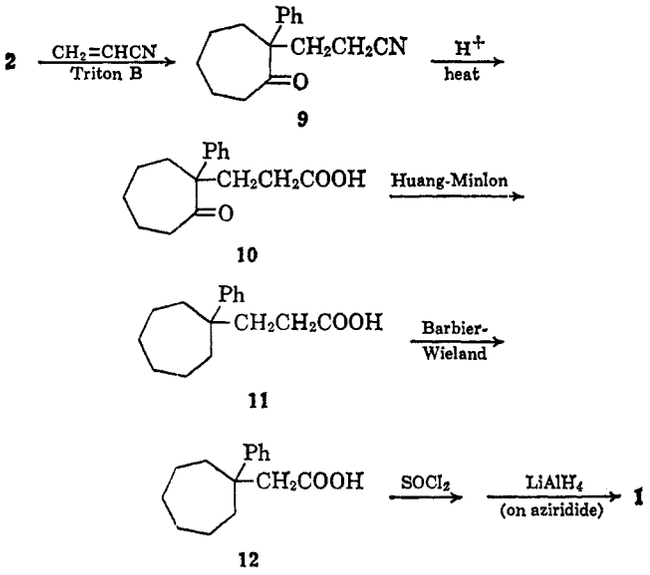
(3) J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, **27**, 3434 (1962).

(4) J. W. Wilt and H. Philip, F. S. C., *ibid.*, **25**, 891 (1960).

(5) R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, **80**, 2896 (1958).

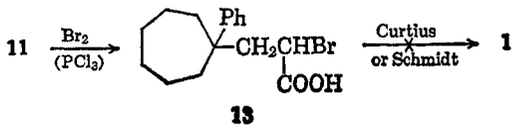
(6) *Cf.* H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 31.

CHART II

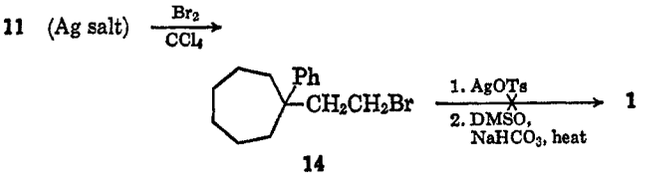


little additional comment.[7] The reduction of the keto acid **10** is of interest because of the extreme resistance of **3** in the same reaction. Even **10** was somewhat resistant, however, and quite forcing conditions were necessary. Under such conditions the yield was rather good (85.6%). It might be further mentioned that **10** has been reported[8] as the product (12% yield) of the hydrolysis of the lactam that resulted from carbamoylation of **2**. The key substance, (1-phenylcycloheptyl)acetic acid (**12**), was investigated thoroughly. Its nmr spectrum was in complete agreement with the structure proposed, with a singlet at δ 2.47 for the α-methylene group of the acid. The 12 cycloheptyl ring protons divided into two multiplets, one at higher field (eight protons) and one at lower field, consisting of the four protons at positions 2 and 7 which experience deshielding by the aromatic group at position 1. This nmr pattern has been observed for all the 1-phenylcycloheptylcarbinyl compounds prepared in this study. The final conversion of the acid chloride of **12** to the required aldehyde **1** was also accomplished using lithium tri-*t*-butoxyaluminohydride,[9] but the aziridide method[10] was superior in yield (59.5% *vs.* 30.9%).

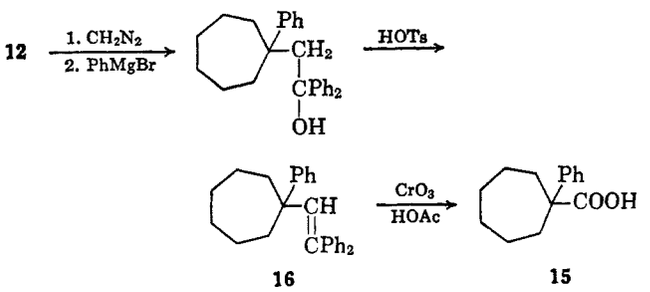
The poorest step in the above sequence was the Barbier–Wieland degradation of **11** to **12** (54.1%). As a result, alternative methods of converting **11** to **1** were briefly investigated. Hell–Volhard–Zelinsky bromination of **11** afforded the α-bromo acid **13** easily. Attempts to convert **13** directly to **1** *via* the Curtius and Schmidt reactions failed. Likewise, hydrolysis of **13** to the α-hydroxy acid could not be achieved.



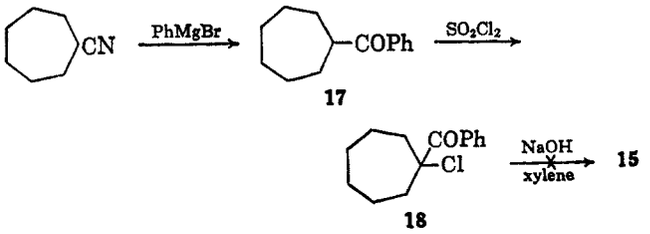
Finally, **11** was converted to the bromide **14** in the Hunsdiecker reaction with the intention of obtaining **1** through oxidation of **14** *via* the tosylate.[11] These plans were quickly dropped when **14** proved to be inert to silver tosylate.



The study of the cationic and carbenic rearrangements in this system required 1-phenylcycloheptanecarboxylic acid (**15**). An earlier report[3] from this laboratory had given the preparation of **15** by another Barbier–Wieland degradation, that of **12** to **15**. The facts following indicate that this earlier preparation was largely in error. Conversion of **12** to 1,1-diphenyl-2-(1-phenylcycloheptyl)ethene (**16**) was successful, as shown. This olefin (60.6% yield) was fully characterized and appeared to possess the structure given.



Oxidation of it with chromium trioxide in acetic acid (a method that gave a 78% yield of benzoic acid from triphenylethylene) gave an acid (purportedly **15**) in 52.4% yield that was grossly similar to the previously reported material, though the melting point reported could not be duplicated (81.5–82° *vs.* 85.5–86°). Because this synthesis of **15** actually involved many steps and two costly degradations, other methods were looked for. A route which looked attractive involved the quasi-Favorskii rearrangement. α-Chlorocyclohexyl phenyl ketone has been converted to 1-phenylcyclohexanecarboxylic acid with sodium hydroxide in hot xylene,[12] and a similar reaction was obviously called for to make **15**. To this end, cycloheptyl phenyl ketone (**17**) was prepared from cycloheptanecarbonitrile and phenyl Grignard reagent. Chlorination of **17** was best achieved using excess sulfuryl chloride as solvent, producing α-chlorocycloheptyl phenyl ketone (**18**) routinely in over 80% yield. Somewhat surprisingly, reaction of **18** under conditions



(7) Much of the sequence was modeled after a similar one by Bachmann, *et al.*: W. E. Bachman and L. B. Wick, *J. Am. Chem. Soc.*, **72**, 3388 (1950); W. E. Bachmann and E. J. Fornefeld, *ibid.*, **73**, 51 (1951).

(8) D. Elad and D. Ginsburg, *J. Chem. Soc.*, 4137 (1953).

(9) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958).

(10) H. C. Brown and A. Tsukamoto, *ibid.*, **83**, 2016, 4549 (1961).

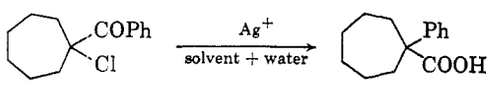
(11) N. Kornblum, W. J. Jones, and G. J. Anderson, *ibid.*, **81**, 4113 (1959).

