was removed in a stream of nitrogen, leaving fine, white needles, which were dried overnight under high vacuum at room temperature; 111 mg. (76.1% yield), m.p. 86–88° with decomposition and gas evolution. An accurate elemental analysis could not be made because the compound lost weight on the analytical balance. Thus, the decomposition in air is very rapid, with apparent loss of nitrogen. On standing in air the white crystals reverted to a pale yellow gum with entrained gas bubbles. An infrared spectrum run after 2 days' standing exhibited bands characteristic of the infrared spectrum of benzophenone. A calculation using the carbonyl group stretching frequency at 1655 cm.$^{-1}$ indicated the presence of 4.5–7.5% benzophenone.

Anal. Calcd. for $C_{20}H_{20}N_2$: C, 83.3; H, 7.0; N, 9.7. Found: C, 79.6; H, 6.5; N, 4.7.

Air oxidation of 2,2,2-triphenylethylhydrazine. A solution of 2,2,2-triphenylethylhydrazine in 30 ml. of reagent benzene prepared by the neutralization of 2,2,2-triphenylethylhydrazine hydrochloride (535 mg., 1.62 mmoles) was heated for 10 hr. under reflux. The benzene was distilled at reduced pressure, leaving 320 mg. of a light yellow oil, whose infrared spectrum, when compared with that of benzophenone, revealed the presence of 12% (13% yield calculated for the stoichiometry in which 1 mole of benzophenone is formed from 1 mole of hydrazine and based on 2,2,2-triphenylethylhydrazine hydrochloride) of benzophenone. Chromatography of 285 mg. of the yellow-orange oil on 15 g. of ethyl acetate–washed alumina, activated overnight at 130°, gave 64 mg. of a hydrocarbon fraction shown by examination of the ultraviolet spectrum to contain no more than 9% (1% yield) of triphenylethylene. Absence of absorption in the infrared at 1380 cm.$^{-1}$ indicated that no significant amounts of 1,1,1-triphenylethane were present. The NMR spectrum gave no evidence of the presence of 1,1,2-triphenylethylene nor dibenzyl, although a maximum at +90 p.p. 10^8 indicated the possible presence of diphenylmethane. The second fraction obtained by elution with 600 ml. of benzene amounted to 145 mg. and the ultraviolet spectrum showed absorption at 252 mμ indicating that it consisted

to the extent of about 33% of benzophenone. No other products were isolated. From another run carried out in a similar fashion, except that air was bubbled through the solution, benzophenone, estimated from the infrared to have been formed in about 20% yield, was isolated as the 2,4-dinitrophenylhydrazone, m.p. 236–238°, and a mixed melting point with an authentic sample, m.p. 240–241°, showed no depression.

Reaction of ethyl 3,3,3-triphenylpropionate and sodium in xylene. The procedure was similar to that used in the preparation of lauroin.[33] A solution of ethyl 3,3,3-triphenylpropionate[34] (5.00 g., 0.0151 mole, m.p. 79–80.5°) in 30 ml. of reagent xylene was added dropwise to a rapidly stirred suspension of 0.7 g. (0.03 g. atom) of freshly-cut sodium in 100 ml. of reagent xylene heated in an oil bath held at 119°. The addition required 5 min. and heating was continued for 30 min., while the reaction flask was constantly swept with nitrogen. The reaction mixture was then cooled to room temperature and 10 ml. of reagent methanol was added to decompose the excess sodium. The xylene solution was extracted with 5% hydrochloric acid and water. The xylene was distilled on the steam bath under reduced pressure, leaving 4.07 g. of a viscous light brown residue. The crude product was chromatographed on 200 g. of untreated alumina. Triphenylmethane (1.50 g., 42% yield, m.p. 89–93°) was eluted with 4:1 hexanebenzene. Several recrystallizations from absolute ethanol gave pure triphenylmethane; m.p. 93–93.5°, reported, m.p. 92.5–93°. An infrared spectrum was identical with a spectrum of authentic triphenylmethane. The NMR spectrum (50% solution in carbon tetrachloride) showed a singlet at −55 p.p. 10^8. The subsequent fractions of the chromatography were not examined.

Anal. Calcd. for $C_{19}H_{16}$: C, 93.4; H, 6.6. Found: C, 93.4; H, 6.9.

URBANA, ILL.

(33) S. M. McElvain, *Org. Reactions*, IV, 256 (1948).

(34) A. T. Blomquist, R. W. Holley, and O. J. Sweeting, *J. Am. Chem. Soc.*, 69, 2356 (1957).

Ring Size Effects in the Neophyl Rearrangement[1,2]

JAMES W. WILT AND BROTHER HERBERT PHILIP, F.S.C.[3]

1-Phenylcyclopentylacetaldehyde (I) and 1-phenylcyclohexylacetaldehyde (II) have been prepared and characterized. The rearrangement percentages upon di-*t*-butyl peroxide-induced decarbonylation in the liquid phase under various conditions have been determined (Table V). The results indicate that the 1,2-phenyl shift is markedly more facile in II than in I. Arguments are presented that this ring size effect results from differences in steric interference with the formation of the requisite transition states and from differences in the hydrogen donor abilities of the aldehydes. The reactions follow the course of other neophyl-type rearrangements and do not appear to involve bridged radicals as intermediates.

The production of a radical site on the cyclohexane ring is generally rather difficult and, in some of the comparisons known, less ready than on the cyclopentane ring, a situation common also to carbonium ion and carbanion formation[4]

on these rings. Cyclopentene, for instance, is three to seven times more reactive than cyclohexene toward addition of trichloromethyl radicals in the photochemical addition of bromotrichloromethane[5] while cyclopentaneazobisnitrile undergoes thermal decomposition at 80° about 11.5 times as fast as does the cyclohexane analog.[6] Commonly these ring size effects have been ascribed to conforma-
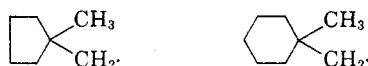
(4) For a survey of much work in these areas, see E. L. Eliel in *Steric Effects in Organic Chemistry*, edited by M. S. Newman, John Wiley and Sons, New York, N.Y., 1956, pp. 121 ff.

