Ring-Size Effects in the Neophyl Rearrangement. VII.[1] The Peroxide-Induced Decarbonylation of (1-Phenylcyclopropyl)- and (1-Phenylcyclobutyl)acetaldehydes

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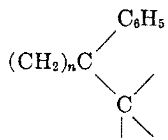
The syntheses of (1-phenylcyclopropyl)acetaldehyde **2** and (1-phenylcyclobutyl)acetaldehyde **3** are described in detail, together with certain other reactions of possible interest. The aldehydes were decarbonylated under free-radical conditions using di-*t*-butyl peroxide (DTBP) as the initiator and in several different reaction environments, *viz.*, neat aldehyde, aldehyde 1 *M* in solvent, and aldehyde in the presence of a mercaptan. The major hydrocarbon product isolated from decarbonylation of **2** was 2-phenyl-1-butene. The hydrocarbons isolated from reaction of **3** were 1-methyl-1-phenylcyclobutane, benzylcyclobutane, 2-phenyl-1-pentene, phenylcyclopentane, phenylcyclopentene, and 1-methyl-3,4-dihydronaphthalene. The variation in the percentage of these products with reaction conditions is discussed. Both **2** and **3** lost carbon monoxide with difficulty under the conditions used and only low yields of hydrocarbons were obtained. The major product from each aldehyde was a high-boiling, carbonyl-containing material apparently resulting from the addition of acyl radicals to the olefins formed in the reaction, as well as by polymerization of these olefins. *No* neophyl rearrangement was observed with **2** and the absence of 1-methyl-1-phenylcyclopropane even in the presence of mercaptan indicated that the (1-phenylcyclopropyl)carbinyl radical probably was not even formed. The neophyl rearrangement *was* found with **3**, but here also ring opening was a major competitive process. With data from the cyclopropyl ring through the cycloheptyl ring now available, the effect of ring size in the neophyl radical rearrangement is summarized.

The present paper completes a series of investigations that we have made into the effect alicyclic rings have upon the migration ability of phenyl in neophyl rearrangements of species **1**. Cationic,[1,3] carbenic,[1,4] and radical[1,5] species have been studied. The results of the radical rearrangement in the small-ring analogs employed in the work reported here are considerably different from the others already published, as are the synthetic routes used to obtain the starting compounds, (1-phenylcyclopropyl)acetaldehyde **2** and (1-phenylcyclobutyl)acetaldehyde **3**. As a consequence, these first two members of the homologous series studied constitute a special class, as indeed they did also in the carbenic study.[4] The cyclopropane derivative was likewise found to be special in the cationic study.[3]



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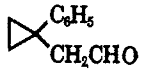
$n + 1 = 3\text{–}7$ (ring size)



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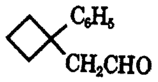

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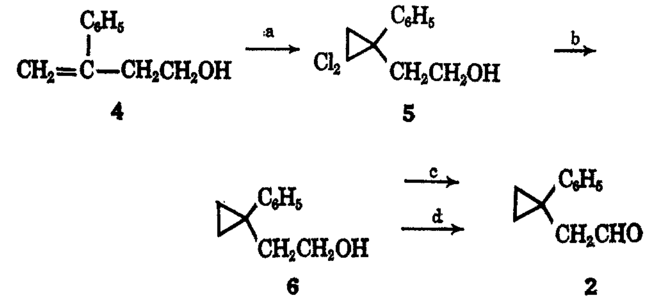
Synthesis of 2.—Two routes were developed for this synthesis. The first of these proceeded as shown in Chart I.

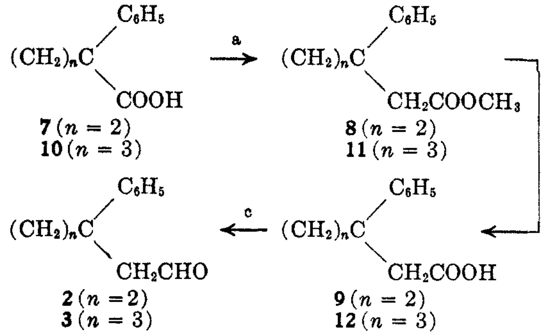
CHART I



a, $Cl_3CCOOC_2H_5 + NaOCH_3$; KOH + heat
b, Na + $CH_3OH + H_2O$
c, CrO_3 + pyridine
d, $Pb(OAc)_4$ + pyridine

The second, and more preferable, route to **2** is given in Chart II, $n = 2$.

Chart II



a, Arndt–Eistert sequence
b, saponification
c, $SOCl_2$; $(CH_2)_2NH + (C_2H_5)_3N$; $LiAlH_4$

(1-Phenylcyclopropyl)acetaldehyde **2** was obtained by both methods (Charts I and II) as a colorless oil with a grass-like odor. It readily oxidized on standing in air, reforming acid **9**. As a result, samples for decarbonylation studies were kept under nitrogen in sealed vials. The various spectra of **2** were consonant with its structure. Although **2** itself had not been prepared before, its 2,4-dinitrophenylhydrazone had been made in this laboratory in 1959 by a different route.[6]

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[1] Paper VI: J. W. Wilt, J. F. Zawadzki and D. G. Schultenover, S. J., *J. Org. Chem.*, **31**, 876 (1966).

[2] Taken from the dissertations of J. F. Z. (1962); a National Science Foundation Fellow, 1959–1962; and L. L. M. (1965), a Petroleum Research Fund Fellow, 1962–1964.

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

[4] J. W. Wilt, J. M. Kosturik and R. C. Orlowski, *ibid.*, **30**, 1052 (1965).

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

[6] J. W. Wilt and Bro. H. Philip, *ibid.*, **24**, 616 (1959).

Synthesis of 3.—(1-Phenylcyclobutyl)acetaldehyde **3** was obtained by the process given earlier in Chart II, $n = 3$, starting with the analogous cyclobutane derivative **10**.[7]

In the present case, homologation was also achieved by the photolytic rearrangement[9] of the diazo ketone in aqueous tetrahydrofuran. Aldehyde **3** was also a colorless, easily oxidized oil with a grass-like odor. It was characterized by the usual data, all of which supported the structure assigned.

Results of Decarbonylation Studies.—The technique for decarbonylation of these aldehydes was patterned after that employed in the higher ring sizes.[1,5] Generally three kinds of reactions were performed: A, decarbonylation of the neat aldehyde at 150–160° with di-*t*-butyl peroxide (DTBP), using 10 to 50 mole % of the peroxide; B, a similar decarbonylation, but of aldehyde 1 *M* in chlorobenzene or *o*-dichlorobenzene; and C, decarbonylation as in A, but with 5 mole % of benzyl mercaptan or thiophenol present.

Early investigations of **2** proved disappointing, no matter which of the above decarbonylation reactions was studied. Even though carbon monoxide was evolved (39–68%), the rate was very slow and a large amount of DTBP was required. Processing the reactions afforded no volatile products, but only a brown, glass-like material. A possible explanation of these results was that *olefins* resulted in the decarbonylation of **2**, and that the residue represented (at least partially) the destruction of these styrene-like olefins by a Kharasch[10] addition of aldehyde to them, as well as by their radically induced polymerization. The results with **2** were, in fact, very much like those obtained in an earlier study[11] from this laboratory of *olefinic* aldehydes in the decarbonylation reaction. The past history of cyclopropane aldehydes in this reaction is varied. While 1-phenylcyclopropanecarboxaldehyde underwent decarbonylation normally, cyclopropanecarboxaldehyde itself did not.[12] Indeed, ring opening during the decarbonylation of cyclopropylacetaldehyde has been reported;[13] thus it was thought quite possible that a similar cleavage would be obtained with **2**. Later work with **2** utilized much shorter reaction times, 1.5 hr compared to the 6–20 hr used previously. This change did allow the isolation of distillable hydrocarbon products, but in a very low yield. Even under these conditions, high-boiling and largely intractable material was the major product. The results of the later study are collected in Table I.