(12) C. L. Stevens and E. Farkas, *ibid.*, **74**, 5352 (1952).

successful in the cyclohexane series afforded little **15**. Use of dioxane[13] as solvent was equally poor. A change to the metal ion promoted[14] Favorskii rearrangement was beneficial. 1-Phenylcycloheptanecarboxylic acid resulted in a pure state quite easily and this became, then, the method of choice for its preparation in this work. While the yield of **15** was not high, the ease of the preparation and the few steps from **17** made it attractive. Table I lists the various media

TABLE I

FAVORSKII REARRANGEMENT OF α-CHLOROCYCLOHEPTYL PHENYL KETONE



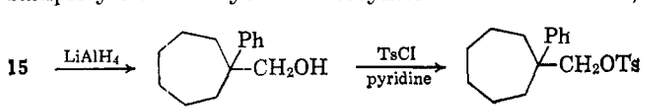
18 **15**

Cosolvent[a]	Temp, °C	Time, hr	Yield, %[b]
Dioxane	0	96	0
Dioxane	55	16	20.0
Dioxane	70–75	5	27.4[c]
Dioxane	80	4	23.4[d]
Dioxane	100	4	20.3
Ethanol	80	4	26.7
Methanol	65	2	11.7[e]

[a] A mixture with distilled water (3:2 solvent–water). The metal salt used was silver nitrate. [b] Based on unrecrystallized acid formed, in relation to silver chloride precipitated. Little loss was observed upon purification. [c] Large-scale preparation (see Experimental Section). [d] The salt used was lead nitrate. [e] The methyl ester of **15** was also formed here in 19.2% yield.

used and yields obtained in this reaction in this work. The remainder of the reaction product was not investigated in detail. It appeared from infrared measurements to be a mixture of the expected α-hydroxy, α-alkoxy (on the occasions of using aqueous alcohol solvents), and olefinic ketones.

With this alternative synthesis of **15** available, a comparison of the "Barbier–Wieland" and "Favorskii" samples of **15** was made. First of all, the latter melted at 127.5–128.5°, considerably higher than the 81.5–82° of the former. Further, the Barbier–Wieland sample was difficult to purify and the highest melting material was obtained with considerable loss. Conversely, the Favorskii acid was obtained in a highly pure state readily from its preparation. Reduction of each sample with lithium aluminum hydride afforded a liquid carbinol (**19**), but only **19** from the Favorskii sample yielded a crystalline tosylate **20**. Further still,



19 **20**

this tosylate acetolyzed to beyond 90% completion (*vide infra*), while the reported[3] solvolytic purity of the tosylate derived from the Barbier–Wieland acid was only 34.5%. The nmr and infrared spectral data also supported the belief that the Barbier–Wieland acid was not pure **15** (Table II). The aliphatic protons of the Barbier–Wieland acid appear to be spread over too great a range and its acid proton is anomalously posi-

(13) B. Tchoubar, *Compt. Rend.*, **235**, 720 (1952).

(14) A. C. Cope and E. S. Graham, *J. Am. Chem. Soc.*, **73**, 4702 (1951). *Cf.* also ref 12.

TABLE II

SPECTRAL COMPARISON OF SAMPLES OF **15**

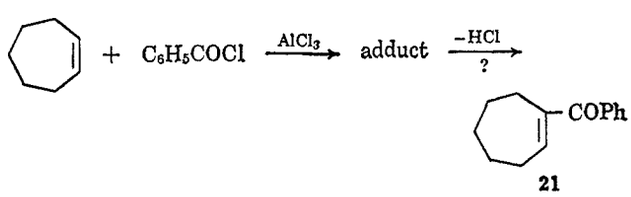
Sample	Proton (δ) Acid	Aromatic	Aliphatic	λc=o, μ
Barbier–Wieland	8.6	7.00–8.10	1.17–3.17[a]	5.82
Favorskii	12.13	7.07–7.50	1.42–2.50[b]	5.90

[a] The integration is difficult to accommodate to the cycloheptyl system. [c] The integration is clearly 4 + 8 protons.

tioned in its nmr spectrum. The aliphatic region and the acid proton of the Favorskii acid, on the other hand, are in good keeping with its structure. The 4 + 8 proton integration of its ring is identical with that of its homolog **12** (*vide supra*). The acid carbonyl absorption in the Favorskii acid is also in better agreement with a proximate phenyl group than it is in the Barbier–Wieland sample. For these reasons it is believed that the Barbier–Wieland degradation of **12** to **15** went awry. What was produced is not known for sure, though certainly *some* **15** was formed, as evidenced by the kinetic work reported earlier. The spectral data imply that some ring opening occurred in the degradation, giving an acid mixture that contained acyclic acids with a remote phenyl substituent and a more complex array of aliphatic protons.

1-Phenylcycloheptanecarboxylic acid (henceforth the Favorskii acid, **15**) proved difficult to derivatize. As a result, **15** was converted *via* the Arndt–Eistert sequence into **12**, giving further assurance to the structure assigned to each acid, as two entirely different synthetic sequences had been used in their preparation.

In closing this description of the synthesis of acid **15**, it is worth noting at least one of the alternative methods that failed. Cycloheptyl phenyl ketone (**17**) was sought *via* the olefinic ketone **21**. This latter has been reported[15] to result by a Darzens addition of benzoyl chloride to cycloheptene followed by dehydrochlorination. This reaction was complex and at least five major substances resulted when the reported procedure was tried in the present work. One of them did appear to be **21**, but the reaction mixture certainly did not warrant separation attempts.



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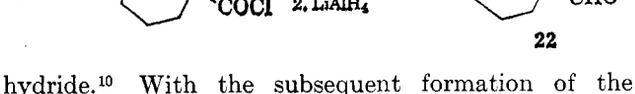
Conversion of acid **15** to 1-phenylcycloheptanecarboxaldehyde (**22**) was accomplished by way of reduction of the N-acylaziridine with lithium aluminum



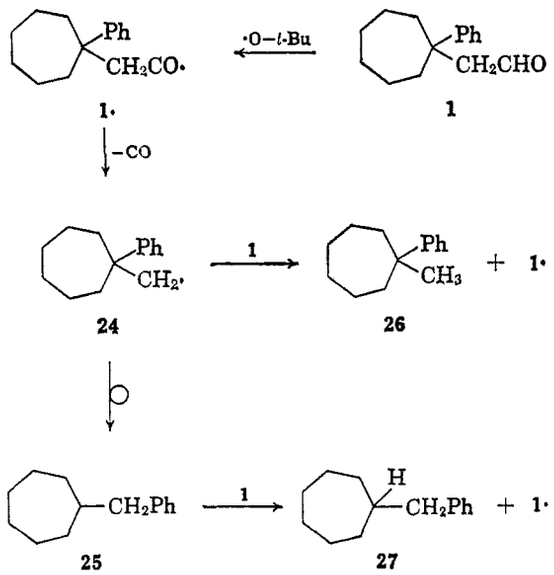
22

hydride.[10] With the subsequent formation of the tosylhydrazone **23** of the aldehyde, the substrates for all the intended rearrangement studies were at hand: **1** for the radical study, **20** for the cationic study, and **23** for the carbenic study.

The rearrangement of the 1-phenylcycloheptylcarbinyl radical (**24**) was brought about by the de-

(15) N. Jones, H. T. Taylor, and E. Rudd, *J. Chem. Soc.*, 1342 (1961).

CHART III



carbonylation of **1** with di-*t*-butyl peroxide (DTBP) according to Chart III. Because several similar studies have been reported in detail,[4,16] only the more interesting aspects of the present rearrangement will be mentioned. Most of these are gathered in Table III.

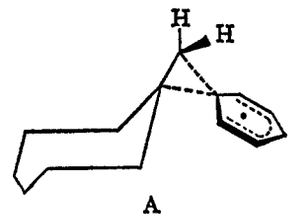
TABLE III

DECARBONYLATION OF (1-PHENYLCYCLOHEPTYL)ACETALDEHYDE (1) AT 160–163°[a]

	Run 1[b]	Run 2[c]
Time,[d] min	300	240
% CO evolved[e]	84.4	83.7
Half-time,[f] min	74	18
% hydrocarbon yield[e,g]	81.6	80.0
% rearrangement[h]	88.7	47.2
% recovery of 1[i]	12.5	0

[a] Bath temperature. [b] Neat aldehyde (10 mmoles). [c] Neat aldehyde (10 mmoles) containing 5 mole % benzyl mercaptan. [d] From time of addition of DTBP. Three equal injections totaling 30 mole % DTBP were made. [e] Based on consumed **1**. [f] Time for one-half the CO to be evolved. [g] The hydrocarbons were **26** and **27**, with a trace of olefinic material in run 1 (see text). [h] Per cent of **27**. [i] Per cent of 2,4-DNP of **1** isolated from reaction mixture.