tional strain differences between these rings.[4,7] Some recent studies give apparently opposite conclusions, however. Cyclohexane adds to formaldehyde in greater yield than does cyclopentane in a radical process with di-*t*-butyl peroxide[8] and the peroxide of cyclohexanecarboxylic acid decomposes nearly twice as fast as the cyclopentane analog in carbon tetrachloride.[9] There does not, however, appear to be any data on the ease of radical production on cycloalkyl rings by rearrangement. Two earlier studies are inconclusive in this regard. In the first,[10] the decarbonylation of cyclohexanecarboxaldehyde and cyclopentylacetaldehyde led to no observed rearrangement (cyclohexyl ⇌ cyclopentylcarbinyl) in either case, only the parent skeletal hydrocarbons being obtained. In the second,[11] neither of the radicals shown (likewise produced by decarbonylation of the alde-

hydes) underwent rearrangement.[12] Thus far, only aryl (and not alkyl) rearrangement has been reported in the radical-chain decarbonylation re-

action.[13] For this reason, it was felt that the decarbonylation reaction involving aryl migration *from* a cycloalkyl ring would be a suitable system in which to study various cycloalkyl radicals and the differences among them arising from ring size and conformation. Such rearrangements (1,2-phenyl shifts) in decarbonylations are well known and the reaction has been of interest to several workers in the field since its discovery.[14] While both steric and electronic factors seem operative in this rearrangement, the evidence favors the former as the more important.[15] Thus, an investigation of the neophyl rearrangement in substances containing incorporated cycloalkyl rings would help also to delineate the steric requirements of this process in addition to providing information on cyclic radicals as mentioned above. This report concerns the synthesis of the cyclopentyl and cyclohexyl model compounds (I and II following) and their behavior upon decarbonylation. Work

is in progress on analogous compounds in other ring sizes.

RESULTS

The aldehydes I and II proved elusive in synthesis. Many routes were attempted and at length most rejected, although a new aldehyde synthesis was developed in the course of this research.[16] Because the skeletal systems desired are quite

(5) For a table of olefin reactivities toward trichloromethyl radicals, see C. Walling, *Free Radicals in Solution*, John Wiley and Sons, New York, N.Y., 1957, p. 254. This increased rate, however, reflects wholly or in part the ground state energy difference between the two cyclic olefins. From heat of hydrogenation data [G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 146 (1936) and M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *J. Am. Chem. Soc.*, **59**, 831 (1937).] It has been shown that cyclopentene is less stable than cyclohexene by 1.7 kcal./mole. These addition processes, then, do not bear significantly on the relative stabilities of the intervening substituted cyclopentyl and cyclohexyl radicals themselves.

(6) C. G. Overberger, H. Biletch, A. B. Finestone, J. Liker, and J. Herbert, *J. Am. Chem. Soc.*, **75**, 2078 (1953).

(7) Such conformational strain differences are predicated on the unreal planar cyclopentane ring. What puckering exists in this ring has been disregarded as unimportant to the comparisons made. That the nature and degree of the nonplanarity in the cyclopentane ring is of importance to its chemistry is indicated by F. V. Brutcher, Jr., T. Roberts, S. J. Barr, and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4915 (1959).

(8) G. Fuller and F. Rust, *J. Am. Chem. Soc.*, **80**, 6149 (1958). This report was preliminary and made no comparisons, but the reaction would seem to depend on the relative ease of hydrogen abstraction from the cycloalkanes by the *t*-butoxy radical.

(9) H. Hart and D. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959). This result is of special interest in view of the results with the azonitriles,[6] although the rate-determining steps may differ in each case.

(10) F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **76**, 3732 (1954).

(11) M. A. Muhs, dissertation (University of Washington, 1954) quoted by H. Breederveld and E. C. Kooyman, *Rec. trav. chim.*, **76**, 305 (1957).

(12) Interestingly, rearrangement was observed when these radicals were produced in the Kolbe electrolysis reaction. For a discussion of this point see the journal reference in footnote 11.

(13) With certain cyclic structures alkyl double bond participation may occur, however. Thus, while cyclohexene-4-carboxaldehyde decarbonylated to cyclohexene exclusively, norbornene-5-carboxaldehyde yielded both norbornene and nortricyclene (J. W. Wilt, A. Wysocki, and A. Levin, unpublished work).

(14) The rearrangement of a radical in solution was first demonstrated by W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944) with the β-phenylisobutyl radical in a cobaltous chloride-Grignard reaction. This β-phenylisobutyl moiety was termed neophyl, apparently first by F. C. Whitmore, C. A. Weisgerber, and A C. Shabica, Jr., *J. Am. Chem. Soc.*, **65**, 1469 (1943) and gave rise to the term neophyl rearrangement for the reaction observed. This rearrangement during the decarbonylation of aldehydes was first recorded by S. Winstein and F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **69**, 2916 (1947) and has been studied in related series by W. H. Urry and N. Nicolaides, *J. Am. Chem. Soc.*, **74**, 5163 (1952); D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952); and F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **75**, 2532 (1953).

(15) See E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Henry Holt and Co., New York, N. Y., 1959, pp., 755 ff. Although steric compression in the radical and an overall transition to an electronically preferred radical assist rearrangement markedly, neither is necessary for rearrangement since L. H. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959) has found that the 2-phenylethyl-1-C[14] radical rearranges to the 2-phenylethyl-2-C[14] radical to the extent of 2–5% in the decarbonylation reaction.

(16) J. W. Wilt and Bro. H. Philip, F.S.C., *J. Org. Chem.*, **24**, 616 (1959).

prone to ionic rearrangements of the Wagner-Meerwein type,[17] synthetic procedures were designed so that reactions which placed charge on the carbinyl carbon (α to the cycloalkyl ring) were avoided. The route used, actually a modified Hershberg[18] synthesis, is shown in the following diagram.
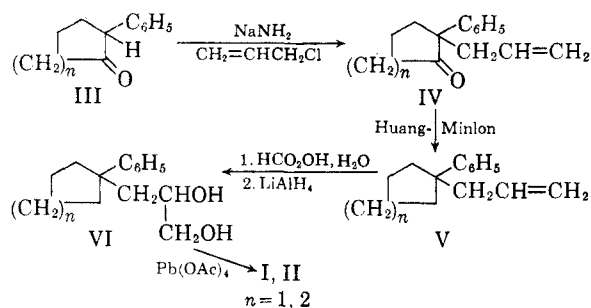
The appropriate 2-phenylcycloalkanone (III-5, III-6[19]) was alkylated in the α-position[20] using allyl chloride with sodium amide as the condensing agent. The yields and properties of the ketones (IV) so produced, together with their 2,4-dinitrophenylhydrazone derivatives, are given in Table I. The basic medium of this step introduced the possibility of an allylic shift in the position of the double bond in IV. No absorption at 7.3 μ (C—CH$_3$) was noted in these products, however, and the rearrangement was therefore considered absent. The Huang-Minlon[21] reduction of the ketones proceeded acceptably to the hydrocarbons (V), whose properties are given in Table II. Here, interestingly, some allylic shift was detected in the infrared spectra of the hydrocarbons at 7.3 μ. Presumably, lengthy contact with hot alkali under these conditions isomerized the material in part. While the degree of rearrangement was seemingly slight as evidenced by the shallow C—methyl absorption, this point was not checked and the products were used as obtained. The hydroxylation of the allylic double bond to give the diols (VI) was achieved quite satisfactorily with performic acid, using with slight modification the literature procedures.[22] It was found that basic workup of the glycol formates led to discoloration