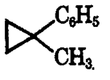
TABLE I

DECARBONYLATION[a] OF (1-PHENYLCYCLOPROPYL)ACETALDEHYDE **2**

	—Decarbonylation	type—	
	A[b]	B[c]	C[d]
% CO evolved[e]	34	. .	47
% yield of hydrocarbons[e]	12	. .	. .
% 2-phenyl-1-butene (**15**)[f]	93[g]	65	62

[a] At 160° for 1.5 hr with 50 mole % (final) DTBP added. Results are the average of several experiments in each case. [b] Neat aldehyde. [c] Aldehyde 1 *M* in chlorobenzene. [d] Neat aldehyde in the presence of 5 mole % thiophenol or benzyl mercaptan. [e] Based on aldehyde not recovered. [f] In distillable product. The remainder of the volatile product resisted identification. It has been included in the hydrocarbon yield, however. [g] ±2% (variation noted with different gc columns).

2-Phenyl-1-butene (**15**) was identified by comparison with a known sample using spectral methods and gas chromatography. The unknown 7 ± 2% of products (which represents, however, only a 0.84% yield of material) consisted of at least four substances, none of which was identified because of the lack of material. Studies showed, however, that *none* of the following possible products was present: 1-methyl-1-phenylcyclopropane (**16**), benzylcyclopropane (**17**), 1-methyleneindane (**18**), 1-methylindene (**19**), 2-phenyl-2-butene **20** (*cis* or *trans*), 2-methyl-3-phenyl-1-propene (**21**), phenylcyclobutane (**13**), 1-phenylcyclobutene (**22**), or 3-phenyl-1-butene (**23**). All of these materials were prepared and checked by gas chromatography against the unknown products, using several column substrates. When reaction conditions were



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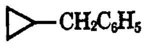

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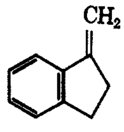

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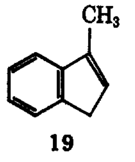

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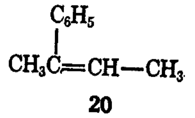
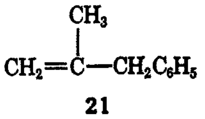


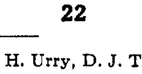
$CH_3C(C_6H_5){=}CH{-}CH_3$

20



$CH_2{=}C(CH_3){-}CH_2C_6H_5$

21



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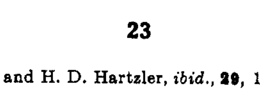

$CH_2{=}CH{-}CH(C_6H_5){-}CH_3$

23

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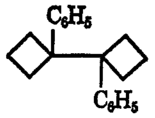
[7] An interesting early attempt to prepare **3** involved the use of 1-phenylcyclobutyl potassium. Because curious results were obtained, the details are given briefly here; they are given more fully in the Experimental Section. A Ziegler cleavage[8] of methyl 1-phenylcyclobutyl ether was attempted using liquid sodium–potassium alloy as the cleavage reagent in 1,2-dimethoxyethane solvent. The reaction mixture was then treated with allyl bromide. The halide was ineffectual in capturing any organometallic intermediate, because processing the reaction gave only phenylcyclobutane (**13**) and a solid product that appeared from its analysis and molecular weight to be $C_{20}H_{22}$. Its infrared spectrum was devoid of functional group absorption and this spectrum together with the nmr spectrum led to the suggested structure, bis(1-phenylcyclobutane) (**14**). It would appear that a 1-phenylcyclobutyl radical resulted in the Ziegler cleavage of the ether and that it then reacted with solvent or dimerized to give the observed products faster than it was further reduced to the carbanion.



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[8] As performed on the cyclopentane and cyclohexane analogs by G. W. Wheland and R. D. Kleene, *J. Am. Chem. Soc.*, **63**, 3321 (1941).

[9] L. Horner, E. Spietschka and A. Gross, *Ann.*, **573** 17 (1951). For a cogent discussion of diazo ketone transformations, *cf.* W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 118–139.

[10] M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

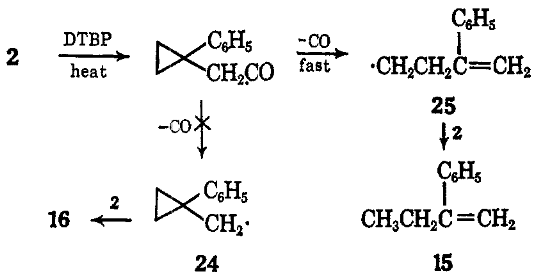
[11] J. W. Wilt and A. A. Levin, *ibid.*, **27**, 2319 (1962).

[12] D. I. Schuster and J. D. Roberts, *ibid.*, **27**, 51 (1962).

[13] W. H. Urry, D. J. Trecker and H. D. Hartzler, *ibid.*, **29**, 1663 (1964) Others have found ring opening to be a major reaction of such radicals; E. Renk, P. D. Shafer, W. H. Graham, R. H. Mazur and J. D. Roberts, *J. Am. Chem. Soc.* **82**, 1987 (1961); E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963); D. E. Applequist and J. A. Landgrebe, *J. Am. Chem. Soc.*, **86**, 1543 (1964); and J. H. Kochi and H. E. Mains, *J. Org. Chem.*, **30**, 1862 (1965). These last workers found that the cyclopropylcarbinyl radical was not trapped as such by butadiene at −8° but rather underwent ring opening. It might be expected that ring opening would be even faster in our case because radical **25** has phenyl conjugated with the double bond.

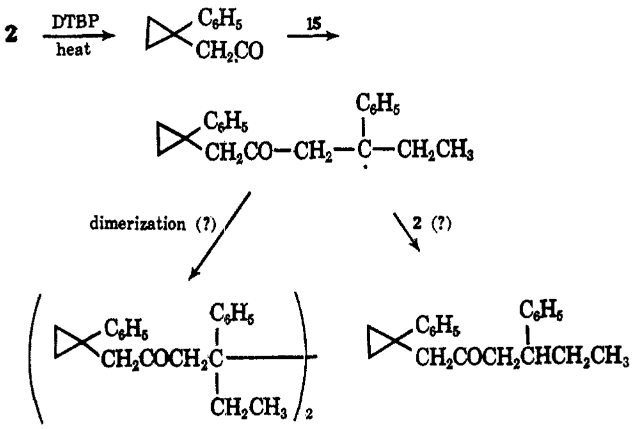
changed to types B and C, an increased amount of unknown material was formed, but again none of the above was present. It is noteworthy that **16** and **17** were *never* observed, and particularly that **16** was not found even though mercaptan was present in study C. Such results argue against the intermediacy of the (1-phenylcyclopropyl)carbinyl radical (**24**) in the decarbonylation. Rather it would appear, at least at 160°, that the acyl radical undergoes decarbonylation *concertedly*[11,13] with ring opening to radical **25**, as shown in Chart III.

CHART III



Because their structures are not all known, it cannot be claimed that all the products are accounted for by the pathway above, but the pathway does rationalize the formation of the major hydrocarbon product **15**. The high-boiling, thermosetting residue that was the major reaction product from **2** perhaps represents the subsequent destruction of **15** by the peroxide-promoted addition[10] of **2** (see Chart IV).