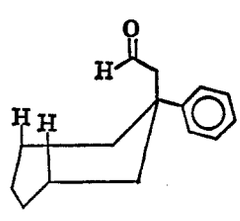
The decarbonylation of **1** proceeded excellently, giving 1-methyl-1-phenylcycloheptane (**26**) and benzylcycloheptane (**27**) together with a trace of olefinic hydrocarbons in run 1 derived from radical **25** by disproportionation.[17] The olefinic products were not observed in run 2 because disproportionation reactions were obviated by use of the excellent chain-transfer agent, benzyl mercaptan. The extent of the rearrangement of **24** (88.7%) matches that observed[4] for the cyclohexyl analog (89%), indicating that the two rings are similar in their abilities to adopt the Ar_1-3 transition state (shown for the cycloheptyl case as A) required of this rearrangement.[16] There appears to be little of the resistance to the formation of this state in the cycloheptyl instance that characterized the cyclopentyl analog (63% rearrangement[4]). This



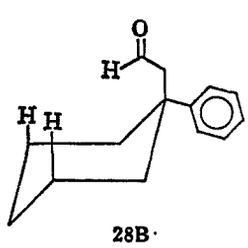
A

is borne out by a study of molecular models which indicated that the rotation of the phenyl ring in **24** has no hindrance from adjacent ring hydrogens and that it is, in fact, quite comparable to the cyclohexyl example in this respect. The ring-size effect, seven ≈ six > five for the neophyl radical rearrangement is therefore in agreement with the conformational explanation previously advanced.[4] The similarity of the cycloheptyl and cyclohexyl cases is further exemplified by the extent of rearrangement observed in the presence of benzyl mercaptan (run 2). The decrease to 47.2% rearrangement with **1** is close to the 50% rearrangement observed in the earlier study of the cyclohexyl compound. In the present work the 20 mole % of mercaptan used earlier was changed to 5 mole %. This still led to the decreased rearrangement, but it was different in that a fourfold *accelerated* decarbonylation rate was observed here. The catalysis of decarbonylations by mercaptans has been reported.[18] The change in product composition in run 2 is also further evidence against bridged radical *intermediates* in these reactions, as has been discussed.[4,16]

Three points of difference should be mentioned with regard to the behavior of **1** and its cyclohexyl analog.[4] The yields of carbon monoxide and hydrocarbon were better from **1** by some 35%. No acetone from the DTBP initiator was found in the decarbonylation of **1**, while 37–41% yields of acetone formed in the decarbonylation of (1-phenylcyclohexyl)acetaldehyde (**28**), and **1** decarbonylated about twice as fast as did **28**. No positive answer can be given for these differences, but a rationale may be advanced. Granted that conformations other than those shown exist, and that these others would not involve the steric effect discussed below, still both **1B** and **28B** are chair conformers with phenyl equatorial and they must therefore be of major importance. Examination of stereomodels showed that rotation of the acetaldehyde chain in each com-



1B



28B·

pound as shown places the aldehydic hydrogen in proximity to neighboring axial hydrogens, and more so in the more rigid **28B** than in **1B** (in fact, in **28B** the aldehydic hydrogen approaches to *within* the van der Waals radii of the axial hydrogens). This steric shielding may be enough to block the approach of radicals to **28** to effect chain initiation and chain transfer, retarding their rates relative to those for **1**. With

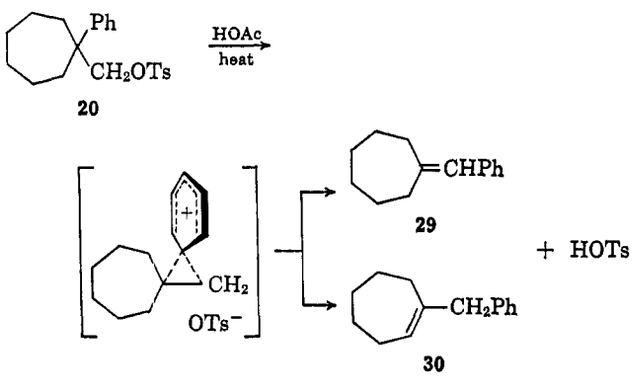
(16) J. W. Wilt and C. A. Schneider, *J. Org. Chem.*, **26**, 4196 (1961).

(17) Such products were not detected in our earlier studies[4,16] because of the less sensitive gc techniques used at that time. Disproportionation products in decarbonylation were first observed by C. Rüchardt, *Chem. Ber.*, **94**, 2599 (1961).

(18) K. E. J. Barrett and W. A. Waters, *Discussions Faraday Soc.*, **14**, 221, 255 (1953).

these rates retarded for **28**, acetone would form from the initiating *t*-butoxy radical and competitive processes could occur instead of chain transfer, lowering the yields of products as stated and increasing reaction time.

On the basis of the previous study of this type,[3] the acetolysis of 1-phenylcycloheptylcarbinyl tosylate (**20**) was expected to, and apparently did, take the course shown, involving phenyl participation in the



ejection of the tosylate ion leaving group. While the products **29** and **30** of the acetolysis were not of especial interest (they had been isolated and identified in the earlier study[3]), they were recovered and their identity was ensured by gas chromatographic analysis. Greater interest lay in ascertaining the rate constants and activation parameters so that the earlier data could be confirmed or rejected. The new data is summarized in Table IV. These data confirm the conclusion of the earlier study[3] in that the ring-size effect in the cationic rearrangement is seven > six > four > five, as claimed. Several values of the former study have been corrected, nonetheless. With the better kinetic data now available, the values of the "ring-size" and "phenyl" effects in this system are raised from 15[3] to 30 and decreased from 523[3] to 429, respectively. Because the latter value requires the kinetic rate constant for the *brosylate* derivative, the present *tosylate* value was increased by three, the usual factor relating the two arenesulfonates in solvolysis. The kinetic activation parameters now nicely fit the general pattern observed in the other ring sizes, especially a negative entropy of activation. The entropic values had ranged from 0 to −3.3 eu in the other compounds, and the even more negative value found in the cycloheptyl analog may represent the greater loss of conformational mobility in this ring as the transition state for rearrangement is achieved. The earlier doubts about the validity of the cycloheptyl ring-size data seem, then, to have been justified in part. The true data reveal **20** to be somewhat more solvolytically reactive than was reported, with activation parameters in accord with the other ring sizes, rather than in anomaly. However, the products previously reported were correct and the previous kinetic data was about that expected for the admittedly impure substrates used. The results incidentally support the earlier mentioned (*vide supra*) belief that acid **15** produced by the Barbier–Wieland degradation of **12** was indeed a mixture.

The investigation of the rearrangement of aldehydes **1** and **28** has shown a close similarity between the cycloheptyl and cyclohexyl rings in the rearrangement of the phenyl group. This same similarity was exhibited in the acetolysis study between **20** and 1-phenylcyclohexylcarbinyl tosylate: k_1 (25°), 1.02 *vs.* 0.32 × 10^{-6} sec^{-1}; ΔH^*, 24.6 *vs.* 25.7 kcal/mole; ΔS^*, −3.5 *vs.* −2.0 eu; "ring-size effect," 30 *vs.* 8.9; "phenyl effect," 429 *vs.* 652. This emphasizes once more that the neophyl rearrangements are sterically controlled. Whether the alicyclic ring in a 1-phenylcycloalkylcarbinyl compound is essentially flat or puckered determines more of the rearrangement process than does the electronic state of the migration terminus.

