from which 9-*o*-nitrophenylanthracene was isolated as yellow coralloid crystals or needles, m.p. 150–151°, by repeated recrystallizations from cyclohexane.

Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.45; H, 4.42; N, 4.79.

Reduction and Deamination of Nitrophenylanthracenes and Dinitrophenylanthracenes.—A solution or a suspension of 0.150 g. (0.005 mole) of the nitro or 0.210 g. (0.005 mole) of the dinitro compound in glacial acetic acid was treated with 0.791 g. or 1.582 g. of stannous chloride dihydrate and 0.5–1.0 ml. of concentrated hydrochloric acid. The mixture was heated on the steam bath with stirring until the characteristic yellow color of the nitro compound disappeared and then was concentrated under reduced pressure. The residue was digested with 5–10 ml. of concentrated hydrochloric acid and the solid was removed by filtration and diazotized in 5–10 ml. of 50% hypophosphorous acid.[31] After standing overnight, the reaction mixture was extracted with benzene and the extracts were concentrated and dried by distillation. Chromatography on alumina using hexane or a mixture of hexane and benzene gave the corresponding hydrocarbon. The yields of 9-phenylanthracene were 26% for the *ortho* isomer, 56% for the *meta*, and 15% for the *para* isomer while the yields of 9,10-diphenylanthracene amounted to 6%, 64% and 57% for the *ortho*, *meta*, and *para* isomers, respectively. After a single recrystallization, identity was established by mixture melting points and by comparison of the infrared spectra

(31) N. Kornblum and D. C. Iffland, *J. Am. Chem. Soc.*, **71**, 2137 (1949).

of authentic 9-phenyl- and 9,10-diphenylanthracene with those of the experimental samples.

Phenylation of 9-Phenylanthracene.—Ten milliliters of an aqueous solution of benzenediazonium chloride prepared in the usual manner from aniline (0.700 g., 0.0075 mole) was added with stirring to a solution of 0.254 g. (0.001 mole) of 9-phenylanthracene and 0.170 g. (0.001 mole) of cupric chloride dihydrate in 40 ml. of acetone. Decomposition of the diazonium salt was accompanied by precipitation of a crystalline solid. After 2 hr. at 35°, the reaction mixture was cooled and 0.083 g. (25%) of 9,10-diphenylanthracene, m.p. 246–248° (lit.[26] 249–250°), was isolated by filtration. Identity was confirmed in the manner described previously.

p-Nitrophenylation of 9-Phenylanthracene.—An aqueous solution of *p*-nitrobenzenediazonium chloride, prepared in the usual manner from 4.14 g. (0.03 mole) of *p*-nitroaniline and diluted with water to a volume of 100 ml., was added with stirring to 2.54 g. (0.01 mole) of 9-phenylanthracene and 2.55 g. (0.015 mole) of cupric chloride dihydrate dissolved in 400 ml. of acetone. Decomposition of the diazonium salt afforded 2.04 g. (54%) of yellow solid, m.p. 282–290°. Recrystallization from benzene-ethanol gave yellow plates of 9-*p*-nitrophenyl-10-phenylanthracene, m.p. 296–297°.

Anal. Calcd. for $C_{26}H_{17}NO_2$: C, 83.18; H, 4.57; N, 3.73. Found: C, 83.01; H, 4.67; N, 3.59.

Reduction, diazotization, and deamination of 0.300 g. (0.001 mole) of 9-*p*-nitrophenyl-10-phenylanthracene by the procedure described afforded 0.118 g. (58%) of 9,10-diphenylanthracene, m.p. 250–252° (lit.[26] 249–250°). Identity was confirmed by the usual methods.

Rearrangement of the 1,2,2-Triphenylethyl Radical

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　　2,3,3-Triphenylpropionaldehyde has been prepared by the lithium aluminum hydride reduction of *N*-(2,3,3-triphenylpropionyl)azridine. The *t*-butyl peroxide-catalyzed decarbonylation of this aldehyde in *o*-dichlorobenzene solvent at 155–185° yielded monomeric products (15%), consisting of 1,1,2-triphenylethane (95%) and triphenylethylene (5%), and a dimeric product (85%) whose infrared and n.m.r. spectra were in accord with those of 1,1,2,3,4,4-hexaphenylbutane. When the decarbonylation was conducted in the presence of thiophenol the yield of monomeric products increased to 37% and that of the dimeric product decreased to 22%. Uniquely labeled 2,3,3-triphenylpropionaldehyde-2-C^{14} was decarbonylated under similar conditions (thiophenol) and at several temperatures. Permanganate oxidation (not attended by subsequent phenyl migration) of the labeled 1,1,2-triphenylethane products afforded benzophenone samples whose radioactivity assays indicated that the intermediate 1,2,2-triphenylethyl radical had undergone 5% phenyl migration during decarbonylation at 155–165° and 14% at 176–184°. Subjection of 1,2,2-triphenylethane-1-C^{14} to the conditions of decarbonylation at 155–165° and 176–184° yielded samples of starting material, oxidative degradation of which indicated that 2.1% phenyl migration had occurred at the lower and 2.5% at the higher temperature. The oxidation of 1,2,2-triphenylethane-1-C^{14} to benzophenone using chromic oxide was attended by about 10% phenyl migration. Application of this degradation to the labeled 1,1,2-triphenylethane and 1,1,2,3,4,4-hexaphenylbutane products from the decarbonylation of 2,3,3-triphenylpropionaldehyde-2-C^{14} afforded benzophenone samples having identical radioactivity assays, suggesting that equivalent extents of phenyl migration had attended the oxidation of each hydrocarbon. The observed phenyl 1,2-rearrangement in the 1,2,2-triphenylethyl radical provides the second example of a radical 1,2-shift which is *not* accompanied by the formation of a more stable radical intermediate or by the relief of steric compression on the carbon atom adjacent to the radical site. The application of these techniques to the question of nonclassical, bridged radical intermediates is discussed.