CHART IV



Investigation of this residual material was not overly rewarding. The infrared spectrum did show carbonyl, however, at 5.84 μ and C-methyl at 7.3 μ. Extraction with ethanol separated two equal fractions, a soluble one (mp 80–90°) with a molecular weight (Rast) of 331, and an insoluble one (mp 154–180°) with a molecular weight (Rast) of 614, in fair agreement with the structures above (292 and 582). The weights of the two fractions represented *ca.* 80% of the weight of **2** used in the reaction. The carbon monoxide percentages (Table I) are in accord with about 1–2 acyl units combined with one decarbonylated unit. Some of the residue could be polymer as well, because **15** (a styrene) underwent polymerization when heated with DTBP. The infrared spectrum of this polymer possessed certain similarities to (though it was not identical with) that of the residue. The presence of such polymer could account for the high experimental values for the molecular weights as well as the thermosetting nature of the residue. No claim is made, nonetheless, for these structures other than that they represent reasonable ones.[14]

Decarbonylation of the cyclobutyl example **3** was even more complex. Again the extent of decarbonylation was modest and mostly high-boiling material was formed. The results are gathered in Table II. The formation of these products is rationalized as shown below. The identity and composition of the hydrocarbon product was established by independent synthesis of each substance and spectral and gas chromatographic comparison of a mixture of them with the decarbonylation reaction mixture. The high-boiling (and principal) product, which showed carbonyl absorption at 5.88 μ and which was very similar to the major product from **2** (*vide supra*) is therefore again viewed as an aldehyde–olefin addition[10] product mixed with polymers of the olefins present. On the basis of the assigned pathway, the formation of these various hydrocarbons illustrates some interesting chemistry. (See Chart V.)

TABLE II

DECARBONYLATION[a] OF (1-PHENYLCYCLOBUTYL)ACETALDEHYDE **3**

	Decarbonylation type		
	A	B	C
% CO evolved[b]	48	60	..
% yield of hydrocarbon[b]	6	..	..
Product composition[c]			
1-Methyl-1-phenyl cyclobutane (**26**)	36	9	52
2-Phenyl-1-pentene (**27**)	35	23	15
Benzylcyclobutane (**28**)	4	Trace	Trace
Phenylcyclopentane (**29**)	19	19	8
1-Phenylcyclopentene (**30**)	3	24	14
1-Methyl-3,4-dihydronaphthalene (**31**)	2	25	11

[a] Conditions and decarbonylation type as in Table I, except that C involved a total of 40 mole % DTBP. [b] Based on aldehyde not recovered. [c] Values are to nearest per cent and are of distillable product only.

Ring opening, the sole reaction established for the cyclopropyl analog **2**, was somewhat less important in the case of **3**, because products with the cyclobutane ring retained were identified (**26**, **28**). This is no doubt due to the decreased ring strain present in the cyclobutane ring relative to the cyclopropane ring. It is noteworthy that the neophyl rearrangement *does occur* here, though to a limited extent,[15] as evidenced by the detection of benzylcyclobutane **28**. The amount of this rearranged product decreased as the decarbonylation type was changed from A to C in keeping with the observation that the neophyl rearrangement has uniformly been found to decrease in the presence of mercaptan.[1,5,16] In the presence of

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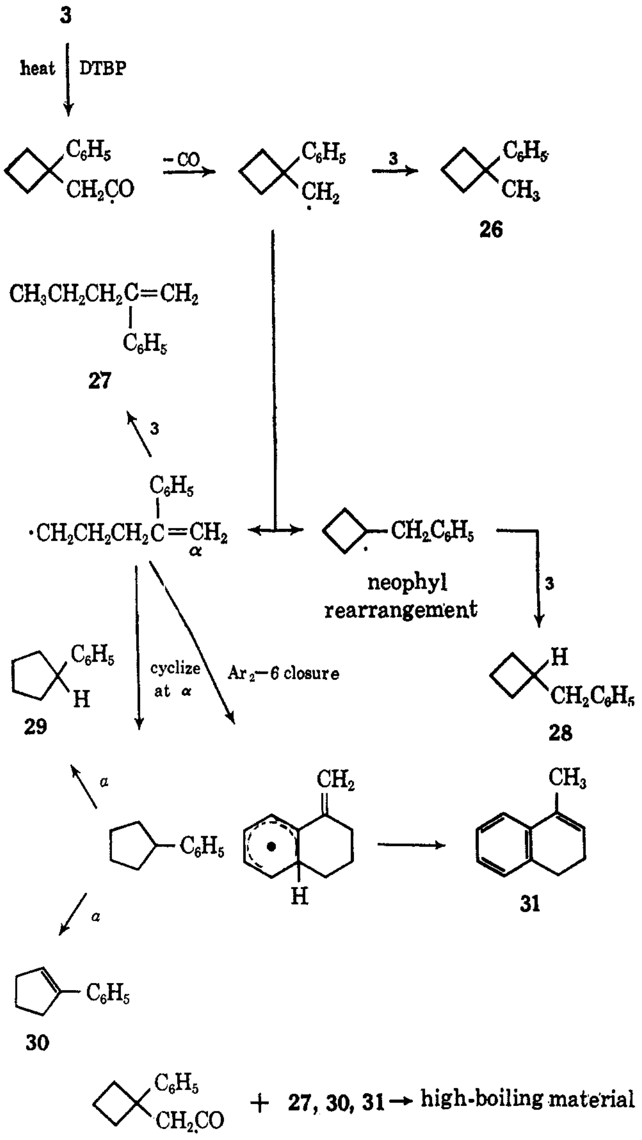
[14] Because olefin products are so destroyed in the reactions of both **2** and **3**, their true yield cannot be calculated, but, obviously, if the residue is of the nature claimed, the olefin yields are considerably higher than those given in the tables.

[15] It is possible that some neophyl rearrangement was undetected, because the 1-benzylcyclobutyl radical could have undergone reactions other than formation of **28** (*e.g.*, dimerization or ring opening), but no volatile product other than **28** was found which possessed such a rearranged skeleton.

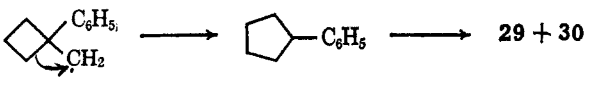
[16] L. H. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959).

CHART V



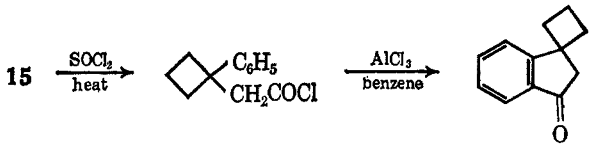
[a] Disproportionation or reaction with 3 or other species.

mercaptan the nonrearranged **26** became the major hydrocarbon product, as would be expected, though ring opening was still highly competitive, as witnessed by the significant percentages of **27** and **29–31**. Less expected, however, was the *decrease* in neophyl rearrangement with dilution (study B). Normally the opposite is found.[1,5,17] The decrease in **26** was expected, but the major result otherwise appeared to be an increase in cyclization processes leading to higher percentages of **29–31**. The finding of phenylcyclopentane **29** among the products suggested the possibility of the long-sought (and still never found) alkyl migration in an intramolecular radical rearrangement,[18] as shown.



This possibility cannot be completely excluded, but the significant amounts of these products even in the presence of mercaptan (type C study) argue against it. They are probably better explained as cleavage-recombination products (see flow sheet earlier). A similar result has been discussed for the 2-bornyl radical.[19]

The decarbonylation of **3** at times gave a product of longer retention time in gas chromatography than the hydrocarbons. This compound was later found to be 2-(1-phenylcyclobutyl)ethanol, present as a minor contaminant in **3**. An early belief that this substance was 3,3-trimethyleneindanone-1 **32** was disproved through comparison with an authentic sample made as shown. The possibility of **32** was a real one, however, because such products (*viz.*, ketones) have been found in other decarbonylation studies,[13] but usually such ketone formation becomes important only at lower temperatures (*ca.* 100°) where loss of carbon monoxide from acyl radicals is slower and there is more time for such alternative reactions.