This view was further supported by the results of the last of the rearrangement studies reported here, the rearrangement of tosylhydrazone **23** under "carbenic" conditions. An earlier report[1] has given the results of such reactions in the lower homologs of **23**. From that study the products from 1-phenylcyclohexanecarboxaldehyde tosylhydrazone (**31**) are given in Table V for comparison with those from **23**. As is seen, the similarity of the two homologs in this reaction also supports the view that steric effects (namely conformational effects) rather than electronic ones govern these rearrangements. Mechanistically, the decomposition of **23** can be viewed as an aprotic Bamford–Stevens reaction. Abundant literature[19] exists in this area and an extended discussion will not be given here. There are, however, certain features of the reaction that warrant mention. The acetolysis of **20**, the acid-catalyzed dehydration of 1-benzylcycloheptanol and the carbenic decomposition of **23** are alike in that olefins **29** and **30** are formed and in proportions of about 30:70, respectively, in each case. Such results augur a common precursor, most probably the 1-benzylcycloheptyl cation (**32**). Late evidence has indeed been presented[20] that the Bamford–Stevens reaction is sensitive to the reaction medium and can

TABLE IV

ACETOLYSIS OF 1-PHENYLCYCLOHEPTYLCARBINYL TOSYLATE (**20**)

Temp, ±0.05°	$10^6 k_1$ sec^{-1}
25.00	1.02 ± 0.01
33.35	3.08 ± 0.01[a]
43.80	12.4 ± 0.5
47.20	18.7 ± 0.01
	ΔH^* = 24.6 ± 0.1 kcal/mole[b]
	ΔS^* = −3.5 ± 0.2 eu[c]

[a] Lit.[3] 2.31 × 10^{-6} sec^{-1} at 35°. [b] Lit.[3] for brosylate, 26.4 ± 0.5 kcal/mole. [c] Lit.[3] for brosylate, +4.5 ± 1.0 eu.

TABLE V

THE "CARBENIC" DECOMPOSITION OF TOSYLHYDRAZONES **23** AND **31**[a]

Compd	Hydrocarbon yield, %	Composition[b]
23	93	**29** (13%)
		30 (30%)
		1-Phenylcyclooctene (**33**, 57%)
31[c]	95	Benzalcyclohexane (10%)
		1-Benzylcyclohexene (31%)
		1-Phenylcycloheptene (59%)

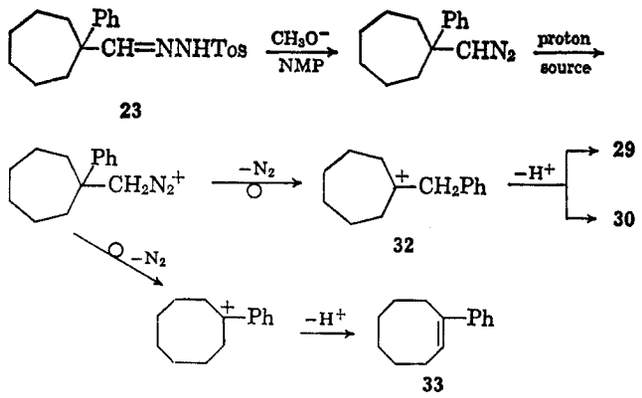
[a] In N-methyl-2-pyrrolidone with sodium methoxide at 180°. [b] To the nearest per cent. [c] *Cf.* ref 1.

(19) *Cf.* ref 1 for further references.

(20) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 659 (1965).

switch from a carbenic to a cationic mechanism. Although the use of N-methyl-2-pyrrolidone and sodium methoxide has been reported[21] to give carbenic decomposition of tosylhydrazones, the results found here could also be accommodated by the scheme shown in Chart IV. The proton source could be the parent

CHART IV



tosylhydrazone **23**, as has been observed in other examples.[20,22] The similarity in the formation of **29** and **30** from **23**, **20**, and 1-benzylcycloheptanol could then be rationalized by this scheme. A feature that differentiates the reactions of **20** and **23** is the absence of 1-phenylcyclooctene (**33**) in the acetolysis of the former. This can be explained by noting that the acetolysis proceeds with anchimeric assistance to the departure of the tosylate ion leaving group (*vide supra*). Because phenyl participates better than does a ring electron pair in **20**, ion **32** is rather quickly reached and no chance is afforded the formation of **33**. The "carbenic" process involving **23**, when viewed as an alternative cationic process, actually resembles a deamination, in that a diazonium ion is involved. The ready departure of nitrogen from this precursor is undoubtedly well in advance of the migrating neigh boring group, and, therefore, the anchimeric ability of the migrating group is less important. Statistically, ring expansion should be twice as frequent as phenyl migration. In both the cases of **23** and **31** (Table V) it is seen that ring expansion is indeed the major process, although it falls short of the theoretical 67%. This is no doubt due to some slight anchimeric character still remaining in the loss of the nitrogen which favors phenyl migration. If the decomposition of **23** is then viewed as one involving an energetic cation, insertion products might normally be expected. None were, in fact, formed to any significant degree. There are, interestingly, no cases of insertion reported in aprotic Bamford–Stevens reactions where phenyl migration is involved.[1] Either the insertion products are unstable and yield other products, or the phenyl migration and ring expansion are too fast. In the case of N-methyl-2-pyrrolidone as solvent, the cation produced (Chart IV) could be somewhat stabilized by this aprotic, high dielectric solvent to the extent that the lower energy processes of phenyl migration and ring expansion completely exclude the higher energy one of insertion.

(21) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).
(22) Unpublished work from this laboratory.

Experimental Section

All melting and boiling points are uncorrected for stem exposure. The former were taken on a calibrated Fisher-Johns block. Spectra were determined on Perkin-Elmer Models 21 and 37 (KBr Infracord), Beckman IR-5A (infrared), Cary Model 14 (ultraviolet), and Varian A-60 (nmr) instruments. Nmr data refer to carbon tetrachloride solutions with internal TMS standard and are in δ units (parts per million). The integrations were in agreement with the assignments given. Unless the range is given, only centers of multiplets are listed. Only infrared absorptions of structural significance are given. Gas chromatography was performed on a Wilkens Aerograph A-90-P instrument. A helium gas flow of 60 cc/min was employed. Signals were recorded in quantitative work on a Sargent SR-GC 1-mv recorder equipped with a disk integrator. Microanalyses were done by the Micro-Tech Laboratories, Skokie, Ill., and by Galbraith Laboratories, Knoxville, Tenn. In preparations that were performed a number of times, a representative procedure is given.

2-Phenylcycloheptanone (**2**).—Reaction of phenyldiazomethane with cyclohexanone led to this ketone, as reported[23] [45%, bp 117° (0.8 mm), n^{28}D 1.5402, mp 22.5–23.5°, λ^{neat} 5.85 μ (>C=O); lit.[23] bp 115–118° (0.8 mm), n^{25}D 1.5425, mp 21–23°]. The *in situ* formation of phenyldiazomethane from oxidation of benzalhydrazone[23] was found superior to its formation from azibenzil.[24] The semicarbazone (mp 155–156.5°, lit.[25] mp 155–156.5°) and 2,4-dinitrophenylhydrazone (mp 171–172°, lit.[26] mp 171–172.5°) further characterized ketone **2**. Attempts to prepare 7-benzal, 7-*m*-nitrobenzal, and 7-furfurylidene derivatives resulted in failure for the first two and a crude derivative (mp 71.5–74° from ethanol) from the third after a 1-week reaction time.

2-Allyl-2-phenylcycloheptanone (**3**).—Preparation was by the method described earlier[4] for its lower ring homologs [79.8%, n^{25}D 1.5410, d^{28}_4 1.035, bp 119° (0.9 mm), λ^{neat} 5.87 (>C=O) and 6.09 μ (C=C)]. No C–CH_3 absorption was shown.