　　Intramolecular rearrangements during free-radical reactions are neither so plentiful nor so extensively studied as those occurring during carbonium ion reactions. Several investigators have documented the tendency of 2-arylethyl radicals to undergo varying extents of aryl 1,2-migration, whether the radicals were produced by the action of cobaltous chloride and Grignard reagents on β-arylalkyl halides,[2-4] by the peroxide-

catalyzed decarbonylation of β-arylpropionaldehydes,[5-11] by the thermal decomposition of 2-arylethyl-azo derivatives,[12,13] during the addition of thiol com-

(2) W. H. Urry and M. S. Kharasch, *J. Am. Chem. Soc.*, **66**, 1438 (1944).
(3) W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).
(4) W. B. Smith and J. D. Anderson, *ibid.*, **82**, 656 (1960).
(5) S. Winstein and F. M. Seubold, Jr., *ibid.*, **69**, 2916 (1947).
(6) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).
(7) F. M. Seubold, Jr., *ibid.*, **75**, 2532 (1953).
(8) L. M. Slaugh, *ibid.*, **81**, 2262 (1959).
(9) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960).
(10) J. W. Wilt and M. Philip, *ibid.*, **25**, 891 (1960).
(11) C. Rüchardt, *Ber.*, **94**, 2609 (1961).
(12) C. G. Overberger and H. Gainer, *J. Am. Chem. Soc.*, **80**, 4556, 4561 (1958).
(13) D. Y. Curtin and T. C. Miller, *J. Org. Chem.*, **25**, 885 (1960).

pounds to α-arylalkenes,[14] by the peroxide-catalyzed β-hydrogen abstraction from alkylbenzenes,[15] during the high-pressure thermal alkylations of monoalkyl-benzenes with olefins,[16] or by heating alkylbenzenes with halogen- or sulfur-containing promotors.[17] Aryl migrations involving 1,5-[18,19] and 1,6-interactions[19] also have been reported. Analogous alkyl 1,2-shifts have apparently never been clearly observed,[20] and hydrogen 1,2-shifts have been shown specifically not to occur in systems involving 2-arylethyl[8,9,20] as well as other[21-23] radical intermediates.

All but one of the reported 2-arylethyl radical re-arrangements have involved systems where the re-arranged radical is more stable than its unrearranged precursor, or where steric compression on the β-carbon is relieved during the migration process. That such factors are not prerequisites for aryl migration, how-ever, has been convincingly demonstrated by Slaugh,[8] who found that the 2-phenylethyl-1-C[14] radical rear-ranged to the 2-phenylethyl-2-C[14] radical to the extent of 2.3–5.1% before its final conversion to ethylbenzene. Here the rearranged radical and its precursor have identical steric and stability features, and the phenyl migration must be determined only by the intrinsic tendency of the 2-phenylethyl radical to rearrange and by its lifetime as an intermediate. That 2-alkylethyl radicals fail to rearrange[3,6,20] further supports the con-tention that steric and stability factors alone are not definitive in engendering such 1,2-migrations.

The exclusive occurrence of aryl (as opposed to alkyl) 1,2-rearrangements of radicals has been explained by several investigators[3,4,7,8,10-12,15,17] in terms of res-onance-stabilized bridged radical intermediates such as I, analogous to the widely postulated "symmetrical phenonium ion" (II). Overberger and Gainer,[12] study-

I   II   III
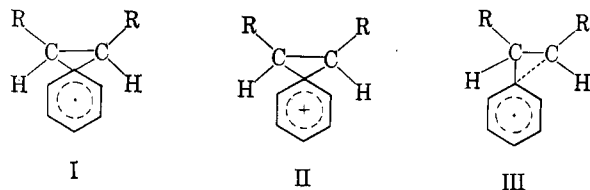
ing neophyl radicals generated from azo compounds, provided evidence against phenyl participation in the rate-determining step of radical formation. Seubold[7] has argued against bridged radicals on grounds that the phenyl migration observed during decarbonylation of β-phenylisovaleraldehyde increased under conditions of dilution with an inert[24] solvent. Smith and Anderson,[4] on the other hand, proposed the intervention of unsym-metrically bridged 2-phenylethyl radicals (III, analo-gous, presumably, to "unsymmetrical phenonium

ions")[25-27] in their studies with 2-phenylethyl-1-C[14] radicals generated by action of Mg–CoCl2 on 2-phenyl-ethyl-1-C[14] bromide, and Rüchardt[11] has argued for bridged intermediates to rationalize relative migration tendencies within p-substituted neophyl radicals. A recent physical organic textbook[28] argues in favor of bridged radical intermediates, and it has been recently stated[4] that "Until the appearance of...(stereoselec-tivity)...data the question of a bridged free radical must be considered unsolved."