and generally unsatisfactory material. On the other hand, acidic conditions were considered unsafe, as pinacol rearrangements were likely. The diols were therefore obtained by reductive hydrolysis of the intermediate formates with lithium aluminum hydride.[23] The properties of the diols are given in Table III. The last step, the oxidative cleavage of the diols to the required aldehydes (I and II), involved reaction with lead tetraacetate in benzene.[24] The cleavages were satisfactory, although the conditions for the cleavage of VI-6 were not considered optimum and the yield of II could probably be increased. Periodic acid cleavage led to iodinated intractable substances and was not investigated further. The properties of the aldehydes and their derivatives are listed in Table IV. While the absence of rearrangement in this route rests ultimately upon the found identity of the hydrocarbon mixtures of VII and VIII (from the decarbonylation of I and II) with authentic mix-

tures (see Experimental), two additional facts substantiate this belief. The autoxidation of II led in excellent yield to 1-phenylcyclohexylacetic acid identical in melting point with that reported[25] for this substance prepared in another way. The 2,4-dinitrophenylhydrazone of II from this route was identical with a sample obtained earlier in this study by a published route.[16] The autoxidation of I, however, led in quantitative yield to an acid having the correct analysis for 1-phenylcyclopentylacetic acid but melting at 88–89°. The literature value[26] is 120°. We believe the earlier compound is an isomer, obtained by a rearrangement in the Friedel-Crafts-type reaction used in its production,[27] and that our sample is correctly this acid.

(17) For the parent neophyl system, see S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, J. Am. Chem. Soc., 74, 1113 (1952). Unpublished work by one of us (J.W.W.) in the cyclic analogs indicates comparable rearrangement reactivity in these compounds also.
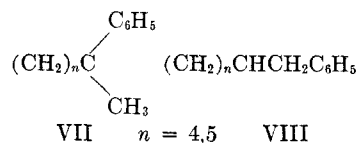
(18) E. B. Hershberg, Helv. Chim. Acta, 17, 351 (1934).

(19) The numeral refers to the type of compound, the number to the cyclopentyl (5) or cyclohexyl (6) example.

(20) The position of alkylation here is in accord with several literature studies: a similar alkylation by V. Boekelheide and W. M. Schilling, J. Am. Chem. Soc., 72, 712 (1950); the increased acidity of hydrogen alpha to both an aromatic ring and the carbonyl group, A. C. Cope, H. L. Holmes, and H. O. House, Organic Reactions, IX, 109 (1957); and the Haller rule that alkylations generally occur at the carbon already more alkylated, A. Haller and E. Benoist, Ann. Chim. (Paris), 17, 25 (1922).

(21) Huang-Minlon, J. Am. Chem. Soc., 68, 2487 (1946).

(22) J. D. Roberts and C. W. Sauer, J. Am. Chem. Soc., 71, 3927 (1949) and W. R. Newhall, J. Org. Chem., 23, 1274 (1958).

(23) This rapid and effective method of hydrolysis of ester functions has found much use in the steroid field (see e.g., H. Hirschmann and M. A. Daus, J. Org. Chem., 24, 1114 (1959)) and is to be recommended generally.

(24) R. J. Speer and H. R. Mahler, J. Am. Chem. Soc., 71, 1133 (1949).

(25) G. F. Woods, E. B. Carton, H. F. Lederle, L. H. Schwartzmann, and G. F. Woods. J. Am. Chem. Soc., 74, 5126 (1952).

(26) M. A. Saboor, J. Chem. Soc., 922 (1945).

(27) In the earlier study[26] (1-carbomethoxycyclopentyl)-acetyl chloride was treated with benzene in the presence of aluminum chloride. An ester, purportedly methyl 1-phenylcyclopentylacetate, was obtained and saponified to the acid melting at 120°. In view of the rearrangements obtained by Woods[25] and others [see C. D. Nenitzescu and J. Gavat, Ber., 70, 1883 (1937) for example] in attempts to synthesize 1-phenylcyclohexyl acetic acid by Friedel-Crafts methods, we feel Saboor's reaction led to isomerization at some point.
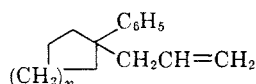
TABLE I

2-Phenyl-2-allylcycloalkanones (IV)

$$\underset{O}{(CH_2)_n}\underset{}{\overset{C_6H_5}{\underset{CH_2CH=CH_2}{|}}}$$
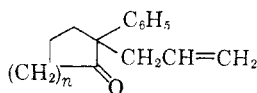
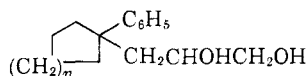|					Analyses			
				Yield,	Calculated		Found	
n	B.p./mm.	n_D^t	d_4^{20}	%	C	H	C	H
1[a]	116°/1.0	1.5390[23]	1.046	79	83.96	8.05	83.91	7.98
2[b]	101°/0.5	1.5365[23]	1.040	85	84.07	8.46	83.93	8.50

[a] 2,4-Dinitrophenylhydrazone, m.p. 134.5–135°. Anal. Calcd. for $C_{20}H_{20}N_4O_4$: N, 14.73. Found: N, 14.75. [b] 2,4-Dinitrophenylhydrazone, m.p. 141–141.5°. Anal. Calcd. for $C_{21}H_{22}N_4O_4$: N, 14.21. Found: N, 14.22.