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.00; H, 8.79.

The 2,4-DNP derivative was very difficultly formed (orange prisms, mp 159–164°). 7-Benzal and 7-furfurylidene derivatives could not be produced. Reduction of **3** was attempted without success by the Clemmenson method (toluene solvent with amalgamated zinc in aqueous acetic acid over a 6-hr period of reflux during which concentrated hydrochloric acid was added in portions); the Huang-Minlon method (a 3-hr reflux in diethylene glycol, with hydrazine and potassium hydroxide, which led primarily to allylic rearrangement of **3** and to an unknown basic material, bp 138–142° at *ca.* 1 mm. Use of sodium instead of the hydroxide was ineffective. Separate attempts to prepare the hydrazone of **3** or its semicarbazone failed; so the failure of the Huang-Minlon process probably is due to this fact.); and the mercaptal method (this derivative was not obtained by any reaction tried between **3** and ethanedithiol or benzyl mercaptan).

2-Allyl-2-phenyl-7-hydroxymethylenecycloheptanone (**5**).—To prove that allylation of **2** went as described to **3**, this derivative was prepared by reaction of **3** (35 mmoles) with ethyl formate and sodium methoxide in benzene under nitrogen (25°, 20 hr).[27] Isolation was achieved *via* the sodium salt, affording **5** as a yellow solid (22%, 2 g, mp 58–61°, deep violet color with alcoholic ferric chloride, readily soluble in 10% aqueous sodium hydroxide). The 2,4-DNP derivative (**6**) was readily prepared and recrystallized from ethyl acetate, mp 193.7–195.3°. The ease of preparation and the analysis suggest a mono derivative of the 7-hydroxymethylene group.

Anal. Calcd for $C_{23}H_{24}N_4O_5$: N, 12.84. Found: N, 12.63.

Unchanged **3** was recovered in 61.5% yield. Regeneration of **3** from **5** was accomplished by refluxing with sodium hydroxide solution (5%, 1 hr). The liberated oil was purified by extraction with ether followed by distillation. The sample of **3** so recovered was identical spectrally with the material used in the preparation of **5**, so the above low yield of **5** did not represent a fractionation of **3** from another isomer, but rather the sluggish reactivity of **3** itself.

2-Allyl-2-phenylcycloheptanol (**7**, **8**).—Reduction of **3** with lithium aluminum hydride and aluminum chloride in ether by a

(23) C. D. Gutsche and E. F. Jason, *J. Am. Chem. Soc.*, **78**, 1184 (1956).
(24) P. Yates and B. L. Shapiro, *J. Org. Chem.*, **23**, 759 (1958).
(25) C. D. Gutsche, *J. Am. Chem. Soc.*, **71**, 3513 (1949).
(26) J. W. Huffman and J. E. Engle, *J. Org. Chem.*, **26**, 3116 (1961).
(27) W. S. Johnson and H. Posvic, *J. Am. Chem. Soc.*, **69**, 1361 (1947).

literature method[5] afforded this mixture [83.4%, bp 126–129° (0.6 mm), $n^{26}D$ 1.5517, d^{28}_4 1.042, λ^{neat} 2.87 μ (OH)]. Gc analysis of the product (20% poly-*m*-phenyl ether on firebrick, 256°) showed two components, one being in decided excess.

Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.20; H, 9.54.

The 3,5-dinitrobenzoate derivative was prepared and recrystallized to a constant melting point from ethanol and finally ethyl acetate: mp 133.5–135°.

Anal. Calcd for $C_{23}H_{24}N_2O_6$: C, 65.08; H, 5.70. Found: C, 64.90; H, 5.89.

Tosylation of the mixture of **7** and **8** in pyridine gave a low-melting solid product which was immediately treated with lithium aluminum hydride in ether under reflux for 24 hr. Isolation of the product from this reaction (and many variations of it) led to small amounts of a hydrocarbon material boiling over a large range (96–125° at *ca.* 3 mm) with spectral properties indicating considerable allylic rearrangement of the allyl function. Unfortunately, extended research aimed at developing this reaction into a more promising route to **4** proved fruitless.

β-(2-Keto-1-phenylcycloheptyl)propionitrile (9).[7]—Ketone **2** (167 g, 0.887 mole) was dissolved in dry dioxane (freshly distilled from sodium, 680 ml) and treated with Triton B (18 ml of a 40% solution in methanol) slowly over 10 min. Acrylonitrile (57.2 g, 1.08 moles) in more dry dioxane (85 ml) was then added to the orange-red solution over 1 hr. The temperature rose to 45° during this addition. After the reaction mixture had been stirred overnight at 25°, the solvent was removed under reduced pressure on a steam bath and the residual oil was taken up in ether, washed well with water, and dried over sodium sulfate. Fractionation then gave **9** as a pale yellow, viscous oil [183 g, 86.4%, bp 184° (1.7 mm), $n^{27}D$ 1.5418, λ^{neat} 4.44 (C≡N) and 5.85 μ (>C=O)].

Anal. Calcd for $C_{16}H_{19}NO$: C, 79.64; H, 7.94. Found: C, 79.47; H, 8.05.

An attempt to make the 7-benzal derivative failed (see **3** also).

β-(2-Keto-1-phenylcycloheptyl)propionic Acid (10).[7]—The above nitrile (174.5 g, 0.72 mole), glacial acetic acid (1335 ml), concentrated hydrochloric acid (445 ml), and water (445 ml) were refluxed with stirring for 26 hr under nitrogen. The cooled solution was poured over crushed ice, and the crude acid oiled out as a brown tar that quickly crystallized as a tan solid [177 g, 94%, mp 108.5–110°, lit.[8] mp 105–106°]. This material was used in the following reduction. The analytical sample was recrystallized from aqueous methanol as a colorless solid: mp 109.8–110.3°; λ^{KBr} 3.3–3.9 broad (COO*H*), 5.85 (>C=O), and 5.9 μ (*C*OOH).

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74; neut equiv, 260. Found: C, 73.86; H, 7.75; neut equiv, 263.

The S-benzylisothiouronium salt was easily prepared and recrystalized from hot acetone: mp 145–146.5°.

Anal. Calcd for $C_{24}H_{30}N_2O_3S$: C, 67.57; H, 7.09. Found: C, 67.36; H, 7.08.

β-(1-Phenylcycloheptyl)propionic Acid (11).[7]—The above keto acid (99 g, 0.376 mole), potassium hydroxide (85%, 76.5 g) in water (37 ml), anhydrous hydrazine (Eastman, 95%, 62 ml), and diethylene glycol (410 ml) were stirred and brought to 130° over 1 hr. After further heating for 1.5 hr, more hydrazine (20 ml) was added and the heating was continued for 3 hr. At this point the reflux condenser was removed and the mixture was heated at 190–200° for 26 hr. The cooled solution was poured into cold, dilute hydrochloric acid (5 l.) to precipitate the acid. Recrystallization was effected from hexane (800 ml) to give **11** as white spears [79.3 g, 85.6%, mp 102.5–103.7°, λ^{KBr} 2.92–4.0 (COO*H*) and 5.9 μ (*C*OOH)].

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.00; H, 9.00. Found: C, 77.85; H, 9.00.

The S-benzylisothiouronium salt was recrystallized from ethanol: mp 158–160°.

Anal. Calcd for $C_{24}H_{32}N_2O_2S$: C, 69.86; H, 7.82. Found: C, 68.78; H, 7.33.

(1-Phenylcycloheptyl)acetic Acid (12).—The Barbier–Wieland degradation of **11** commenced with its conversion to the ethyl ester.[28] An 18-hr reaction of **11** (50 g, 0.203 mole) in ethanol (absolute, 250 ml) and benzene (1370 ml) with *p*-toluenesulfonic acid monohydrate (7 g) under reflux with stirring in a system equipped with a Dean–Stark trap led, after the usual processing, to **ethyl (1-phenylcycloheptyl)acetate** [colorless oil, 50.4 g, 90.4%, bp 165° (1.4 mm), $n^{26}D$ 1.5197, d^{24}_4 1.050, λ^{neat} 5.75 (>C=O) and 7.26 μ (C–CH_3)].