Some time ago we examined certain solvolytic[29] and deamination[30] reactions of 1,2,2-triphenylethyl deriva-tives to test the general concept of bridged phenonium ions in carbonium ion reactions. Using double-labeling techniques, it was found that cationic processes in this system proceeded via equilibrating classical carbonium ions (IV) and not through bridged phenonium ions of type II (R = Ph), despite the marked stereoselec-tivity[31,32] observed in many of these reactions. The nonambiguity of the double-labeling criterion compared

$$\overset{\oplus}{Ph_2CH}\text{---}CHPh \rightleftharpoons Ph\overset{\oplus}{CH}\text{---}CHPh_2$$
IV
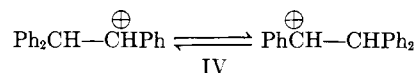
with the stereochemical criterion for bridged inter-mediates has suggested the desirability of investigating the possible existence of bridged 1,2,2-triphenylethyl radicals (I, R = Ph) by similar techniques. Prelimi-nary studies in this direction are described subse-quently.

Discussion

In view of the wide applicability of aldehyde de-carbonylation as a means of generating free radicals, the decarbonylation of 2,3,3-triphenylpropionaldehyde appeared potentially capable of providing the desired 1,2,2-triphenylethyl radical intermediate. This alde-hyde, m.p. 109–111°, proved accessible from the known[33,34] 2,3,3-triphenylpropionic acid via the se-quence of reactions[35]: 2,3,3-triphenylpropionyl chloride (m.p. 96–98°) + ethyleneimine → N-(2,3,3-triphenyl-propionyl)aziridine (m.p. 186.5–187.5°) $\xrightarrow{\text{LiAlH}_4}$ 2,3,3-triphenylpropionaldehyde. Furthermore, since the uniquely labeled 2,3,3-triphenylpropionic-2-C[14] acid can be readily prepared,[34] a precursor was available for the synthesis of 2,3,3-triphenylpropionaldehyde-2-C[14], a labeled analog potentially capable of generating the 1,2,2-triphenylethyl-1-C[14] radical (Va), whose possible rearrangement (eq. 1) might be studied by previously employed techniques.

(14) J. Weinstock and S. N. Lewis, J. Am. Chem. Soc., 79, 6243 (1957).
(15) H. Pines and C. N. Pillai, ibid., 81, 3629 (1959); 82, 2921 (1960).
(16) H. Pines and J. T. Arrigo, ibid., 79, 4958 (1957).
(17) L. H. Slaugh and J. H. Raley, ibid., 82, 1259 (1960); 84, 2640 (1962).
(18) D. F. DeTar and A. Hlynsky, ibid., 77, 4411 (1955).
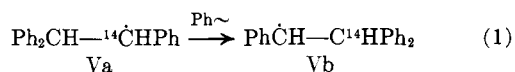(19) S. Winstein, R. Heck, S. Lapporte, and R. Baird, Experientia, 12, 138 (1956).
(20) C. Walling, "Molecular Rearrangements. Part I," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 417 ff.
(21) N. Kornblum and E. P. Eliveto, J. Am. Chem. Soc., 71, 226 (1949).
(22) N. Kornblum and H. E. De La Mare, ibid., 74, 3079 (1952).
(23) H. C. Brown and G. A. Russel, ibid., 74, 3995 (1952).
(24) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, Discussions Faraday Soc., No. 10, 242 ff. and 315 (1951).
(25) J. D. Roberts and C. M. Regan, J. Am. Chem. Soc., 75, 2069 (1953).
(26) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, ibid., 74, 1140 (1952).
(27) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, ibid., 74, 1113 (1952).
(28) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 482.
(29) W. A. Bonner and C. J. Collins, ibid., 75, 5372 (1953); 78, 5587 (1956); C. J. Collins and W. A. Bonner, ibid., 77, 92 (1955).
(30) W. A. Bonner and C. J. Collins, ibid., 78, 5587 (1956); W. A. Bonner and T. A. Putkey, J. Org. Chem., 27, 2348 (1962).
(31) C. J. Collins, W. A. Bonner, and C. T. Lester, J. Am. Chem. Soc., 81, 466 (1959).
(32) C. J. Collins, J. B. Christie, and V. F. Raaen, ibid., 83, 4267 (1961).
(33) E. P. Kohler and G. Heritage, Am. Chem. J., 33, 156 (1905).
(34) W. A. Bonner, J. Am. Chem. Soc., 81, 1181 (1959).
(35) H. C. Brown and A. Trukamoto, ibid., 83, 4549 (1961).

$$Ph_2CH-\overset{Ph\sim}{^{14}\dot{C}HPh} \longrightarrow Ph\dot{C}H-C^{14}HPh_2 \qquad (1)$$
$$\quad\ Va \qquad\qquad\qquad\qquad Vb$$

When 2,3,3-triphenylpropionaldehyde was decarbonylated by heating (170°) in o-dichlorobenzene solvent in the presence of t-butyl peroxide, gas was evolved and two crystalline substances were obtained by chromatographic separation of the crude reaction product. The minor product (15%) proved to be a mixture of monomeric derivatives, 1,1,2-triphenylethane (VI, $ca.$ 95%) and triphenylethylene ($ca.$ 5%). The major product (85%) had the constitution of a "dimeric" hexaphenylbutane derivative, and its infrared and n.m.r. spectra were consistent with the 1,1,2,3,4,4-hexaphenyl isomer (VII).