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It is perhaps relevant to summarize in Table III the extent of the neophyl rearrangement in the hydrocarbon product from decarbonylation of (1-phenylcycloalkyl)acetaldehydes, as found in this and in earlier studies. The effect of ring size is obviously pronounced. The differences among the medium sized rings have been ascribed to steric hindrance.[1,5] In the 1-phenylcyclopentylcarbinyl radical the adjacent hydrogens of the nearly planar cyclopentane ring are shown by stereo models to interfere with the rotation of the phenyl ring. This in turn raises the energy required to reach the Ar$_1$-3 transition state for phenyl migration and allows hydrogen abstraction by the *unrearranged* radical to become more competitive. In the cyclohexyl and cycloheptyl cases rearrangement largely predominates because the alicyclic ring is puckered and the adjacent ring hydrogens are so positioned that they do not interfere with the rotation of the aromatic ring. In addition, *axial strain* is relieved in these rings by rearrangement.

TABLE III

EXTENT OF NEOPHYL REARRANGEMENT IN HYDROCARBON PRODUCTS

Cycloalkyl ring size	% neophyl-rearranged hydrocarbon
3[a]	0
4[b]	4
5[c]	63
6[c]	89
7[d]	88

[a] Ring-opened material is observed instead (see text). [b] Ring-opened material occurs to the extent of 60%. [c] Reference 5. [d] Reference 1.

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[17] F. H. Seubold, *J. Am. Chem. Soc.*, **75**, 2532 (1953); C. Rüchardt, *Chem. Ber.*, **94**, 2599 (1961).

[18] Some attempts *via* decarbonylation: W. von E. Doering, M. Farber, M. Sprecher and K. B. Wiberg, *J. Am. Chem. Soc.*, **74**, 3000 (1952); W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952); F. H. Seubold, *ibid.*, **76**, 3732 (1954); and M. A. Muhs, *Dissertation Abstr.*, **14**, 765 (1954). Quite recently the vinyl group has been shown to rearrange in an intramolecular 1,2 shift, though the study was wisely not of decarbonylation [L. H. Slaugh, *J. Am. Chem. Soc.*, **87**, 1522 (1965)].

[19] J. A. Berson, C. J. Olsen and J. S. Walia, *ibid.*, **82**, 5000 (1960); **84**, 3337 (1962).

On the other hand, the larger difference between the small- and medium-ring compounds is ascribed to ring opening of the former during decarbonylation, this being a consequence of their large ring strain. Normally the acyl radicals involved in such reactions at higher temperatures (>140°) decarbonylate readily. The 1-phenylcycloalkylcarbinyl radicals so formed then can suffer neophyl rearrangement or hydrogen abstraction reactions, but in the cases of the three- and four-membered ring analogs the acyl radicals lead to hydrocarbon product by fragmentation to olefinic radicals and carbon monoxide, either to the exclusion of decarbonylation without ring opening (as in the cyclopropyl case) or in competition with it (as in the cyclobutyl case). No rates of rearrangement, however, can be calculated from our data because the kinetics of the decarbonylation are unknown, but in the small ring cases it is evident that decarbonylation with ring opening is faster than is just decarbonylation itself. This leads to a marked decrease in the percentage of neophyl-rearranged hydrocarbon product, because once ring opening occurs the opportunity for a 1,2-phenyl shift is lost.

Experimental Section

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 certain absorptions are given (in microns). Nmr data was obtained on Varian A-60 and A-60A instruments. Tetramethylsilane was used as an internal standard and the values are in ppm (δ units). Normally the compounds were about 10% solutions in carbon tetrachloride. The symbols used are s, singlet, d, doublet, t, triplet, q, quartet, and m, multiplet. At times higher order splitting was apparent but the symbols refer to the gross appearance of the signal. Gas chromatography was performed on an Aerograph A-90P instrument using helium as the carrier gas at *ca.* 60 ml/min. Analyses were carried out by Micro-Tech Laboratories, Skokie, Illinois, and by Galbraith Laboratories, Knoxville, Tennessee. In the case of several preparations of a material only a representative procedure is given.

3-Phenyl-3-buten-1-ol (4).—This alcohol was obtained from 3-phenyl-3-buten-1-yl acetate which was prepared as described[20] [62%, bp 144–145° (13 mm), n^{20}D 1.5233, $d^{23.5}_4$ 1.060, λ^{neat} 5.74 (C=O), 8.1 ($\mathrm{O\overset{|}{C}{=}O}$), 6.11, 11.1 (>C=CH$_2$), δ[21] 1.9 s (C$H_3$COO–), 2.75 t (=CC$H_2CH_2$–), 4.11 t (=CCH$_2CH_2$OAc, J_{AX} = 8 cps), 5.07 m ($({}^{H}_{\mathrm{H}}{>}\mathrm{C{=}C}{<}_{\mathrm{CH_2-}})$), 5.3 m ($({}^{\mathrm{H}}_{\mathrm{H}}{>}\mathrm{C{=}C}{<}_{\mathrm{C_6H_5}})$), 7.25 s (ArH), lit.[20] bp 135° (13 mm), n^{20}D 1.5233].

Its saponification in aqueous alcoholic potassium hydroxide, as reported,[20] led to alcohol 4 [colorless oil, 84%, bp 130–131° (13 mm), n^{20}D 1.5583, d^{23}_4 1.031, λ^{neat} 2.97 (OH), 6.11, 11.2 (<C=CH$_2$), 3,5-dinitrobenzoate mp 72.5–75°, lit.[20] bp 130–131° (13 mm), n^{20}D 1.5581, 3,5-dinitrobenzoate mp 77–78°].

2-(2,2-Dichloro-1-phenylcyclopropyl)ethanol (5).—3-Phenyl-3-buten-1-ol (4, 22.5 g, 0.15 mole) was slowly added to a stirred suspension of *freshly prepared* sodium methoxide (16.5 g, 0.3 mole) in hexane (60 ml) cooled in ice. Ethyl trichloroacetate (63.3 g, 0.32 mole) was next added dropwise, under nitrogen, to the cold, stirred mixture. The reaction was allowed to come to room temperature with stirring overnight. Water (60 ml) was added and the red organic phase was separated and washed with dilute (5%) hydrochloric acid, brine, aqueous sodium bicarbonate, and again brine. The material was dried and distilled to give a forecut [6.5 g, bp 140–170° (4 mm)], followed by the major portion [slightly yellow oil, 20.5 g, bp 172–174° (5 mm), n^{25}D 1.5266, λ^{neat} 5.73 (C=O), 7.92 ($\mathrm{-O\overset{|}{C}{=}O}$), hydroxamic acid test positive]. Though it was an ester, the exact nature of this material was not established. Rather, the product (27 g) was saponified under reflux (4 hr) with aqueous, alcoholic potassium hydroxide. The deep red solution was processed *via* ether extraction, washes, and finally distillation to give a forecut of crude **5** [2.1 g, bp 95–104° (0.8 mm)] and the main portion of chloro alcohol **5** [16.6 g, bp 119–124° (0.45 mm)]. This oil soon solidified and after recrystallization from hexane (100 ml) formed white, waxy plates (12 g, mp 63–65°, 34.7% from olefinic alcohol **4**). The analytical sample was redistilled [bp 130° (0.8 mm), mp 64–65°, n^{27}D (supercooled) 1.5546, λ^{melt} 2.98 (OH), δ 1.5–2.5 m (ring CH_2, -CH_2CH$_2$OH), 3.4 t (–CH$_2$CH_2OH, J_{AX} = 6 cps), 7.23 s (ArH)].