TABLE II

1-Phenyl-1-allylcycloalkanes (V)

$$(CH_2)_n\overset{C_6H_5}{\underset{CH_2CH=CH_2}{|}}$$

					Analyses			
				Yield,	Calculated		Found	
n	B.p./mm.	n_D^t	d_4^{20}	%	C	H	C	H
1	98°/2.9	1.5340[26]	0.958	63	90.26	9.74	90.49	9.57
2	90°/0.8	1.5315[23]	0.964	70	89.94	10.06	90.05	10.10

TABLE III

1-Phenyl-1-(β,γ-dihydroxypropyl)cycloalkanes (VI)

$$(CH_2)_n\overset{C_6H_5}{\underset{CH_2CHOHCH_2OH}{|}}$$

					Analyses			
				Yield,	Calculated		Found	
n	B.p./mm.	n_D^t	d_4^{20}	%	C	H	C	H
1[a]	162°/1.2	1.5482[23]	[b]	75	76.32	9.15	76.44	9.05
2[c]	165°/0.4	1.5457[23]	[b]	90	76.88	9.46	76.63	9.66

[a] Mono-p-nitrobenzenesulfonate, m.p. 72–73°. Anal. Calcd. for $C_{20}H_{23}NO_6S$: C, 59.24; H, 5.72. Found: C, 58.81; H, 5.40. [b] Too viscous to measure in a densitometer. [c] No crystalline derivative was obtained.

TABLE IV

1-Phenylcycloalkylacetaldehydes (I,II)

$$(CH_2)_n\overset{C_6H_5}{\underset{CH_2CHO}{|}}$$
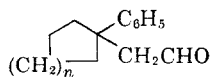
					Analyses			
				Yield,	Calculated		Found	
n	B.p./mm	n_D^t	d_4^{20}	%	C	H	C	H
1[a,b]	106°/1.0	1.5352[22]	1.065	60	82.93	8.57	82.69	8.37
2[c,d]	112°/0.5	1.5395[22]	1.080	32	83.14	8.95	82.95	9.09

[a] 2,4-Dinitrophenylhydrazone, m.p. 132–133°. Anal. Calcd. for $C_{19}H_{20}N_4O_4$: N, 15.21. Found. N, 15.25. [b] Oxidizes in air to the acid (100%), m.p. 88–89°. Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.26; H, 7.69. [c] 2,4-Dinitrophenylhydrazone, m.p. 163–164°. Anal. Calcd. for $C_{20}H_{22}N_4O_4$: N, 14.65. Found: N, 14.53. [d] Oxidizes in air to the acid (85%), m.p. 85–86°. Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.36; H, 8.31.

TABLE V

DECARBONYLATION OF ALDEHYDES

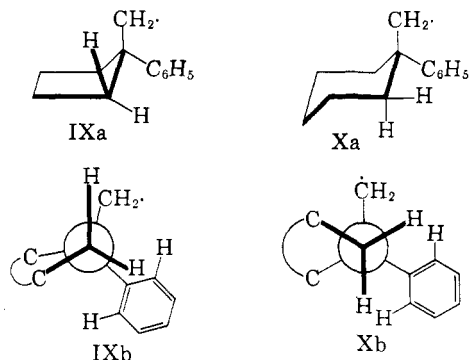| Acetaldehyde	Expt.	Temp. (Bath)	Time (Hr.)	% CO	Hydrocarbons (% VII, VIII)	Rearrangement[a] (% VIII in VII, VIII)
1-Phenylcyclopentyl (I)	I-1	140°	4	87	74	63[b]
	I-2	190°	2	91	70	71[b]
	I-3[c]	132°	20	77	58	92[b]
	I-4[d]	160°	22	64	64	<3[b]
1-Phenylcyclohexyl (II)	II-1	140°	9	48	47	89
	II-2	190°	8	43	41	91
	II-3[c]	132°	20	43	42	94
	II-4[d]	160°	23	22	21	50

[a] Maximum error for I, 2.5%; for II, 1%. See Experimental. [b] With β-phenylisovaleraldehyde, 57% at 130°, 150°; 63% at 170°; ~80% when 1M in chlorobenzene (see F. H. Seubold, Jr. footnote 14); and ". . . rearrangement decreases as benzyl mercaptan is added" (see S. Lapporte, Lit.[38]). [c] Aldehyde 1M in chlorobenzene. [d] Benzyl mercaptan (20 mole-%) added initially.

The decarbonylations of I and II were initiated with di-t-butyl peroxide and carried out in the usual fashion.[14,28] The results of these reactions are given in Table V where literature data on the rearrangement of β-phenylisovaleraldehyde to mixtures of iso- and t-butylbenzene has also been included for comparison purposes.

Discussion. The results in Table V indicate several things, each of which will be discussed in turn: (1) the size of the ring in the decarbonylated radicals does affect rearrangement percentages, the radical $(CH_2)_5C(C_6H_5)CH_2$· (Xa following) rearranging more than the radical $(CH_2)_4C(C_6H_5)$-CH_2· (IXa following); (2) the rearrangement of IXa shows the greater temperature dependence; and (3) bridged radicals are not significantly involved in either case.

Ring size effect. I approximates somewhat β-phenylisovaleraldehyde in the amount of rearrangement observed, while II has significantly more rearrangement. If steric compression at the quaternary carbon center in the generated radical (*i.e.*, IXa or Xa) were the predominant factor in determining rearrangement, then the results obtained here and elsewhere would indicate the following order of increasing β-compression: neophyl< IXa<Xa<β,β,β-triphenylethyl.[29] A study of molecular models substantiates this order, though the models of the cycloalkyl radicals do not appear different in this regard to the degree indicated by their different rearrangement percentages. While increased β-compression undoubtedly raises the potential energy of a radical compared with some standard (in this case the neophyl radical), in certain structures the free energy barrier to rearrangement may also be raised and the net effect is no increase in rearrangement. When the greater strain is not counterbalanced by a raised barrier, rearrangement increases. IXa and Xa below illus-

(28) These reactions undoubtedly follow the path given by earlier workers and discussed in Walling (ref. 5), pp. 278-280.

(29) D. Y. Curtin and M. J. Hurwitz, ref. 14, found 100% rearrangement of this radical in decarbonylation.

trate these points. The cyclopentane ring, while nonplanar and somewhat flexible, still maximizes adjacent bond oppositions compared with the strainless cyclohexane ring. In Newman[30] projection such maximized and minimized bond opposition states may be represented by the following structures (IXb and Xb). The chair form of the cyclo-


hexane ring has been used for Xa–Xb and the phenyl group has been placed in the more likely equatorial position because of its size. These representations show, as do the actual models (Fisher Taylor-Hirschfelder scale models), that rotation of the aromatic ring about its C-1 bond is severely restricted in IXa because of the interference between the *ortho* ring hydrogens and the adjacent cyclopentane ring hydrogen (as is seen in IXb). Such rotation is relatively free in Xa, however, and is in fact comparable to that in the neophyl radical itself. Since migration of the phenyl group to the carbinyl carbon atom will be easiest when the overlap of the orbitals involved is maximized, the lowest-lying transition states for the rearrangement may be shown by XI and XII for the 5- and 6-case, respectively. These states require that the plane of the migrating phenyl group lie perpendicular to the axis of the exocyclic bond of the cycloalkane. As rotation of the phenyl group about its C-1 bond to achieve such geometry is restricted in IXa, while much less so in Xa, the rate of conversion of Xa to

(30) M. S. Newman, *J. Chem. Ed.*, 32 344 (1955).