$$Ph_2CH-CH_2Ph \qquad\qquad \overset{Ph\quad\ Ph}{Ph_2CH-CH-CH-CHPh_2}$$
$$\qquad VI \qquad\qquad\qquad\qquad\qquad VII$$
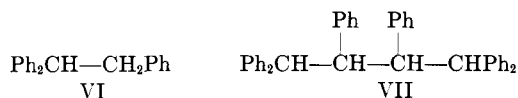
The results of the decarbonylation may be interpreted in terms of the following steps[36] (eq. 2–9).

$$t\text{-}Bu_2O_2 \longrightarrow 2t\text{-}BuO\cdot \qquad (2)$$

$$t\text{-}BuO\cdot \longrightarrow Me\cdot + Me_2CO \qquad (3)$$

$$RCH{=}O + t\text{-}BuO\cdot \longrightarrow R-\dot{C}{=}O + t\text{-}BuOH \qquad (4)$$

$$RCH{=}O + Me\cdot \longrightarrow R-\dot{C}{=}O + CH_4 \qquad (5)$$

$$R-\dot{C}{=}O \longrightarrow R\cdot + CO \qquad (6)$$

$$R\cdot + RCH{=}O \longrightarrow VI + R-\dot{C}{=}O \qquad (7)$$

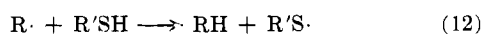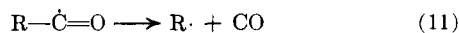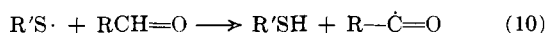$$2R\cdot \longrightarrow VI + Ph_2C{=}CHPh \qquad (8)$$

$$2R\cdot \longrightarrow VII \qquad (9)$$

$$R = Ph_2CH-\overset{|}{\dot{C}HPh}$$
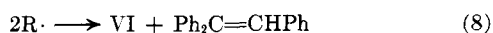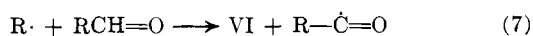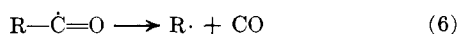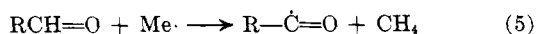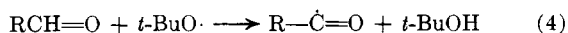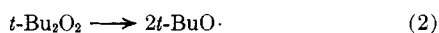
The low yield of monomeric hydrocarbon VI was somewhat surprising, suggesting a high activation energy for step 7 and indicating that the majority of acyl radicals must here be formed by steps 4 and 5.

In view of this low yield of monomeric product VI and our inability (see following) to find a means of degrading the dimeric product VII without further phenyl rearrangement, we sought a means of increasing the yield of VI. The ability of mercaptans to catalyze aldehyde decarbonylations was first demonstrated by Waters,[37] who rationalized this observation in terms of the chain sequence 10, 11, and 12.
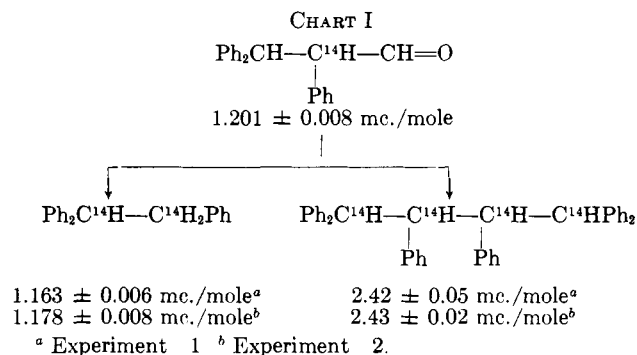
$$R'S\cdot + RCH{=}O \longrightarrow R'SH + R-\dot{C}{=}O \qquad (10)$$

$$R-\dot{C}{=}O \longrightarrow R\cdot + CO \qquad (11)$$

$$R\cdot + R'SH \longrightarrow RH + R'S\cdot \qquad (12)$$

Additionally, chain transfer constants for mercaptans[38,39] in the polymerization of styrene are much greater than those for aldehydes,[40] suggesting that mercaptans donate hydrogen to free radicals (eq. 12) more readily than do aldehydes. While this latter factor is capable of reducing the lifetime of free-radical intermediates and hence curtailing aryl 1,2-migration,[8] decarbonylation in the presence of mercaptans nevertheless appeared promising as a means of increasing the

(36) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 278, 469.
(37) E. F. P. Harris and W. H. Waters, $Nature$, $\mathbf{170}$, 211 (1952).
(38) C. Walling, $J. Am. Chem. Soc.$, $\mathbf{70}$, 2561 (1948).
(39) R. A. Gregg, F. R. Alderman, and F. R. Mayo, $ibid.$, $\mathbf{70}$, 3740 (1948).
(40) R. A. Gregg and F. R. Mayo, $ibid.$, $\mathbf{75}$, 3530 (1953).

yield of 1,1,2-triphenylethane in the present case. When 2,3,3-triphenylpropionaldehyde was decarbonylated in the presence of benzyl mercaptan (5 mole %) the yield of monomeric hydrocarbons increased 3-fold and the yield of the dimeric product VII decreased from 73 to 22%. An even greater enhancement of monomer yield (37%) occurred using thiophenol. Variation in aldehyde concentration had little effect on monomer yield (37–42%), and 1,1,2-triphenylethane again proved to be the principal component ($ca.$ 75%) of the monomer mixture.