Anal. Calcd for $C_{11}H_{12}Cl_2O$: C, 57.16; H, 5.23. Found: C, 57.10, H, 5.31.

The 3,5-dinitrobenzoate derivative was prepared (mp 115.2–116.2°, white waxy crystals after recrystallization from ethyl acetate, ethanol and some water).

Anal. Calcd for $C_{18}H_{14}Cl_2N_2O_6$: C, 50.84; H, 3.31. Found: C, 50.76; H, 3.18.

2-(1-Phenylcyclopropyl)ethanol (6).—Chloro alcohol **5** (15.5 g, 0.067 mole) was stirred in methanol (300 ml) and water (10 ml) and treated with small pieces of sodium (34.5 g, 1.5 g-atoms) through a condenser at such a rate as to produce a gentle reflux. More sodium (14 g, 0.61 g-atom) was then added quickly and the mixture was stirred for 3 hr and allowed to stand overnight. Water (600 ml) was then added *cautiously* and the organic phase extracted with ether. The extracts were neutralized, dried, and distilled. The dechlorinated product was a colorless, viscous oil [8.85 g, 81.2%, bp 116–126° (2.3 mm)], followed by a middle fraction, and then recovered **5** (2.55 g). The latter fractions were recycled through the above preparation. From **5** (81.4 g) there was finally obtained **6** [38 g, bp 91° (0.9 mm), $n^{24.5}$D 1.5332, negative Cl test by Na fusion, λ^{neat} 2.98 (OH), δ 0.7 m (cyclopropyl CH_2), 1.71 t (–CH_2CH$_2$OH), 3.46 t (–CH$_2$CH_2OH, J_{AX} = 7 cps), 2.47 s (OH), 7.2 s (ArH)].

Anal. Calcd for $C_{11}H_{14}O$: C, 81.43; H, 8.70. Found: C, 81.16; H, 8.90.

The 3,5-dinitrobenzoate was prepared and recrystallized from ethanol–ethyl acetate (mp 68–70°).

Anal. Calcd for $C_{18}H_{16}N_2O_6$: C, 60.76; H, 4.53. Found: C, 60.43; H, 4.62.

(1-Phenylcyclopropyl)acetaldehyde (2).—Oxidation of **6** to the aldehyde **2** was accomplished by several methods, of which the following were preferred. (1) Chromium trioxide (10 g, 0.1 mole) was *carefully* added in portions to pyridine (100 ml) in an ice bath. Alcohol **6** (4.86 g, 0.03 mole) in pyridine (49 ml) was then added all at once, with stirring and with the cooling bath removed. After 4 hr at 25°, the dark reaction material was poured into water (800 ml) and extracted with ether (one 150-ml portion, six 50-ml portions). The ether extracts were combined, neutralized, dried, and distilled (Piros–Glover spinning-band column) to yield **2** as a colorless oil with a grass-like odor [1.45 g, 30.2%, bp 82° (1.25 mm), n^{23}D 1.5319, λ^{neat} 3.64, 5.75 (–CH=O), δ 0.9 m (cyclopropyl CH$_2$), 2.5 d (–CH_2CHO), 9.61 t (–CH$_2$CHO, J_{AX} = 2.5 cps), 7.2 s (ArH), homogeneous on several gc columns].

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.26: H, 7.36.

The 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol (yellow needles, mp 115.5–116.5°, mixture melting point undepressed with analyzed material from another route).[6]

Starting alcohol **6** was recovered (20%) in the above method as a higher boiling distillation fraction. (2) To a magnetically stirred solution of **6** (9.21 g, 0.057 mole) in dry pyridine (320 ml) was added lead tetraacetate (25.2 g, 0.057 mole) at room temperature.[22] The solution (protected from atmospheric moisture) was stirred for 4 hr, during which time its color changed from red to dark yellow. Further lead tetraacetate (2 g) was then added and the solution was stirred for another 6 hr. The pyridine was removed by distillation (aspirator) and the residue was extracted with ether (250 ml). The ether was neutralized, washed, and dried. The oil remaining after removal of the ether was dissolved in benzene (20 ml) and chromatographed on an 8-in. column of neutral alumina (benzene eluent, 80 ml). Distillation of this material then gave **2** (3.85 g, 42.3%) identical with that described. The aldehyde oxidized readily in air to acid **9**.

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(20) E. G. E. Hawkins and R. D. Thompson, *J. Chem. Soc.*, 370 (1961).

(21) If more than one kind or proton is indicated, the resonance is that of the italicized one. Coupling constants are to the nearest cycles per second.

(1-Phenylcycloalkyl)acetic Acids, 9 and 12.—1-Phenylcyclopropanecarbonitrile[23] and 1-phenylcyclobutanecarbonitrile[23] were hydrolyzed to the acids. Their acid chlorides were then prepared and added to 3 *M* excess, ethereal diazomethane (dried overnight over KOH, distilled material) at 0°. The reaction was allowed to proceed overnight in an explosionproof refrigerator. The ether and excess diazomethane were then removed by distillation (aspirator). The oil remaining was the diazo ketone, which was not further purified [λ^{neat} 4.71, 6.1 (-COCHN$_2$) for the cyclopropyl case and 4.72, 6.09 for the cyclobutyl case]. If the diazomethane was not dried thoroughly, impure diazo ketone resulted, being contaminated with methyl esters. The excess diazomethane was very necessary, for, if unchanged acid chloride was present, the diazo ketones underwent methanolysis rapidly in the next step. These troubles, if uncorrected, necessitated costly refractionations of products later, so care in the preparation and use of the diazomethane was stressed. Under carefully controlled conditions, diazo ketones were produced which showed no infrared spectral evidence of ester contamination and no tendency to react with methanol. Such diazo ketones were then treated as follows. The appropriate diazo ketone (0.109 mole) was dissolved in absolute methanol (170 ml) and to it was added a small amount of silver benzoate in triethylamine catalyst[24] with magnetic stirring at room temperature. Reaction times varied with the sample and showed induction effects, but 87–100% nitrogen was obtained in 2–8 hr with portionwise addition of catalyst to the black solution whenever the gas evolution slackened. The material was then processed by filtration and removal of volatile material by distillation (aspirator). The remaining oil was taken up in ether, neutralized, washed, and distilled to yield either **methyl (1-phenylcyclopropyl)acetate** (**8**) [58%, bp 107–108° (4 mm), 93–94° (1.4 mm), $n^{26}\text{D}$ 1.5122, $d^{26}{}_4$ 1.061, λ^{neat} 5.7 (C=O), δ 0.96 s (cyclopropyl CH$_2$), 2.52 s (-C*H*$_2$COOCH$_3$), 3.5 s (-CH$_2$COOC*H*$_3$), 7.2 m (ArH)] or **methyl (1-phenylcyclobutyl)acetate** (**11**) [63%, bp 112–114° (3.5 mm), 97–98° (1.4 mm), $n^{26}\text{D}$ 1.5130, $d^{23}{}_4$ 1.047, λ^{neat} 5.7 (C=O), δ 1.67–2.6 m (cyclobutyl CH$_2$), 2.67 s (-C*H*$_2$COOCH$_3$), 3.4 s (-CH$_2$COOC*H*$_3$), 7.1 s (ArH)].

Anal. Calcd for $C_{12}H_{14}O_2$ (**8**): C, 75.76; H, 7.42. Found: C, 75.85; H, 7.49.