IXa→   →(CH$_2$)$_n$Ċ—CH$_2$C$_6$H$_5$←   ←Xa

XI   XIII, $n = 4$

       XIV, $n = 5$ XII
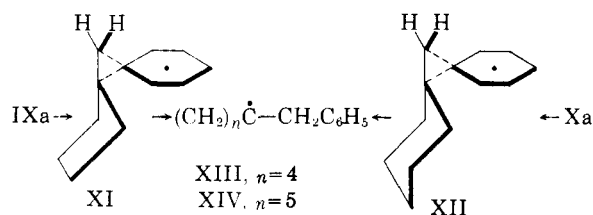
XIV should be (and is) faster than that of IXa to XIII.[31] The similarity of IXa to the neophyl radical, moreover, becomes fortuitous. While the conversion IXa → XIII probably has the higher activation enthalpy, the entropy change would seem less unfavorable because IXa is more strained than the neophyl radical. The apparent net effect is to equate the systems in rearrangement.

The rearrangements above are in competition with processes involving abstraction of hydrogen by the radicals from the solvent, leading to unrearranged hydrocarbons. If this abstraction is easier in one of the systems than the other, the amount of rearrangement will accordingly decrease. Three observations indicate that such indeed is the case: (a) the rates of decarbonylation; (b) the rates of autoxidation; and (c) the presence of acetone from the initiator. At 140° I (pure liquid) decarbonylated nearly four times faster than II (pure liquid) (see Table V). Decarbonylation under these conditions is a free-radical chain process[28] and its rate is determined largely by the rates of primary initiation and chain transfer. Initiation was more effective with I since only ∼3 mole per cent di-t-butyl peroxide sufficed for 90% of the carbon monoxide evolved, while II required seven-fold more peroxide for less decarbonylation (see Experimental). Therefore initiation and transfer steps are presumably faster with I and imply that the aldehydic hydrogen is more readily homolyzed in I than II. The same conclusion is reached when the rates of autoxidation (a reaction also involving hydrogen abstraction from the aldehyde[32]) are compared. I was oxidized quantitatively in air in twelve hours, while II was oxidized in 85% yield in air in seven days. In a similar way, the formation of acetone is informative here. The amount of acetone resulting from di-t-butyl peroxide-initiated processes is determined by the cleavage of t-butoxy radicals in competition with hydrogen-atom transfer with the solvent as

shown.[33] The more acetone found, the more difficult the hydrogen abstraction must be. No acetone was found in the reactions with I, while 37–41% yields of acetone (based on initial di-t-butyl peroxide) were found with II.[34] The longer chain length apparent with I was no doubt due to the *primary* nature of the chain carrier IXa, while with II the chain would be propagated most frequently by the *tertiary* radical XIV, as rearrangement was so extensive here. This argument is irrelevant, however, to the autoxidation rate and the acetone amounts produced and does not exclude the postulated greater hydrogen-donor ability of I.[35]
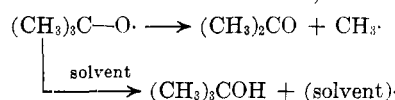
$(CH_3)_3C$—$O\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot$

$\xrightarrow{\text{solvent}} (CH_3)_3COH + (\text{solvent})\cdot$

Temperature dependence. With a 50° increase in temperature, the rearrangement of II rose 2%, while that of I rose more than 12%, a six-fold greater response (all values relative to the 140° experiments, see Table V). The greater temperature dependence of rearrangement in I is in accord with the postulated greater $\Delta H^{\pm}$ here.[31] Calculations[36] show that the difference in activation enthalpies for rearrangement and abstraction processes with IXa (*i.e.*, $\Delta(\Delta H^{\pm}) = \Delta H^{\pm}_{\text{rearrangement}} - \Delta H^{\pm}_{\text{abstraction}}$ is ∼1 kcal. mole^{-1} greater than the analogous difference with Xa.

Absence of bridged radicals. The neophyl rearrangement is not synchronous with decarbonylation as the amount of rearranged product is inversely related to the initial aldehyde concentration.[37] Active chain transfer agents (*e.g.*, mercaptans) also affect this rearrangement, allowing hydrogen abstraction by the unrearranged radical faster than does the aldehyde itself and consequently decreasing the extent of rearrangement.[38] The decarbonylations of I and II were investigated

(31) The work reported here does not allow a quantitative determination of entropic and enthalpic factors in these rates. An inspection of the above representations of the radicals involved (or their actual models), however, indicates that the transformation Xa → XIV would probably have a larger $-\Delta S^{\pm}$ than IXa → XIII, as both XI and XII are comparably constrained at the reaction zone, while Xa has a higher entropy (because staggered) than IXa (eclipsed). The *rate* for Xa → XIV is greater than IXa → XIII and therefore the former process would have the smaller $\Delta H^{\pm}$ for rearrangement at a given temperature.

(32) Ref. 5, p. 401.

(33) G. A. Russell, *J. Org. Chem.*, 24, 300 (1959).

(34) Because equal mole per cents of initiator were ultimately present in each system, the acetone in the decarbonylation of II did not arise from thermal decomposition of excess initiator. In fact, the di-t-butyl peroxide was "in excess" with I more than II because initiation was so much more efficient in the former (see text).

(35) The lower hydrogen-donor ability of II is most probably steric in origin, although the exact nature of the effect is obscure. Speculatively, the axial position of the —CH$_2$CHO in II might render aldehydic hydrogen abstraction by bulky radicals (such as XIV) more difficult.

(36) See the doctoral thesis of Bro. H. Philip, F.S.C. (Loyola University), 1959, p. 61–62.

(37) F. H. Seubold, Jr., ref. 14. Other instances of rearrangement involving neophyl-like substances have also indicated that rearrangement is not concerted with radical generation, but rather is a step-wise process involving discrete unrearranged and rearranged radicals. See J. Weinstock and S. N. Lewis, *J. Am. Chem. Soc.*, 79, 6243 (1957) and C. G. Overberger and H. Gainer, *J. Am. Chem. Soc.*, 80, 4561 (1958).