To assay phenyl migration in the 1,2,2-triphenylethyl radical, a means for degrading the hydrocarbon products VI and VII into benzophenone without subsequent rearrangement was required. Direct oxidation of VI with potassium permanganate has been shown to proceed without rearrangement.[34] Permanganate oxidation of the dimeric product VII, however, proved ineffectual, as did several other degradative techniques. Oxidation of VII with chromic oxide–acetic acid afforded benzophenone in low yield, but was found to proceed with 10% phenyl migration when applied to 1,1,2-triphenylethane-2-C^{14}. Our studies of the phenyl migration occurring prior to the formation of VII accordingly have an uncertainty due to possible phenyl rearrangement during its subsequent degradation to benzophenone.

The decarbonylation in the presence of thiophenol of 2,3,3-triphenylpropionaldehyde-2-C^{14} afforded the usual mixture of hydrocarbon products (Chart I). The

CHART I

$$\overset{}{Ph_2CH-C^{14}H-CH{=}O}$$
$$\overset{|}{Ph}$$
$$1.201 \pm 0.008 \text{ mc./mole}$$

$$Ph_2C^{14}H-C^{14}H_2Ph \qquad\qquad \overset{}{Ph_2C^{14}H-C^{14}H-C^{14}H-C^{14}HPh_2}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad \overset{|}{Ph} \quad\ \overset{|}{Ph}$$

1.163 ± 0.006 mc./mole[a]   2.42 ± 0.05 mc./mole[a]
1.178 ± 0.008 mc./mole[b]   2.43 ± 0.02 mc./mole[b]

[a] Experiment 1   [b] Experiment 2.

slight difference ($ca.$ 3%) in the specific radioactivities of the monomeric hydrocarbon product and the starting aldehyde suggest a normal isotope effect during the abstraction step (12). Oxidation with permanganate of the 1,1,2-triphenylethane products from similar decarbonylations afforded benzophenone derivatives whose radioactivity assays indicated (Table I) that 4.9% (corrected, following) phenyl migration had occurred during the lifetime of the intermediate triphenylethyl radical when the decarbonylation was conducted at 155–165°, and 13.9% (corrected) rearrangement had occurred at 176–184°. We have no similar data regarding concomitant hydrogen migration within the present 1,2,2-triphenylethyl radical, but on the basis of earlier studies[8,9,21-23] we assume it is negligible in the present case. 1,1,2-Triphenylethane-2-C^{14} itself, when subjected to these conditions of the decarbonylation, was found to undergo 2.1% rearrangement at the lower temperature and 2.5% at the higher temperature. This phenyl migration, which has been subtracted from the total in the figures quoted earlier, apparently re-

sults from the generation of 1,2,2-triphenylethyl radicals by a displacement reaction involving either RS· or t-BuO·radicals (eq. 13). A similar displacement

$$Ph_2CHCH_2PH + RS· \text{ (or } t\text{-BuO·)} \longrightarrow$$
$$Ph_2CH\dot{C}HPh + RSH \text{ (or } t\text{-BuOH)} \quad (13)$$

reaction has been reported by Wang and Cohen.[41] Our finding of up to 14% phenyl migration, even in the presence of thiophenol,[8] in the case of the 1,2,2-triphenylethyl radical confirms the disclosure of Slaugh[8] that radical stability factors and relief of steric strain are not uniquely important in determining free radical rearrangements. It is interesting that our rearrangement involved a more stable and presumably longer lived secondary benzyl radical, whereas Slaugh's example involved a less stable, shorter lived primary 2-phenylalkyl radical. The greater extent of phenyl migration in our radical intermediate appears to be a logical consequence of its longer lifetime.

Degradation (chromic oxide–acetic acid) of the dimeric hexaphenylbutane products (VII) from similar decarbonylations of 2,3,3-triphenylpropionaldehyde-2-C^{14} revealed similar extents of phenyl migration to those observed when the monomeric products from the same reactions were similarly degraded (Table III). If one assumes ioentical extents of phenyl migration (and, therefore, lifetimes) for 1,2,2-triphenylethyl radicals following either the dimerization path (eq. 9), the disproportionation path (eq. 8), or hydrogen abstraction paths (eq. 7, 12), these results suggest that the chromic oxide–acetic acid oxidations of both hydrocarbons VI and VII were attended by identical extents of subsequent phenyl rearrangement. We are aware of no other reported instances of phenyl migration during a chromic oxide–acetic acid oxidation.

Having now established the occurrence of significant phenyl 1,2-migration during the lifetime of the 1,2,2-triphenylethyl radical, we presently hope to examine the possibility of nonclassical bridged radical intermediates in this system by employing our previous double-labeling techniques.

Experimental

2,3,3-Triphenylpropionic Acid.—The crude acid was prepared *via* the action of phenylmagnesium bromide on methyl α-phenylcinnamate in the manner previously described,[34] m.p. 212–214°, lit.[34] m.p. 220.5°.