Anal. Calcd for $C_{13}H_{16}O_2$ (**11**): C, 76.44; H, 7.89. Found: C, 76.15; H, 7.91.

The catalyst used to obtain ester **8** was a filtered solution of dry, freshly made silver benzoate (11 g) in triethylamine (160 ml) and for **11**, 22 g in 260 ml. Esters **8** and **11** (0.066 mole) were then saponified by refluxing them with potassium hydroxide (0.1 mole) in water (65 ml) and ethanol (95%, 80 ml) for 15–20 hrs. The alcohol was removed on a rotary evaporator and the alkaline residue was extracted with ether, which extracts were discarded. The boiled aqueous phase then was acidified and the liberated oil was allowed to solidify. Recrystallization was effected from 50% aqueous ethanol. In this way either **9** or **12** was obtained from the appropriate ester: **(1-phenylcyclopropyl)acetic acid** (**9**) [79%; mp 52–53°; λ^{KBr} 2.86–4.0, 5.83 (-COOH); δ 0.87 m (cyclopropyl CH$_2$), 2.54 s (-C*H*$_2$COOH), 7.2 m (Ar H), acid proton overlooked. *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87, neut equiv, 176.2. Found: C, 74.69; H, 7.01, neut equiv, 173.3.], from which the S-benzylisothiuronium salt was prepared (mp 156.5–158°. *Anal.* Calcd for $C_{19}H_{22}N_2O_2S$: C, 66.64; H, 6.48. Found: C, 66.85; H, 6.55.), and **(1-phenylcyclobutyl)acetic acid** (**12**) [88%; mp 75–76°; λ^{KBr} 2.86–4.0, 5.86 (-COOH); δ 1.67–2.67 m (cyclobutyl CH$_2$), 2.8 s (-C*H*$_2$COOH), 7.2 s (ArH), 10.3 s (-COO*H*). *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42, neut equiv, 190.2. Found: C, 75.47; H, 7.51; neut equiv, 188.2.], from which the S-benzylisothiuronium salt was prepared (mp 160–161°. *Anal.* Calcd for $C_{20}H_{24}N_2O_2S$: C, 67.38; H, 6.79. Found: C, 67.38; H, 6.79.).

Acid **9** was also formed from aldehyde **2** on standing in air a few days. The sample was identified by mixture melting point and spectral comparison with **9** made by Arndt-Eistert's method. **12** was also prepared from its diazo ketone as follows. 1-Phenylcyclobutyl diazomethyl ketone (2.32 g, 12 mmoles) was dissolved in tetrahydrofuran (150 ml) and water (130 ml). Irradiation at 2537 A with a low pressure ultraviolet light source was carried out for 4 days, during which time the theoretical volume of nitrogen was evolved.[9] The tetrahydrofuran was then removed on a rotary evaporator and the oil so liberated was taken up in ether. The ether solution was treated with aqueous sodium bicarbonate (10%, three 35-ml portions) and the alkaline material was then acidified. The oil produced soon solidified and it was recrystallized from aqueous alcohol (48%, mp 77–78°).

(1-Phenylcycloalkyl)acetaldehydes, 2 and 3.—Acids **9** and **12** were converted to their acid chlorides [87%, bp 88–90° (1 mm), $n^{24}\text{D}$ 1.5357, $d^{24}{}_4$ 1.141, λ^{neat} 5.5 (-COCl), and 97%, bp 95–96° (1.5 mm), $n^{24}\text{D}$ 1.5362, $d^{24}{}_4$ 1.129 λ^{neat} 5.5, from **9** and **12**, respectively]. These acid chlorides were then reduced to the aldehydes by the N-acylaziridine method.[25] The method was followed as described; thus details are omitted here. From **9** was obtained aldehyde **2** (68%, identical with sample described earlier, $d^{29}{}_4$ 1.036). From **12** was produced **(1-phenylcyclobutyl)acetaldehyde** (**3**) [colorless oil with a grass-like odor, 82%, bp 86–87° (0.6 mm), 93–94° (1.2 mm), $n^{31}\text{D}$ 1.5279, $d^{24}{}_4$ 1.026, λ^{neat} 3.61, 5.75 (-CH=O), δ 1.67–2.5 m (cyclobutyl CH$_2$), 2.73 d (-C*H*$_2$CHO), 8.95 t (-CH$_2$C*H*O, J_{AX} = 6 cps), 7.2 s (ArH), homogeneous on several gc columns].

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.61; H, 7.94.

The 2,4-dinitrophenylhydrazone of **3** formed bright yellow needles from ethanol (mp 119–120°).

Anal. Calcd for $C_{18}H_{18}N_4O_4$: N, 15.81. Found: N, 15.85.

Upon standing in air for one day **3** was oxidized to **12** (by mixture melting point comparison).

Methyl 1-Phenylcyclobutyl Ether.—After this part of the work had been completed, the preparation of this ether appeared.[26] Our sample was prepared similarly, except that methyl iodide was employed and a small amount of N-methylpyrrolidone (an effective catalyst) was admixed with the benzene solvent. The ether was obtained as a colorless oil with a pleasant odor [81%, bp 55–57° (2 mm), $n^{26}\text{D}$ 1.5130, $d^{23}{}_4$ 0.9931, λ^{neat} 8.7, 9.8 (-OCH$_3$), δ 1.5–2.67 m (cyclobutyl CH$_2$), 2.82 s (-OCH$_3$), 6.83–7.67 m (ArH), lit.[26] bp 36° (0.02 mm)].

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.25; H, 8.56.

The ether decomposed on gc columns around 200° to 1-phenylcyclobutene [λ^{neat} 5.91 (C=C in this compound), another (unidentified) material and methanol].

Cleavage of Methyl 1-Phenylcyclobutyl Ether.—Into a magnetically stirred suspension of sodium–potassium alloy (7.8 g, approximately 6.3 g of potassium, 0.161 g-atom) in freshly distilled, dry 1,2-dimethoxyethane at room temperature was added methyl 1-phenylcyclobutyl ether (12 g, 0.074 mole) in a small volume of further solvent. The mixture became cloudy and turned dark yellow as a solid precipitated. After 40 min the color deepened to a wine red. In another 30 min this color lightened, so allyl bromide (24 g, 0.198 mole) was quickly added. The solution became warm and briefly refluxed. When cool, isopropyl alcohol (15 ml) was cautiously added, followed by water (60 ml). The organic phase (immiscible because of the very alkaline water phase) was separated and reduced in volume on the rotary evaporator. The residue was taken up in pentane (90 ml), dried, filtered and air evaporated to give a mass of crystals saturated with a pleasant-smelling oil. The oil was decanted and distilled to give **phenylcyclobutane** (**13**) [2.58 g, 26%, bp 35.5–37° (1.1 mm), $n^{25}\text{D}$ 1.5223, $d^{23}{}_4$ 0.950, δ 1.67–2.67 m (cyclobutyl CH$_2$), 3.17–3.83 m (cyclobutyl $-\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H}$), 7.27 s (ArH), lit.[23] bp 101–102° (41 mm), $n^{20}\text{D}$ 1.5277, $d^{20}{}_4$ 0.9378] and a higher-boiling fraction (1.1 g) of recovered starting ether together with further crystals which separated upon standing. These crystals were combined with those obtained earlier and all were washed well with cold pentane and recrystallized from aqueous dioxane. The following data indicated that this product was **bis(1-phenylcyclobutane)** (**14**) [7.4 g, 42%, mp 106–107°, bp 164–166° (0.4 mm), λ^{KBr} no functionality other than monosubstituted aromatic ring and cyclobutyl ring, 10.91, δ 1.33–3.0 m (cyclobutyl CH$_2$), 6.75 m (*ortho* ArH), 7.05 m (other ArH)].