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.42; H, 9.69.

Treatment of this ester (50 g, 0.18 mole) in dry ether (375 ml) with phenylmagnesium bromide (from magnesium, 17.72 g, 0.73 g-atom, and bromobenzene, 119.6 g, 0.76 mole, in dry ether, 350 ml) under reflux for 2 days gave, after the customary work-up, the tertiary alcohol. The alcohol was not isolated but was immediately treated further with *p*-toluenesulfonic acid monohydrate (7 g) in benzene (1 l.) under reflux in a system equipped with a Dean–Stark trap. After 2 hr the requisite water had formed and the benzene solution was neutralized, dried, and evaporated to yield the diphenylethylene derivative. Oxidation of this crude material was performed in isooctane (160 ml) and glacial acetic acid (560 ml). To this solution at 40° was added in portions and with stirring a solution of chromium trioxide (70 g, 0.70 mole), water (52 ml), and more glacial acetic acid (375 ml) at such a rate as to keep the temperature below 50° (about a 45-min addition time). After the addition was completed, the reaction material was stirred at 48° for another 1.5 hr. The excess oxidant was decomposed by the cautious addition of methanol (100 ml). After having been concentrated under vacuum, the green material was taken up in water (1 l.) and extracted with ether (four 250-ml portions). The ether extracts were combined and treated with aqueous sodium hydroxide (10%, five 125-ml portions). The alkaline solution was then poured into a mixture of hydrochloric acid (10%) and ice, precipitating **12** as fine, off-white crystals. The crude acid was recrystallized from ethanol (Norit) as a colorless, crystalline solid [25.5 g; 54.1% from **11**; mp 92–93.2°; λ^{KBr} 2.95–3.9 (COO*H*) and 5.85 μ (*C*OOH); nmr, δ 1.3–1.7 (m) (some CH_2 groups of ring), 1.8–2.3 (m) (CH_2 groups at positions 2 and 7 of ring), 2.47 (s) (–CH_2COOH), 7–7.3 (m) (Ar–*H*), and 10.83 broad (COO*H*)].

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; neut equiv, 232.3. Found: C, 77.77; H, 8.73; neut equiv, 233.2.

The S-benzylisothiouronium salt was prepared and recrystallized from aqueous alcohol: mp 142–144°.

Anal. Calcd for $C_{23}H_{30}N_2O_2S$: C, 69.31; H, 7.59. Found: C, 68.41; H, 7.13.

(1-Phenylcycloheptyl)acetaldehyde (1).—This aldehyde was prepared from the acid above (4.65 g, 0.02 mole) by first obtaining the acid chloride through reaction with thionyl chloride in the usual way. The acid chloride was not overly stable and it was used directly after removal of the thionyl chloride under vacuum in the reduction to **1** by the method of Brown and Tsukamoto.[10] The aldehyde was a colorless oil [2.57 g, 59.5%, $n^{23}D$ 1.5418, bp 122° (0.85 mm), λ^{neat} 3.66 and 5.81 μ (–CHO)].

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.38; H, 9.17.

The yellow 2,4-DNP was readily prepared and recrystallized from ethanol–ethyl acetate: mp 165–166.5°.

Anal. Calcd for $C_{21}H_{24}N_4O_4$: N, 14.13. Found: N, 14.18.

The preparation of **1** using lithium tri-*t*-butoxyaluminohydride[9] was less satisfactory (30.9% yield).

Miscellaneous Work Aimed at the Synthesis of 1.—The bromination of acid **11** (10 g, 0.041 mole) was achieved at −80° by the addition of bromine (7 g, 0.044 mole) and phosphorus trichloride (1 drop). The reaction was then allowed to proceed at room temperature for 6 hr. Further phosphorus trichloride (1 drop) was then added and the mixture was heated at 90° overnight and at 100° for another 2 hr. Hot hexane (60 ml) was added and the hot mixture was filtered and allowed to cool. The α-bromo acid **13** crystallized as white needles [7.2 g, 54.7%, mp 110.3–111.3° after recrystallization from hexane, λ^{KBr} 2.9–3.85 (COO*H*) and 5.9 μ (*C*OOH)].

Anal. Calcd for $C_{16}H_{21}BrO_2$: Br, 24.58. Found: Br, 24.64.

The bromo acid was unchanged after a week long reflux with aqueous potassium hydroxide (*ca.* 10%), followed by acidification. The Schmidt reaction on **13** and the Curtius reaction on its acid chloride were tried a number of times and with several modifications of each method. In no instance were other than traces of an aldehyde observed. Treatment of the dried silver salt of **13** (11.2 g, 0.032 mole) in dry carbon tetrachloride with bromine at reflux in the usual manner[29] led to **β-(1-phenylcycloheptyl)ethyl bromide [14**, 3.6 g, 40.5%, bp 159–164° (1.8 mm),

(28) The method used was that of E. B. Carton, H. F. Lederle, L. H. Schwartzman, and G. F. Woods, *J. Am. Chem. Soc.*, **74**, 5126 (1952).

(29) J. W. Wilt, *ibid.*, **77**, 6397 (1955).

λ^{KBr} 17.1 and 17.9 μ (C-Br)]. Subsequent failure of this bromide to react with silver tosylate in acetonitrile[11] in the dark at 0–5° for 24 hr (no silver bromide) stopped further work with **14**.

1,1-Diphenyl-2-(1-phenylcycloheptyl)ethene (16).—The Barbier–Wieland degradation of **12** was performed as describd above. The crude olefin was not, however, immediately oxidized as was done before. Rather it was chromatographed on alumina (petroleum ether, bp 30–60°, as eluent), to afford **16** (from 18.6 g, 0.08 mole, of **12** there was obtained 13.0 g, 60.6%, of **16**) as large, transparent crystals [mp 73–73.5° from methanol; λ^{KBr} 6.0, 11.83, and 12.09 μ (-CH=C<) and aromatic monosubstitution absorptions; nmr, δ 1.33–2.1 (m) (ring CH_2 groups) and 6.42–7.33 (m) (Ar*H* and -C*H*=C<)].

Anal. Calcd for $C_{27}H_{28}$: C, 91.99; H, 8.01. Found: C, 91.95; H, 8.12.

Oxidation of the olefin was then performed as before to yield the **Barbier–Wieland 15** (from 13.2 g of **16** there was obtained 4.0 g, 52.4%, of this sample of **15**). The acid was recrystallized three times from aqueous alcohol: mp 81.5–82° (lit.[3] mp 85.5–86°). Its infrared and nmr spectra (partial) appear in Table II.

Cycloheptyl Phenyl Ketone (17).—Preparation was made in 80% yield from cycloheptanecarbonitrile (Aldrich) and phenyl Grignard reagent [bp 185° at (35 mm), lit.[30] bp 115–117° (0.1 mm)]. The ketone as homogeneous at 195° on an SE-30 column and afforded a 2,4-DNP derivative melting at 168–169° (lit.[30] mp 170–171°). An oxime was prepared: mp 99–101°.

Anal. Calcd for $C_{14}H_{19}NO$: N, 6.45. Found: N, 6.15.

Likewise, a tosylhydrazone was made in the usual way[1] (70%, mp 100–100.5° from aqueous methanol).

Anal. Calcd for $C_{21}H_{26}N_2O_2S$: C, 68.07; H, 7.07. Found: C, 68.71; H, 7.28.