2,3,3-Triphenylpropionyl Chloride.—A mixture of thionyl chloride (200 g.), benzene (25 ml.), and the prior 2,3,3-triphenylpropionic acid (20 g.) was heated under reflux for 1 hr., then stripped of volatile components under reduced pressure. The resulting pale yellow oil crystallized on standing and was recrystallized from hexane to yield 17 g. (80%) of rectangular prisms. Three additional recrystallizations afforded the pure acid chloride, m.p. 96–98°.

Anal. Calcd. for $C_{21}H_{17}OCl$: C, 78.62; H, 5.34. Found: C, 78.46; H, 5.38.

N-(2,3,3-Triphenylpropionyl)aziridine.—The procedure employed was adapted from that of Brown and Trukamoto.[35] The prior acid chloride (2.83 g.) in benzene (50 ml.) was stirred dropwise over a period of 30 min. into an ice-cooled ether–benzene (1:1, 50 ml.) solution of triethylamine (1.8 ml.) and ethyleneimine (1.0 ml.). Stirring was continued at 0° for 30 min., then at room temperature for 30 min., whereupon the amine hydrochloride precipitate was filtered and washed with hot acetone. Solvent evaporation from the combined filtrates and washings yielded 3.2 g. of white solid. A portion (1 g.) of the crude product was chromatographed on 50 g. of acid-washed silica, using

ether–hexane (1:10) as eluent. Evaporation of the first 1.25 l. of eluent left 0.54 g. of white solid, fraction A. The next liter of eluent yielded 0.37 g. of white solid, fraction B.

The infrared spectrum of fraction A showed a sharp C–H bending frequency at 1474 cm.$^{-1}$, characteristic of aziridine derivatives.[42] The spectrum showed no N–H stretching frequencies expected for primary and secondary amides (3100–3600 cm.$^{-1}$),[43] but displayed a strong carbonyl absorption band at 1676 cm.$^{-1}$. The n.m.r. spectrum of fraction A showed an octet of bands centered at 1.85, a quartet of bands (4.45, 4.65, 4.76 and 5.95) centered at 4.95, and a complex of bands between 7.0 and 7.5 p.p.m. Their relative intensities were consistent with the N-(2,3,3-triphenylpropionyl)-aziridine structure, octet–quartet–complex (2:1:8). After two recrystallizations from a mixture of benzene and pentane, pure N-(2,3,3-triphenylpropionyl)aziridine was obtained, m.p. 186.5–187.5°.

Anal. Calcd. for $C_{23}H_{21}ON$: C, 84.37; H, 6.47. Found: C, 84.56; H, 6.70.

The infrared spectrum of fraction B showed a sharp absorption at 3310, the N–H stretching frequency, and a strong carbonyl band at 1646, the secondary amide region of the spectrum, as well as a strong peak at 661 cm.$^{-1}$, the organo-halogen region of the spectrum.[44] A positive halogen test was observed on sodium fusion. The compound appeared to be N-(2-chloroethyl)-2,3,3-triphenylpropionamide, arising from the reaction of the acid chloride with 2-chloroethylamine, formed in turn by the action of the hydrochloric acid by-product on ethylenimine.[42]

The yields of the desired aziridine were improved in subsequent preparations by using a greater excess of triethylamine. It was found that the aziridine need not be isolated and purified, but could be converted in its crude form directly into 2,3,3-triphenylpropionaldehyde as described subsequently.

2,3,3-Triphenylpropionaldehyde.—The following procedure was adapted from that of Brown and Trukamoto.[35] An ether suspension (100 ml.) containing 200% excess of lithium aluminum hydride was stirred dropwise over a period of 30 min. into an ice-cooled ether–benzene (200 ml., 1:1) solution of crude N-(2,3,3-triphenylpropionyl\aziridine prepared from 5.14 g. of 2,3,3-triphenylpropionyl chloride. Stirring at 0° was continued for 30 min., whereupon the excess hydride was destroyed by cautious addition of chilled 5 N sulfuric acid. The organic layer was separated and processed as usual, being washed with dilute sodium bicarbonate. Solvent evaporation afforded 4.54 g. (99%) of thick sirup. This was chromatographed on 300 g. of acid-washed silica with benzene as eluent. Evaporation of the first 600 ml. of eluent left 2.2 g. (48% based on acid chloride) of white solid which proved homogeneous in thin layer chromatography. Pure 2,3,3-triphenylpropionaldehyde, m.p. 109–111°, was obtained after two recrystallizations from a mixture of hexane and benzene.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.33. Found: C, 88.11; H, 6.34.

The 2,4-dinitrophenylhydrazone was prepared in the usual way and recrystallized three times from a mixture of hexane and benzene, m.p. 230–232°.

Anal. Calcd. for $C_{27}H_{22}N_4O_4$: C, 69.51; H, 4.75; N, 12.01. Found: C, 69.27; H, 4.96; N, 12.03.