Anal. Calcd for $C_{10}H_{12}$ (**13**): C, 90.80; H, 9.20. Found: C, 90.78; H, 9.22.

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(22) R. E. Partch, *Tetrahedron Letters*, 3071 (1964).

(23) F. H. Case, *J. Am. Chem. Soc.*, **56**, 715 (1934).

(24) M. S. Newman and P. F. Beal, III, *ibid.*, **72**, 5163 (1950).

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

(26) D. D. Roberts, *J. Org. Chem.*, **30**, 23 (1965).

Anal. Calcd for $C_{20}H_{22}$ (**14**): C, 91.54; H, 8.45, mol wt, 262. Found: C, 91.36; H, 8.70, mol wt (Rast), 225.[27]

The material resisted oxidation with hot aqueous potassium permanganate (evidence of quaternary nature) and formed a nitro derivative[27] (mp of crude material 74–76°). At most only traces of 1-allyl-1-phenylcyclobutane appeared in the several cleavages performed as above on methyl 1-phenylcyclobutyl ether, as judged by weak allyl absorption in the infrared spectrum of **13** before fractionation.

Preparation of Reference Compounds.—All reference compounds were purified until essentially homogeneous by glpc analysis. The following olefins were prepared (albeit in low yield) by the Wittig reaction of methylenetriphenylphosphorane[28] on the appropriate aldehyde or ketone (Table IV). Purification was effected *via* Girard-T reagent and distillation. **1-Methyl-1-phenylcyclocyclopropane** (**16**) was obtained from α-methylstyrene, as reported[33] [50%, bp 66–67° (11 mm), n^{21}_{D} 1.5152, λ^{neat} 9.73, 9.86 (cyclopropyl), δ 0.60 m, 0.77 m (cyclopropyl CH_2), 1.3 s ($-CH_3$), 7.1 m (ArH), lit.[33] bp 71° (20 mm), n^{21}_{D} 1.5152]. **Benzylcyclopropane** (**27**) was prepared as reported[34] by the Huang-Minlon reduction of cyclopropyl phenyl ketone [75%, bp 190° (atm), n^{25}_{D} 1.5130, δ 0–1.17 m (all cyclopropyl H), 2.48 d ($-CH_2C_6H_5$, J_{AX} = 7 cps), 7.13 s (ArH), lit.[34] bp 188° (atm), n^{25}_{D} 1.5130]. **Phenylcyclobutane** (**13**) has been described earlier herein. **1-Phenylcyclobutene** (**22**)[3], **phenylcyclopentane** (**29**),[4] and **1-phenylcyclopentene** (**30**)[4] were available from an earlier study. **1-Methylindene** (**19**) **and 1-methyl-3,4-dihydronaphthalene** (**33**) were prepared by dehydration of 1-methyl-1-indanol[35] and 1-methyl-1-tetralol.[35] Both were colorless oils [**19**, 54% from 1-indanone, bp 82.5–83° (11 mm), n^{27}_{D} 1.5605, d^{27}_{4} 0.974, λ^{neat} 6.14 (C=C), 7.2 ($C-CH_3$), δ 2.07 m ($-CH_3$), 3.13 t ($-CH_2-$), 6.03 m ($C{=}CH-$), 7.2 m (ArH), lit.[36] bp 76–78° (11 mm), n^{25}_{D} 1.5587; **31**, 83% from 1-tetralone, bp 88° (5 mm), n^{26}_{D} 1.5727, d^{23}_{4} 1.004, λ^{neat} 6.05 (C=C), 7.23 ($C{=}CH_3$), δ 2.0 m ($-CH_3$), 2.25 m (allylic $-CH_2-$), 2.7 m (benzylic $-CH_2-$), 5.77 m ($C{=}CH-$), 7.05 m (ArH), lit.[37] bp 122–123° (30 mm), n^{25}_{D} 1.57288, d^{35}_{4} 0.9882]. Catalytic hydrogenation of these olefins yielded the expected 1-methylindan and 1-methyltetralin, establishing the fact that no skeletal rearrangements accompanied the dehydrations. **2-Phenyl-*cis*- and *trans*-2-butene** (**20**) were obtained in a mixture containing some **15** by dehydration of 2-phenyl-2-butanol with hot sulfuric acid (33%, 8 hr).[36] The mixture [74%, bp 75–78° (13 mm), n^{25}_{D} 1.5337, d^{25}_{4} 0.911, lit.[38] bp 74.5–77° (13 mm), n^{20}_{D} 1.5340, d^{20}_{4} 0.914] was analyzed by glpc on a Carbowax 20 M column at 166° and comprised 19% **15**, 10.5% *trans*-**20**, and 70.5% *cis*-**20**, this last being collected [δ 1.77 d (4-CH_3), 2.0 m (1-CH_3), 5.77 q ($-C{=}CH-$, $J_{\mathrm{H,\,4\text{-}CH_3}}$ = 7 cps, $J_{\mathrm{H,\,1\text{-}CH_3}}$ = *ca.* 1 cps), 7.2 m (ArH)]. **1-Methyl-1-phenylcyclobutane** (**26**) resulted by addition of 1-phenylcyclobutylcarbinyl tosylate (8.4 g, 26.5 mmoles, mp 89.5–91°, lit.[3] mp 97–98°) in dry tetrahydrofuran (40 ml) to a cold solution of lithium aluminum hydride (1.25 g, 33 mmoles) in further tetrahydrofuran (30 ml). After the addition, more lithium aluminum hydride (1.25 g) was added. The mixture was then stirred at 25° for 40 hr and refluxed for 1 hr. The excess hydride was decomposed by the cautious addition of dilute hydrochloride acid and then water. The filtered solution was extracted with ether and processed to give **26** as a colorless, fragrant oil [2.61 g, 67%, bp 38–39° (1 mm), n^{26}_{D} 1.5120, d^{23}_{4} 0.924, λ^{neat} 7.25 ($C-CH_3$), δ 1.45 s ($-CH_3$), 1.67–2.67 m (cyclobutyl CH_2), 7.2 s (ArH), lit.[39] bp 69° (8 mm), n^{20}_{D} 1.5132, d^{20}_{vac} 0.9192]. **Benzylcyclobutane** (**28**) was prepared by the Huang-Minlon reduction of cyclobutyl phenyl ketone, following the procedure used earlier for **17**. The product was a colorless, pleasant-smelling oil [63%, bp 52–53° (1.9 mm), n^{26}_{D} 1.5124, 0.920, δ 1.5–2.17 m (all cyclobutyl H), 2.62 m ($-CH_2C_6H_5$), 7.1 s (ArH), lit.[40] bp 218–219° (736 mm), n^{20}_{D} 1.5265, d^{20}_{4} 0.9556]. The two pairs of hydrocarbons **16**, **26** and **17**, **28** exhibited hydrogen out-of-plane deformation in their infrared spectra at 13.1 and 13.5–13.7 μ, respectively. This useful differentiation of 1-methyl-1-phenylcycloalkanes from benzylcycloalkanes has been mentioned in an earlier work[5] for larger cycloalkanes and the present illustration indicates the difference exists regardless of the ring size of the alicycle.