(38) S. Lapporte, unpublished work mentioned by S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, 12, 138 (1956); L. H. Slaugh, ref. 15.

in this regard also. Both concentration changes and added mercaptan did affect the extent of rearrangement noticeably (see Table V). A decrease in the initial concentration of I and II from the pure liquids (5.8 and 5.4M, respectively) to 1M solutions in chlorobenzene increased the rearrangement in each case to nearly the same value. These rearrangement percentages may be the limiting values in chlorobenzene, as this solvent does undergo radical attack itself[39] and could allow a path (although a more difficult one) for abstraction of hydrogen by the unrearranged radicals leading to unrearranged product. The addition of benzyl mercaptan lowered the percentage of rearrangement in both cases, although significantly less in II. The amount of mercaptan added (20 mole per cent) was much greater than that employed in earlier studies,[40] where concentrations of 3 mole per cent effected striking *catalysis* of decarbonylation. The reaction of the acyl radicals with excess mercaptan to regenerate the parent aldehyde would perhaps account for the *slower* rate and decreased percentage of carbon monoxide evolution observed under our conditions. Presumably the high concentration of thiol radicals that resulted in our cases also led to increased disulfide (dimer product), as reflected in the heavier pot residues in these runs (see Experimental). The merit of the excess mercaptan is seen, nonetheless, in the convincing demonstration that these rearrangements can be controlled dramatically in this manner. The virtual disappearance of rearrangement in I contrasts with the equalization of rearrangement and nonrearrangement with II. As hydrogen abstraction from I itself competed favorably in rate with the rearrangement of IXa, it is not surprising that abstraction from the much more active donor material, benzyl mercaptan, effectively swamped out the rearrangement process in this instance. With Xa, however, rearrangement was faster than the abstraction of hydrogen from II and, apparently even in the presence of mercaptan, proceeded at an equal rate with abstraction, illustrating the ease of skeletal rearrangement here. The effects of concentration changes and added mercaptan are thus those noted by others[37,38] for the neophyl rearrangement itself. Hence, in the present processes also the rearrangements proceed through the primary radicals (IXa and Xa), discretely produced and rearranging with a certain rate to the tertiary radicals (XIII and XIV). Bridged radicals, such as XI and XII, are not involved as reaction intermediates but probably as activated complexes in the transitions of the primary radicals during rearrangement.

Investigations are under way in other rearrangement reactions involving 1,2-phenyl shifts to see if the ring size effect 6>5 is operative to the same extent found in these decarbonylations.

EXPERIMENTAL

All melting and boiling points are uncorrected. The combustion analyses were performed by the Galbraith Laboratories, Knoxville, Tennessee. Infrared spectra were determined on a Perkin-Elmer Model 21 Spectrophotometer with sodium chloride optics and were taken on the pure liquids unless otherwise stated. Vapor phase chromatographic work was done on a Perkin-Elmer Model 154 Fractometer using a silicone oil column. Because the synthetic steps followed were usually identical in both ring series, general descriptions of the procedures are given below. Several preparations of all the substances described were carried out, but the departures from the given procedure were slight.

2-Phenylcycloalkanones (III). 2-Phenylcyclopentanone was obtained by the method of Mousseron[41] and by that of Arnold.[42] The former method was found preferable, both in yield (70%) and in quality of product (colorless solid, m.p. 37–38°, semicarbazone m.p. 213–214° dec., lit.,[42] m.p. 37°, semicarbazone m.p. 213° dec.). 2-Phenylcyclohexanone was also obtained in two ways: the phenyl Grignard method of Newman[43] and the oxidation method of Price.[44] Neither route was very successful in our hands, although the latter was preferred because commercially available starting material could be used (Matheson, mixed *cis-trans* 2-phenylcyclohexanol). The ketone was obtained therefrom in a 70% yield, with 30% conversion, as a colorless solid (m.p. 64–65°, 2,4-dinitrophenylhydrazone, m.p. 137–138°, lit.,[44] m.p. 63°, 2,4-dinitrophenylhydrazone m.p.[43] 139°).

2-Phenyl-2-allylcycloalkanones (IV). The appropriate 2-phenylcycloalkanone (1 mole) in dry ether-benzene solution (1:1 by volume, 200 ml.) was added dropwise to a stirred, refluxing suspension of sodium amide (Farchan, 42.9 g., 1.1 moles) in more dry ether-benzene solution (200 ml.). Reflux was continued for 8 hr. To the cooled solution, allyl chloride (freshly distilled, 84 g., 89 ml., 1.1 moles) dissolved in further dry ether-benzene solvent (100 ml.) was added dropwise and with stirring. After 10 hr. of further reflux, water was added cautiously to the cooled mixture. The organic phase was separated, washed with water, and dried over sodium sulfate. The solvents were removed by distillation and the product ketones obtained by vacuum distillation of the residual oil. The physical constants, yield data, analyses, and derivatives of these substances are given in Table I. The infrared spectra of the products were consistent with their proposed structures, having carbonyl (5.75–5.85 μ) and unconjugated carbon-carbon unsaturation (6.09 μ) absorption. C-methyl absorption at 7.3 μ was absent, indicating no allyl to propenyl isomerization during this reaction.

1-Phenyl-1-allylcycloalkanes (V). The appropriate 2-phenyl-2-allylcycloalkanone (0.068 mole), diethylene glycol (90 ml.), hydrazine hydrate (85%, 33.5 ml.) and potassium hydroxide (12.9 g., 0.23 mole) dissolved in water (12 ml.) were refluxed together for three hours. Water was then removed by use of a Dean-Stark separator until the pot temperature reached 200°, whereupon reflux was continued for 6 hr. longer. The reaction mixture was cooled, poured into cold water (700 ml.), and extracted with ether. The extracts were washed with water and dried over sodium

(39) A. L. Beckwith and W. A. Waters, *J. Chem. Soc.,* 1665 (1957).

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

(41) M. Mousseron, R. Jacquier, and H. Christol, *Compt rend.,* 236, 927 (1953).

(42) R. T. Arnold, J. S. Buckley, and E. M. Dodson, *J. Am. Chem. Soc.,* 72, 3154 (1950).

(43) M. S. Newman and M. D. Farbman, *J. Am. Chem. Soc.,* 69, 1550 (1944).

(44) C. C. Price and J. V. Karabinos, *J. Am. Chem. Soc.,* 62, 1160 (1940).

sulfate. Removal of the ether by distillation left the hydro-carbons as residual oil which was then fractionated. The physical properties of these substances are given in Table II. Their infrared spectra showed absorption at 6.09 μ (C=C) and a slight peak at 7.3 μ (C—CH₃). No trace of carbonyl absorption was present. The C—CH₃ absorption indicated allyl to propenyl isomerization had occurred under these reaction conditions. The weak intensity of the peak, however, indicated this isomerization was minor.