The 2,3,3-triphenylpropionaldehyde-2-C^{14} employed in the following experiments was prepared by application of the former sequence of reactions to 2,3,3-triphenylpropionic-2-C^{14} acid.[34]

The Decarbonylation of 2,3,3-Triphenylpropionaldehyde.—The procedure employed was adapted from that described by Slaugh.[8] A solution of this aldehyde (1.00 g.) and freshly distilled t-butyl peroxide (0.15 ml., 20 mole %) in o-dichlorobenzene (5.0 ml.) was immersed in an oil bath preheated to 170° and fitted with a steam condenser to allow for escape of volatile reaction products. The gases evolved were collected in a graduated cylinder inverted over a brine solution. After gas evolution had subsided, the reaction mixture was quickly cooled to room temperature, treated with additional fresh peroxide (0.15 ml.), and again heated to 170°. This procedure was repeated three times, yielding a total of 84 ml. (98% based on carbon monoxide)

(41) C. H. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 1924 (1957).

(42) R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds," Interscience Publishers, Inc., New York, N. Y., 1960, p. 7.

(43) A. D. Cross, "Introduction to Practical Infrared Spectroscopy," Butterworths Scientific Publications, London, 1960, pp. 57–75.

(44) N. R. Jones and C. Sandorfy, "Techniques of Organic Chemistry," Vol. IX, W. West, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 564–580.

of gas. The major portion of the solvent was removed by evaporation at reduced pressure and the residual crude product was chromatographed on 100 g. of alumina using hexane as eluent. Evaporation of the first 150 ml. of eluent yielded a viscous oil, 0.119 g., fraction A, which partially crystallized on standing for 1 week. Evaporation of the last 500 ml. of eluent (enriched in benzene) yielded 0.674 g. of white solid, fraction B.

Thin layer chromatographic investigation of fraction A revealed the presence of two components whose R_f values and spot colors were identical with those of authentic 1,1,2-triphenylethane and triphenylethylene. Mixtures of these hydrocarbons behaved similarly to fraction A upon thin layer chromatography on alumina using a variety of eluents. Fraction A was recrystallized three times from methanol to yield a white solid, m.p. 54.5–55.5°, whose infrared spectrum was superimposable on that of authentic 1,1,2-triphenylethane with reported m.p. 55–55.5°.[34] The mixture of the two monomers, 1,1,2-triphenylethane and triphenylethylene, constituted a 15% yield from the starting aldehyde.

Fraction B was recrystallized three times from hexane–benzene, affording white crystals, m.p. 210–213°. Their infrared spectrum was generally similar to that of 1,2,2-triphenylethane, although characteristic methylene C–H stretching bands (2940–2915, 2870–2845 cm.$^{-1}$)[43] were seemingly absent. Only two relatively weak bands appeared in these regions of the spectrum (2900 and 2930), in contrast to three stronger bands at 2880, 2925, and 2939 and a weak band at 2859 cm.$^{-1}$ present in the spectrum of 1,2,2-triphenylethane. The n.m.r. spectrum of the solid contained two overlapping bands at 4.14 and 4.17 and a complex of bands between 6.5 and 7.5 p.p.m. The ratio of integrated band intensities was consistent with a hexaphenylbutane structure, aromatic (complex)–aliphatic (doublet) 15:2.

Anal. Calcd. for $C_{40}H_{34}$: C, 93.34; H, 6.66; mol. wt., 514.7. Found: C, 93.31; H, 6.78; mol. wt. (Rast), 484.

The structure most consistent with the previous data appeared to be 1,1,2,3,4,4-hexaphenylbutane. The absence of methylene absorption bands in the infrared spectrum, we believe, makes other hexaphenylbutane isomers less likely, in that each of these contains a methylene group. The hydrocarbon, $C_{40}H_{34}$, was the principal product of the decarbonylation reaction (75% based on aldehyde, Table I).

The aldehyde decarbonylation was repeated in the same solvent under a variety of reaction conditions, results of which are shown in Table I.

Table I

THE DECARBONYLATION OF 2,3,3-TRIPHENYLPROPIONALDEHYDE

Aldehyde (m olality)	*t*-Butyl peroxide (mole %)	Temp., °C.	Gas evolved (% of theoretical amount of CO)	—Hydrocarbon yield, %— Mono- meric	Di- meric	Total
0.074	39	153	102			71
.128	20	165	95			72
.538	20	170	98	15	75	90
.250	15	180	85	1	58	59
.192	15	180	114	11	62	73

The Mercaptan-Catalyzed Decarbonylation of 2,3,3-Triphenylpropionaldehyde.—The procedure for the decarbonylation of the aldehyde in the presence of mercaptans was similar to that described earlier. A mixture of 2,3,3-triphenylpropionaldehyde (0.55 g.), freshly distilled *t*-butyl peroxide (40 mg.), and benzyl mercaptan (13 mg., 5 mole %) in *o*-dichlorobenzene solvent (0.75 ml.) was placed in a bath preheated at 180°. Decarbonylation was vigorous, yielding 48 ml. (114% based on carbon monoxide) of gas. The monomer and dimer hydrocarbon products were separated chromatographically as before. The mixture of monomers (166 mg., 33%) was further separated by gas chromatography (silicone rubber column, 250°), and found to consist of 1,1,2-triphenylethane (29%, based on aldehyde) and triphenylethylene (4%). The dimeric hydrocarbon product was obtained in 32% yield. The decarbonylation was repeated under similar reaction conditions employing thiophenol as catalyst. The results of these experiments are listed in Table II. In each case 1,1,2-triphenylethane represented the principal component (*ca.* 74%) of the monomer mixture.