TABLE IV

OLEFINS MADE BY WITTIG REACTIONS

					$-\overset{\vert}{C}{=}CH_2$[a]	
Olefin	Yield	Bp (mm), °C	n^{t}_{D}	d^{t}_{4}	λ	δ
15[b]	9	179–180° (atm)	1.5210[g]	0.902[h]	6.1	5.0
					11.2	5.1
18[c]	24	41–42° (0.7)	1.5778[i]	0.999[i]	6.05	4.92
					11.51	5.33
21[d]	6	29–38° (0.4)	1.5036[g]	0.889[g]	6.02	4.72
					11.22	
23[e]	22	32–33° (2.1)	1.5113[j]	0.992[j]	6.1	4.9
					10.96	5.1
27[f]	29	199° (atm)	1.5159[g]	0.903[h]	6.1	5.0

[a] The remainder of the spectrum was in agreement with the structure in each case, though minor impurities were evident in some of the compounds. [b] Lit.[29] bp 181° (atm), n^{25}_{D} 1.5264, d^{25}_{4} 0.8868. [c] Lit.[30] bp 91–93° (17 mm.) [d] Lit.[31] bp 175.8° (760 mm), n^{20}_{D} 1.5083, d^{20}_{4} 0.8821. [e] lit.[32] bp 157–162° (630 mm), n^{25}_{D} 1.5055. [f] Lit.[29] bp 201° (atm), n^{25}_{D} 1.5195, d^{25}_{4} 0.9042. [g] Reference 26. [h] Reference 23. [i] Reference 27. [j] Reference 28.

2-(1 Phenylcyclobutyl)ethanol.—Reduction of the acid chloride of **12** by lithium aluminum hydride in dry ether in the usual manner afforded the alcohol as a colorless oil in quantitative yield. It was purified by glpc [n^{26}_{D} 1.5362, λ^{neat} 3.02, 9.68 ($-CH_2OH$), δ 1.67–2.5 m (cyclobutyl CH_2, and $-CH_2CH_2OH$), 3.22 t ($-CH_2CH_2OH$), 7.07 m (ArH)].

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77, H, 9.15. Found: C, 81.59; H, 9.09.

3,3-Trimethylene-1-indanone 32.—The above acid chloride of **12** (0.89 g, 4.3 mmoles) in benzene (18 ml) was treated with aluminum chloride (0.63 g, 4.3 mmoles) and refluxed with stirring for 3 hr. The solution was poured with vigorous stirring onto ice and the benzene phase was separated, neutralized, dried, and evaporated. The red oil (mainly **32**, 0.44 g, 60%) was purified by glpc [pale yellow oil, n^{24}_{D} 1.5717, d^{24}_{4} 1.112, λ^{neat} 5.8 (C=O), δ 2.0–2.67 m (cyclobutyl CH_2), 2.8 s ($-CH_2CO-$), 7.1–7.8 m (ArH)].

Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.02. Found: C, 83.02; H, 7.16.

The ketone formed a bright orange 2,4-dinitrophenylhydrazone (mp 253–254.5° from glacial acetic acid).

Anal. Calcd for $C_{18}H_{16}N_4O_4$: N, 15.90. Found: N, 16.62.

Decarbonylation Studies.—The technique and apparatus have been described earlier.[5] The reactions of **2** and **3** with DTBP at 160° for extended times led only to intractable material, so most decompositions were limited to 1.5 hr even though gas was still evolving. The liberated gas was analyzed for carbon monoxide either in a Fisher–Orsat apparatus (cuprous chloride absorbent) or in a Fisher gas analyzer (30 in × 1/4 in column of hexamethylphosphoramide on firebrick followed by a 6 ft × 3/16 in column of activated Molecular Sieve 13). On occasion the reaction material was analyzed directly by glpc. Other times distillation under vacuum isolated the mixture of lower boiling products which was then analyzed by glpc and spectral methods. Most of the decarbonylation data has been given in Tables I and II. The scale of the experiments was 2–30 mmoles of aldehyde, using 10–50 mole % of DTBP. In all cases the composition and yield of the hydrocarbon products were established by comparison with known samples. The identity of the re-

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action products was first surmised by comparison of their glpc retention times with those of likely reference compounds on the following column substrates: silicone rubber SE-30, polyester (Reoplex) and fluorinated ester (Zonyl E-7).[41] With use of the disk-integrated areas of the glpc signals, a synthetic mixture of reference substances could then be prepared such that its glpc matched that of the reaction material, assuming peak areas were proportional to molar concentration. Final substantiation of the composition of the product was through infrared and nmr spectral correlation with the synthetic mixture. The yield of hydrocarbon was determined by direct weight in the larger experiments or by calibration curves of glpc peak area *vs.* mmoles of selected knowns in the smaller ones. The yield was corrected for recovered aldehyde which eluted at longer retention time in the 1.5-hr reactions. For complete data and details of these determinations, the dissertations of L. L. M. and J. F. Z. should be consulted.

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The Formation of Aromatic and Pseudo-Aromatic Compounds in Radiofrequency Discharges

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The formation of aromatic and pseudo-aromatic compounds from nonaromatic species has been observed in a 28-Mc electrodeless discharge. Cyclohexadiene when excited yields an emission spectrum characteristic of benzene and benzene can be isolated in the products. Evidence is presented for the conversion of 1,3-cyclopentadiene to the cyclopentadienide anion and indene to the indenide anion.

Emission spectra of organic molecules have been obtained for some time by the use of electrical discharges,[1] but the technique has not received wide usage and little attention has been paid to the chemical reactions that result.

A large percentage of the work that has been done can be attributed to the efforts of Schüler and coworkers using high frequency, high voltage discharges through organic vapors between internal metal electrodes.[2]

The use of radiofrequency electrodeless discharges for the excitation of the emission spectra and the initiation of chemical reactions with organic molecules appears to be more promising.[3] The use of microwave frequencies (2450 Mc) results in extensive fragmentation.[4] Aside from the obvious advantages associated with the absence of internal electrodes, this technique allows for the continuous variation of excitation frequencies and power levels to obtain optimum conditions.

The emission spectra of a variety of organic compounds were obtained using a 28-Mc electrodeless discharge. With nonaromatic molecules sharp line fragmentation spectra consisting of CH, C_2, and other diatomic molecules were usually obtained. In the case of aromatic compounds, emission spectra of the entire molecule or a modified molecule were obtained. These emission spectra or fluorescence spectra are related to the corresponding absorption spectra in a crude mirror image fashion.[5] This relationship varies from quite precise in some cases to rather crude in others. The emission spectra of benzene and toluene were found to rather precisely mirror the absorption spectra of these molecules, while fluorobenzene was quite different. In all instances, however, the absorption and emission spectra coincided at the $0 \rightarrow 0$ band.

It was found that some nonaromatic compounds when subject to the 28-Mc discharge emitted continuous spectra of the type characteristic of aromatic molecules. Both 1,3- and 1,4-cyclohexadiene emitted a benzene spectrum which could be identified by previously recorded data.[6,7]

No benzene was found in the original dienes as analyzed by gas chromatography but the vapors which had been passed through the discharge showed appreciable amounts of benzene indicating that benzene was formed from the dienes in the discharge. The amount of benzene formed from 1,4-cyclohexadiene (6%) was somewhat greater than that formed from the 1,3-diene (2%). On the other hand, when 1,3-pentadiene vapor was subjected to the 28-Mc discharge, a fragmentation spectrum mainly arising from diatomic molecules was obtained. 1,3-cyclopentadiene, however, was found to emit an aromatic-type continuous emission spectrum and one of the purposes of this research was to establish the origin of the continuous spectra for nonaromatic compounds.

Experimental Section

Determination of Emission Spectra.—Radiofrequency power was supplied by a Johnson Viking II radiofrequency transmitter equipped with a Heathkit Model VF-1 variable frequency oscillator capable of operation over the range 1750 kc to 28 Mc. A frequency of 28 Mc was employed throughout this work.

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