1-Phenyl-1-(β,γ-dihydroxypropyl)cycloalkanes (VI). Into the stirred 1-phenyl-1-allylcycloalkane (0.75 mole) in formic acid (88%, 100 ml.), a solution of hydrogen peroxide (Becco Chemical Division, Food Machinery and Chemical Corpora-tion, 30%, 130 ml.) was added at a rate such that the tem-perature remained below 35°.[45] After the addition, the material was held at 35° for 1 hr. and then stirred for an additional 12 hr. Excess formic acid was removed by vacuum distillation and the residual oil held at 40° and 1 mm. pres-sure for 2 hr. more. The crude product (0.65 mole, calculated as diformate ester) was then taken up in dry ether (100 ml.) and added dropwise to a cold, stirred suspension of lithium aluminum hydride (0.64 mole) in dry ether (300 ml.). After the addition, the material was stirred for 2 hr. and then cau-tiously hydrolyzed with ice-cold hydrochloric acid (5%, 250 ml.). The organic layer was separated, washed with aqueous sodium bicarbonate (10%, 25 ml.), then water, and finally dried over sodium sulfate. The ether solvent was stripped off and the glycols then obtained as viscous oils by vacuum distillation. All attempts to crystallize these substances failed. The properties of the diols are given in Table II. A solid derivative, apparently the mono-*p*-nitro-benzenesulfonate, was obtained from VI-5. No solid deriva-tives were obtained from VI-6. Their infrared spectra showed broad absorption at 2.9–3.0 μ (O—H). No absorption remained at 6.09 μ (C=C), indicating the absence of the olefinic starting material.

1-Phenylcycloalkylacetaldehydes (I, II). Into a stirred solu-tion of the appropriate 1-phenyl-1-(β, γ-dihydroxypropyl)-cycloalkane (0.51 mole) in benzene (300 ml.) was added a slurry of lead tetraacetate (Arapahoe, 226 g., 0.51 mole) in additional benzene (300 ml.). The reaction mixture was then stirred for 12 hr. and hydrolyzed with excess water. The organic phase was separated, washed with water, aque-ous sodium bicarbonate (5%), again with water, and finally dried over sodium sulfate. The benzene was removed by dis-tillation and the residual aldehydes were obtained by frac-tionation of the residues. The properties of these compounds are given in Table IV. Their infrared spectra showed ab-sorption at 5.75–5.85 μ (C=O) and 3.65 μ (aldehyde C—H). The aromatic C—H rocking absorption (out-of-plane de-formation) was found at 13.1 μ, in accord with a phenyl attached to a tertiary carbon (*i.e.*, a quaternary site). This correlation is developed further below.

Autoxidation of the aldehydes. The aldehydes were allowed to stand undisturbed in air (I, 12 hours; II, 7 days). The solid which formed was taken up in aqueous sodium hy-droxide (10%). This solution was extracted with ether and the separated aqueous phase was then heated to remove the last traces of the ether. Acidification with dilute (10%) hydrochloric acid precipitated the corresponding acids in a crystalline state. Recrystallization was effected from ethanol. The yields of these products are included in Table IV.

Preparation of the reference hydrocarbons. 1-Phenyl-1-methylcyclopentane (VII-5). The method of Sidorova and Dudnikova[46] was used to obtain this hydrocarbon (40%, b.p. 97° at 11.2 mm., n_D^{20} 1.5190, d_4^{20} 0.942; MR$_D$ calcd. 51.9, found 51.6; lit.,[46] b.p. 110–112° at 25 mm., n_4^{20} 1.5193,

d_4^{20} 0.9396). The aromatic C—H rocking absorption in the infrared spectrum was observed at 13.1 μ.

1-Phenyl-1-methylcyclohexane (VII-6). This substance was prepared by the method of Linsk[47] as a colorless oil (38%, b.p. 88° at 2 mm., n_D^{25} 1.525, d_4^{20} 0.946); MR$_D$ calcd. 56.4, found 56.4; lit.,[47] b.p. 103° at 9.5 mm., n_D^{20} 1.5278. In the infrared spectrum the aromatic C—H rocking absorption was again found at 13.1 μ.

Benzylcyclopentane (VIII-5). This hydrocarbon was ob-tained by the Huang-Minlon reduction of phenyl cyclo-pentyl ketone.[48] To phenyl cyclopentyl ketone (8.7 g., 50 mmoles) in hydrazine hydrate (85%, 10 ml.) there was added a solution of potassium hydroxide (10 g., 180 mmoles) in diethylene glycol (70 ml.) and water (10 ml.). This mix-ture was refluxed for 1 hr. and the water was then removed with a Dean-Stark separator. Reflux was continued for 3 hr. at 190° (pot temperature), whereupon the material was cooled and poured into cold water (200 ml.). The water solution was treated with ether and the ether extracts were separated, washed, and dried. After removal of the ether, the hydrocarbon was distilled as a colorless oil (4 g., 50%, b.p. 80° at 3 mm., n_D^{20} 1.5180, d_4^{20} 0.930; MR$_D$ calcd. 51.9, found 51.7; lit.,[49] b.p. 234–236° at 750 mm., n_D^{21} 1.5170, d_4^{21} 0.9283). The infrared spectrum of this hydrocarbon showed the aromatic C—H rocking absorption at 13.5 μ.

Benzylcyclohexane (VIII-6). The material used was ob-tained from K and K Laboratories, Long Island, N. Y. A wash with concd. sulfuric acid did not alter the infrared spectrum of this sample and the hydrocarbon was therefore used as received. The aromatic C—H rocking absorption was again noticed at 13.5 μ.

Determination of hydrocarbon structure by the 13.1 μ and 13.5 μ absorption. A correlation was observed in this work between the structure of a hydrocarbon and the position of its aromatic C—H out-of-plane deformation (rocking) ab-sorption. Such correlations are not new, but this one was of value in the analytical process employed in this study.

The partial structure $\mathrm{C_6H_6}$—C—C always gave rise to the

aromatic C—H rocking absorption at 13.1 μ, *e.g.*, I, II, and the pairs IV, V, and VI. The partial structure

$\mathrm{C_6H_5}$—C—C however exhibited this absorption at 13.5

μ, *e.g.* VIII-5 and -6. While these absorption positions may not be unique to the partial structures shown, nonetheless the position of this absorption allowed a simple and ready distinction between unrearranged and rearranged hydro-carbons obtained in this study. A plot of the log transmission at 13.1 μ against the mole per cent of the 1-phenyl-1-methylcycloalkane (VII-5, -6) in mixtures with the ap-propriate benzylcycloalkane (VIII-5 or -6) gave a linear relationship over the concentrations of interest with a maximum deviation of 2.5% for the cyclopentyl compounds and 2.0% for the cyclohexyl compounds. The average devi-ation was 1.6% for the former and 1.3% for the latter.