Earlier preparations of ketone **17** were attempted by addition of benzoyl chloride to cycloheptene (Aldrich) in the presence of aluminum chloride. Both carbon disulfide[31] and methylene chloride[15] were tried as solvents. Dehydrochlorination of the product(s) led to complex mixtures, presumably containing ketone **21**. Consecutive dehydrochlorination and hydrogenation led to a mixture of at least five major products by gc analysis, and only small amounts of the proper 2,4-DNP derivative could be isolated from this mixture. The facts that the procedure used were those in the literature and that little success was achieved preclude detailed descriptions of these attempts.

α-Chlorocycloheptyl Phenyl Ketone (18).—Of the several methods used to chlorinate ketone **17** with sulfuryl chloride,[32] the method of Stevens and Farkas[12] was found to be best. Cycloheptyl phenyl ketone (**17**, 20.2 g, 0.1 mole) was dissolved in freshly distilled sulfuryl chloride (100 ml). An ice bath was kept ready to quell the occasionally vigorous reaction. After this reaction (variable time), the solution was refluxed for 1 day and poured onto excess crushed ice, and the oil was separated, neutralized, and washed. The dried oil was distilled to give **18** as a pale yellow syrup [17.4 g, 74%—though yields were often in the eighties—bp 165–195° (free flame) (10 mm), $n^{20}D$ 1.5688, d^{27}_4 1.2310]. A chloride determination with hot, alcoholic silver nitrate for 1.5 hr indicated purities of over 80%. The chloro ketone was not overly stable and no further work was attempted to purify it.

1-Phenylcycloheptanecarboxylic Acid (15, Favorskii Route).—Both the methods used[12,13] for quasi-Favorskii rearrangement of α-chlorocyclohexyl phenyl ketone failed with **18**. No acid product was found. The successful conversion described here is for a larger scale run. Other data may be found in Table I. Chloro ketone **18** (123.1 g, 0.52 mole if pure **18**) was dissolved in dioxane (freshly distilled from alkali, 900 ml) and to it was added a solution of silver nitrate (170 g, 1.0 mole) in distilled water (100 ml). This larger scale run used less water than was employed in smaller scale preparations (see Table I). The nonhomogeneous mixture was vigorously stirred at 70–75° for 5 hr. The precipitated silver chloride (83.2%) was filtered from the cold solution. Water (3 l.) was added to the filtrate, which was then extracted with four portions of ether (150 ml). The ether extracts were in turn extracted with aqueous sodium carbonate (10%, four 100-ml portions). The basic extracts were boiled briefly and cooled. Acidification with concentrated hydrochloric acid precipitated acid **15** as a tan solid (25.7 g, 27.4% based on silver chloride yield). Recrystallization was easily effected with little loss from 95% ethanol, whereupon **15** resulted as large, transparent, colorless needles (mp 127.5–128.5°) or from petroleum ether–benzene (fine white needles, same melting point). Spectral data (partial) are given in Table II.

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.04; H, 8.31. Found: C, 77.28; H, 8.35.

Attempts failed to make the S-benzylisothiouronium salt, anilide, or amide derivative. Conversion of **15** to its acid chloride with thionyl chloride succeeded (56% of a colorless syrup distilled through a short-path apparatus). The dark yellow diazo ketone [λ^{neat} 4.78 ($COCHN_2$) and 6.11 μ ($COCHN_2$); not distilled] from the acid chloride (0.9 g, 3.8 mmoles) and excess diazomethane was dissolved in a mixture of tetrahydrofuran (150 ml) and water (130 ml) and irradiated with an internal low-pressure ultraviolet light source (Delmar Illuminator, 2537 A) for 3 days.[33] The tetrahydrofuran was removed by vacuum evaporation and the oil so liberated was extracted with ether (three 30-ml. portions). Extraction of this ether solution with sodium carbonate (10%, three 50-ml. portions) and acidification of the alkaline material gave the homologous (1-phenylcycloheptyl)acetic acid (**12**, *ca.* 0.4 g, 45%). The crude acid was recrystallized from ethanol (Norit) to give **12** indistinguishable from the alternatively produced material (*vide supra*) by mixture melting point and infrared determinations.

1-Phenylcycloheptylcarbinol (19) resulted in quantitative yield upon reduction of acid **15** with lithium aluminum hydride in ether [bp 145–155° (1.1 mm); λ^{neat} 2.98 (OH) and 9.4 μ (primary C–O); nmr, δ 1.2–2.33 (m) (ring CH_2 groups), 2.43 (s) (O*H*), 3.22 (s) (-CH_2OH), and 7.27 (m) (Ar*H*)]. The alcohol was a clear, thick, colorless oil with a camphoraceous odor, homogeneous at 180° on an SE-30 column.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.41; H, 9.92.

1-Phenylcycloheptylcarbinyl Tosylate (20).—This derivative was obtained from the carbinol above and tosyl chloride in pyridine [12 hr at 25°; 74.5%; mp 79.5–80.5° from benzene–petroleum ether; λ^{KBr} 7.41 and 8.49 μ (-SO_2-); nmr, δ 1.33–2.33 (m) (ring CH_2 groups), 2.4 (s) (Ar-CH_3), 3.83 (s) (-CH_2-OSO_2-), and 7.4 (m) (Ar*H*)].

Anal. Calcd for $C_{21}H_{26}O_3S$: C, 70.35; H, 7.31. Found: C, 70.25; H, 7.47.

1-Phenylcycloheptanecarboxaldehyde (22).—Acid **15** (18.84 g, 0.086 mole) was converted to its acid chloride with thionyl chloride [17.58 g, 85.9%, bp 145–155° (1.1 mm), λ^{neat} 5.62 μ ($COCl$)] and thence to the aldehyde **22** by the N-acylaziridine method[10] [11.34 g, 75.6% based on acid chloride; bp 122–123° (2.1 mm); $n^{24}D$ 1.5468; d^{24}_4 1.022; λ^{neat} 3.74 and 5.81 μ (-CHO); nmr, δ 1.5–2.33 (m) (ring CH_2 groups), 7.22 (s) (Ar*H*), and 9.2 (s) (-C*H*O)].

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.96. Found: C, 82.56; H, 8.95.

The 2,4-DNP derivative was readily formed (yellow-orange needles, mp 165–165.5° from ethanol–ethyl acetate).

Anal. Calcd for $C_{20}H_{22}N_4O_4$: C, 62.99; H, 5.96. Found: C, 62.81; H, 5.80.

The behavior of the aldehyde on a Carbowax 20M column at 188° was interesting. At an injection temperature of 220°, decarbonylation occurred and (from its infrared spectrum) phenylcycloheptane eluted at *ca.* 14 min, while **22** eluted (pure) at *ca.* 48 min.

1-Phenylcycloheptanecarboxaldehyde tosylhydrazone (23) was prepared in the usual fashion[1] from the aldehyde, tosylhydrazine, and acetic acid in ethanol [77.9%; mp 128.5–129.5° dec from a solute ethanol; λ^{KBr} 3.17 (-NH-), 7.41, 7.64, and 8.55 μ (-SO_2-)].

Anal. Calcd for $C_{20}H_{26}N_2O_2S$: C, 68.07; H, 7.07. Found: C, 68.16; H, 7.24.

Preparation of Reference Compounds.—1-Methyl-1-phenylcycloheptane (26) was prepared by first converting 2-phenylcycloheptanone (**2**) with methyl iodide in the presence of sodium amide[34] to 2-methyl-2-phenylcycloheptanone [colorless oil, 77.8%, bp 143° (1.1 mm) (superheated), $n^{23}D$ 1.5365, d^{26}_4 1.047, λ^{neat} 5.86 (>C=O) and 7.3 μ (C-CH_3), 2,4-DNP (yellow) mp

(30) C. H. Tilford and M. G. Van Campen, Jr., *J. Am. Chem. Soc.*, **76**, 2431 (1954).

(31) R. E. Christ and R. C. Fuson, *ibid.*, **59**, 893 (1937).