Determination of hydrocarbon structure by the 7.3 μ absorp-tion. Because the rearrangement of I gave appreciable un-rearranged product (VII-5), an analytical method based on C—CH₃ absorption was devised. A plot of the log trans-mission at 7.3 μ (C—CH₃ absorption) against the mole

(45) On one occasion this temperature was apparently not adequately controlled and a violent (although not ex-plosive) reaction ensued.

(46) N. G. Didorova and E. A. Dudnikova, *Zhur. Obshchei. Khim.*, **23**, 1399 (1953). *Cf. Chem. Abstr.*, **47**, 12268c (1953).

(47) J. Linsk, *J. Am. Chem. Soc.*, **72**, 4256 (1950).

(48) This ketone was kindly supplied by Dr. R. P. Mariella of this department and was a sample prepared as in R. P. Mariella and R. Raube, *J. Am. Chem. Soc.*, **74**, 521 (1952).

(49) Y. I. Denisenko, *J. Gen. Chem. (U.S.S.R.)*, **9**, 1068 (1939). *Cf. Chem. Abstr.*, **33**, 8578² (1939).

per cent of VII-5 in mixtures with VIII-5 was linear over the concentrations of interest with a maximum deviation of 1.0% and an average deviation of 0.7%. This served as a supplementary check on the analysis based on absorption at 13.1 μ. As II gave primarily rearranged product (little C—CH₃), this additional check was not used in the cyclohexane series.

Decarbonylation of the aldehydes (I and II). A solution of di-t-butyl peroxide (0.47 g., 0.6 ml., 3 mmoles, n_D^{20} 1.3890) in the appropriate aldehyde (I or II, 30 mmoles) was heated in a Wood's metal bath held at some constant temperature (see Table V for the specific temperatures used). Portions of more peroxide (to a limit of 9 mmoles) were added periodically, although such additions were not needed for I because of its rapid rate of decarbonylation. The gas liberated in the reaction was passed through a cold trap (−80°) and collected over water. Analysis of the gas for carbon monoxide was performed in a Fisher-Orsat apparatus using cuprous chloride absorbent. When no further gas was evolved, distillation was commenced under reduced pressure, all volatile materials being collected in the cold trap. The distillation was continued until the head temperature decreased, a temperature which in all cases was at least 20° below the boiling point of the parent aldehyde. The purification of the distillate from nonhydrocarbon contaminants was attempted by column chromatography, Girard-T separations, steam distillation, and permanganate oxidations. None of these methods were satisfactory. The distillate was, however, effectively and simply purified by the following technique: distillate (1 g.) was taken up in petroleum ether (10 ml.) and extracted twice with concd. sulfuric acid (10 ml.). The organic phase was separated and washed with sodium bicarbonate solution (10%), then with water, and dried over sodium sulfate. The solvent was removed at room temperature under reduced pressure and the residual oil held at 1 mm. for 5 min. This procedure was shown in control experiments not to affect the hydrocarbons VII and VIII in that the infrared spectra of the hydrocarbons and their mixtures were not altered. The purified hydrocarbons were then analyzed by use of infrared by comparison with the calibration curves obtained using authentic samples (see above). In one instance (an early experiment with II),

vapor phase chromatography was employed in the analysis. The silicone oil column failed to resolve the hydrocarbon mixture at the temperature used (225°) although the curve obtained matched that of a synthetic mixture of VII-6 and VIII-6 made up in the proportions indicated by infrared analysis.

The acetone produced in each reaction was determined by the weight of its 2,4-dinitrophenylhydrazone derivatives obtained from the cold trap material: for experiment I-1 (0%), I-2 (0%); II-1 (37%), II-2 (41%), II-3 (37%), all based on the final amount of initiator used. No determinations were made in the other experiments.

The dilution experiments (I-3 and II-3) were performed as above except that the aldehyde (30 mmoles) was dissolved in distilled chlorobenzene (30 ml.). The experiments with mercaptan present (I-4 and II-4) were also performed as above, except that benzyl mercaptan (Eastman, 1.24 g., 10 mmoles) was added initially. The pot residues from all of these reactions were dark viscous materials ranging from 19–25% of the initial aldehyde weight in the case of I to 29–46% in the case of II. These figures do not include the experiments I-4 and II-4 where much of the residue was sulfur-containing material derived from the added mercaptan. The residues contained some unchanged aldehyde in every case as evidenced by the isolation of the correct 2,4-dinitrophenylhydrazone. Other than this, no further work was done on these residues.[50]

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(50) The possibility exists that dimeric hydrocarbons are present in these residues and that the relative rearrangement data might be thereby affected. Such dimer production has been reported by Curtin,[4] although such is normally not the course of the decarbonylation process because the concentration of radicals is kept low by the small amount of initiator present and by control of its rate of homolysis through the use of moderate temperatures for the decarbonylations. The intractable nature of these residues precluded effective work-up, but no crystalline or otherwise easily isolable substances appeared present.

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY, THE UNIVERSITY OF CHICAGO]

Reactions of t-Butyl Peresters. II. The Reactions of Peresters with Compounds Containing Activated Hydrogens[1]

GEORGE SOSNOVSKY AND N. C. YANG

The reactions of t-butyl peresters with esters, ethers, aldehydes, ketones, tetralin, benzyl alcohol, dimethylaniline, and thiophenol were investigated. Cuprous bromide exerts a marked influence on both the nature and the rate in most of these reactions, and some of these reactions may be applied advantageously for preparative purposes.

In a previous communication, the reactions of t-butyl peresters with olefins in the presence of transition metal salts were described.[2] These reactions may be formulated as the displacement of

an allylic hydrogen atom by an acyloxy group. Contrary to the results obtained by conventional free radical reactions, reactions with terminal olefins yielded only one type of allylic esters with terminal unsaturation. In the present investigation, the reactions of t-butyl peresters have been extended to substrates containing activated hydrogen atoms other than olefins. The compounds employed are esters, ethers, aldehydes, ketones, tetralin, benzyl alcohol, dimethylaniline, and thiophenol. Cuprous bromide was found to exert a

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(2) M. S. Kharasch and G. Sosnovsky, *J. Am. Chem. Soc.*, **80**, 756 (1958); M. S. Kharasch, G. Sosnovsky, and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959).