(32) Besides that of Stevens and Farkas,[12] methods tried were those of D. P. Wyman and R. R. Kaufman [*J. Org. Chem.*, **29**, 1956 (1964)]—reaction without solvent below 40° (recovery of **17** only)—and a photoinitiated chlorination (in carbon tetrachloride, 74% yield of **18**).

(33) A procedure patterned after that of L. Maravetz, Dissertation, Loyola University, 1965.

(34) The reaction details followed those of a related preparation by M. S. Newman and M. D. Farbman, *J. Am. Chem. Soc.*, **66**, 1550 (1944).

137–139°; lit.[35] bp 164° (11 mm), $n^{25}D$ 1.5368, d^{25}_4 1.0294, 2,4-DNP (orange) mp 134.6–136°]. This ketone (9.14 g, 0.045 mole), potassium hydroxide (9.15 g), water (4.5 ml), hydrazine (95%, 7.5 g, 0.234 mole), and diethylene glycol (49 ml) were refluxed for 2 hr at 120° and then at 160° for 1 hr. Much foaming occurred. Additional hydrazine (2.5 ml) and further heating at 160° (3 hr) afforded on processing only about 2 ml of hydrocarbon **26**, with a solid (8.0 g, mp 80–90°), apparently the hydrazone, being isolated as well. This solid was treated again as above, this time the temperature being raised eventually to 230° and held there for 2 hr. This technique afforded further hydrocarbon on work-up. 1-Methyl-1-phenylcycloheptane (**26**) was a colorless oil with a fragrant odor [combined weight, 4.55 g, 53.4%; bp 63° (1.25 mm); $n^{25}D$ 1.5300; d^{25}_4 0.964; λ^{neat} 7.3 ($C-CH_3$) and 13.11 μ (characteristic[4] of $C_6H_5-C<$). The properties were unchanged after a wash of **26** with concentrated sulfuric acid.

Anal. Calcd for $C_{14}H_{20}$: C, 89.30; H, 10.71. Found: C, 89.58; H, 10.85.

Benzylcycloheptane (**27**) was prepared by hydrogenation of the mixture of olefins (**29**, **30**, *vide infra*) resulting from the dehydration of 1-benzylcycloheptanol (mp 45–46.5°, lit[36] mp 46.5°). The hydrocarbon **27** was a colorless, fragrant oil [bp 141° (7 mm) (superheated), $n^{22}D$ 1.5238, d^{25}_4 0.925, λ^{neat} 13.37 (characteristic[4] of $C_6H_5-C-C<$); lit.[36] bp 273–274.5° (739 mm), $n^{20}D$ 1.4810, d^{20}_4 0.8820—these literature constants appear to be low for such a compound]. Again these properties were unaffected by a sulfuric acid wash. **Benzalcycloheptane** (**29**) and **1-benzylcycloheptene** (**30**) were available from an earlier study.[3] **1-Phenylcyclooctene** (**33**) was prepared as reported.[37]

Decarbonylation of (1-Phenylcycloheptyl)acetaldehyde (**1**).—This study was performed with essentially no change from the details given before.[4] The yield and composition of the hydrocarbon product were determined by gc and infrared analysis, using calibration data from the pure isomers. The absorptions at 7.3 and 13.1 μ were used. The olefinic products (**29**, **30**) were observed in the gc analysis of run 1 as a slight forepeak of that of the saturated products (poly-*m*-phenyl ether, 20% on firebrick, 256°). No such forepeak was noticed in run 2. The acetone and *t*-butyl alcohol formed were measured by gc methods. Other pertinent data are collected in Table III.

TABLE VI

ACETOLYSIS OF TOSYLATE **20**[a] (47.2 ± 0.05°)

Time, hr	Titrant, ml[b]	% reaction	2.3031 log $a/(a-x)$	10^6k_1, sec^{-1}
0.0	0.0	0.0		
4.42	0.31	25.8	0.301	18.9
5.56	0.37	30.1	0.372	18.5
6.67	0.45	37.5	0.470	19.6
7.0	0.45	37.5	0.471	18.7
8.0	0.52	43.4	0.567	19.7
9.25	0.56	46.6	0.630	18.9
11.0	0.63	52.5	0.733	18.5
12.8	0.69	57.6	0.859	18.6
21.0	0.90	75.0	1.384	18.3
28.0	1.00	83.3	1.612	16.0[c]
47	1.11	91.6	2.610	15.5[c,d]

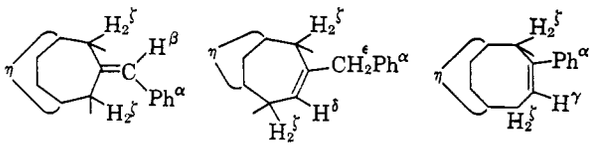
[a] 0.0300 *M* in a stock solution of glacial acetic acid, made from J. T. Baker reagent grade (99.8%, 1000 ml) and acetic anhydride (3 ml.). [b] Sodium acetate in glacial acetic acid, 0.0501 *N*. Brom phenol blue was the indicator. [c] Data omitted from the determination of the rate constant. [d] Average, 18.7 ± 0.01 (the error being the standard deviation).

Acetolysis of 1-Phenylcycloheptylcarbinyl Tosylate (**20**).—The procedure given earlier was followed exactly.[3] One of the kinetic runs is given in Table VI. The activation parameters were calculated as follows: E_a from an Arrhenius plot; ΔH^* from $\Delta H^* = E_a - RT$; ΔS^* from $\Delta S^* = R(\ln k_1 - \ln kT/h) + \Delta H^*/T$. Other data are given in Table IV. The products of a larger scale acetolysis were examined by gc and found to be only **29** and **30** (Carbowax 20 M at 220°) in the same proportion as from the dehydration of 1-benzylcycloheptanol.

Decomposition of 1-Phenylcycloheptanecarboxaldehyde Tosylhydrazone (**23**).—Several reactions were carried out, using the procedure recently described.[1] The reaction material, after removal of solvent, was analyzed by gc, infrared, ultraviolet, and nmr methods. Integration of the gc peaks (Carbowax 20 M, 188°) indicated the reaction product consisted of **29** (12.6%), **30** (30.1%), and **33** (57.3%) in terms of percentage of peak area. A synthetic mixture (SYN) was prepared with these proportions in terms of percentage by volume. As it turned out, this approximation of peak area to volume was a good one. The gc trace and infrared spectrum of SYN were identical with those of the reaction products. The comparisons in the ultraviolet were reaction products, 1.93×10^{-4} *M*, *A* = 1.670, $\lambda_{max}^{isooctane}$ 249 mμ (ϵ 8650); SYN, 1.93×10^{-4} *M*, *A* = 1.549, $\lambda_{max}^{isooctane}$ 249 mμ (ϵ 8040). The nmr comparisons are given in Table VII. All four methods of analysis were in good agreement and give great credibility to the percentage composition ascribed to this reaction mixture.

TABLE VII

NMR COMPARISONS OF REACTION AND SYN MIXTURES



29 **30** **33**

	Assignment, δ	Integration[a] Reaction	Integration[a] SYN
α[b]	7.06	5.0	5.0
β[c]	6.20	0.11	0.11
γ[d]	5.90	0.53	0.44
δ[e]	5.58	0.25	0.26
ϵ[f]	3.22	0.58	0.57
ζ	1.83–2.74	11.8	11.0
η	1.52		
Total protons		18.29	17.38

[a] The *theoretical* values may be obtained as follows: *e.g.*, for protons ϵ there should be 30.1% of two ϵ protons, or 0.602 protons. [b] This integration was used as the standard (*i.e.*, there should be 100% of α protons, or 100% × 5 = 5.0). [c] Singlet with some higher order splitting. [d] Triplet (J = 8.2 cps, empirical value 7–9 [G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, **85**, 2016; 2017 (1963)]). [e] Triplet, with higher order splitting [J = 5.8 cps, empirical value 5.7 (see *d*)]. [f] Calculated from Schoolery's constants as δ 3.32.

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