Table II

DECARBONYLATION OF 2,3,3-TRIPHENYLPROPIONALDEHYDE IN THE PRESENCE OF THIOPHENOL

Aldehyde (molality)	*t*-Butyl peroxide (mole %)	Thio- phenol (mole %)	Temp., °C.	Gas evolved (% of theoretical amount of CO)	Hydrocarbon %— Mono- meric	Di- meric
0.190	5.6	6.2	185	122	37	22
.075	30	8.1	185	172	41	29
.075	30	16.5	180	195	42	21

Oxidation of 1,1,2-Triphenylethane-2-C^{14}.—1,2,2-Triphenylethanol-1-C^{14} was converted by the action of Raney nickel in refluxing ethanol into 1,1,2-triphenylethane-2-C^{14}.[34] This was recrystallized from methanol to give a pure sample, m.p. 55–56°, specific activity 1.90 ± 0.07 mc./mole, which was employed in the following oxidation experiments.

A. With Chromic Oxide.—A solution of the previous hydrocarbon (121 mg.) in acetic acid (5 ml.) was treated with a solution of chromic oxide (600 mg.) in water (1 ml.) and the mixture was heated on the steam bath for 19 hr., then was cooled, made alkaline with sodium hydroxide, and extracted thoroughly three times with ether. The extract was washed, dried, and stripped of solvent to yield a neutral oil, thin layer chromatography of which revealed no starting material. The oil was converted in the usual way to benzophenone 2,4-dinitrophenylhydrazone (180 mg., 106%) which, on recrystallization from dioxane, had m.p. 243–244° and specific activity of 0.193 mc./mole. Thus *ca.* 10% phenyl migration accompanied the oxidative degradation of 1,1,2-triphenylethane with chromic oxide.

B. With Potassium Permanganate.—The previous hydrocarbon was oxidized with potassium permanganate as previously described,[34] affording a sample of benzophenone whose purified 2,4-dinitrophenylhydrazone, m.p. 240–242°, was void of radioactivity. This degradation, involving no subsequent molecular rearrangement, was thus deemed suitable for assessing rearrangement in the 1,1,2-triphenylethane fraction from decarbonylation reactions.

Degradation of 1,1,2,3,4,4-Hexaphenylethane.—A variety of techniques was attempted to find satisfactory conditions for the degradation of the dimeric hydrocarbon (IX) from the decarbonylation reaction. These included attempts at preliminary dehydrogenation using chloranil, preliminary halogenation with N-bromosuccinimide, and direct oxidation (as before) with potassium permanganate. All of these methods failed, and the only applicable degradation proved to be direct oxidation with chromic oxide in acetic acid, as before. Since this oxidation proceeded with 10% molecular rearrangement in the case of 1,1,2-triphenylethane, and since benzophenone yields were quite low (20–25%) and benzoic acid yields negligible in the present case, it was apparent that any estimates of the extent of rearrangement during the formation of the dimeric decarbonylation product could only be approximate.

Effect of Decarbonylation Conditions on 1,1,2-Triphenylethane-2-C^{14}.—The conditions in the following experiment were maintained as close to those of the previous decarbonylation as possible. A solution of 1,1,2-triphenylethane-2-C^{14} (930 mg., m.p. 55–56°, specific activity 0.645 ± 0.005 mc./mole), freshly distilled *t*-butyl peroxide (400 mg.), and thiophenol (148 mg.) in *o*-dichlorobenzene (18 ml.) was divided into two equal portions. Using the previous decarbonylation apparatus, each portion was inserted into its bath, preheated to 160° and 182°, respectively. After 45 min. the flasks were cooled, additional peroxide (200 mg.) was added, and the reactants were again heated at their prescribed temperatures. After a total reaction time of 2 hr. and a second intermittent addition of fresh peroxide, the reactions were stopped, and the products were isolated as before. The crude triphenylethane chromatography fraction (830 mg., 89.5%) contained approximately the same per cent of triphenylethylene (*ca.* 8%) as did that from the decarbonylation. Portions of each triphenylethane sample were converted *via* permanganate oxidation as described into benzophenone 2,4-dinitrophenylhydrazone, which was purified and assayed for radioactivity. The benzophenone derivative from the experiment conducted at 154–159° had a specific activity of 0.0135 mc./mole (2.09%

TABLE III

THIOPHENOL-CATALYZED DECARBONYLATIONS OF 2,3,3-TRIPHENYLPROPIONALDEHYDE-2-C^{14}

Starting aldehyde (A)					
Sp. act., mc./mole	1.365^a	1.365^a	1.201^b	1.201	1.201^b
Concn., M	0.51	0.51	0.50	0.50	0.50
Temperature, °C.	155–165	176–184	155–158	155–158	174–178
t-Bu$_2$O$_2$, mole % of A	30	30	31	31	31
Thiophenol, mole % of A	14	14	11	11	11
VI, sp. act., mc./mole			1.163^b	1.178^b	1.18^a
VII, sp. act., mc./mole			2.42^c	2.43^c	
Oxidant for degradation	KMnO$_4$	KMnO$_4$	CrO$_3$	CrO$_3$	CrO$_3$
Ph$_2$CO from VI, mc./mole	0.0949^b	0.224^d	0.143^d	0.147^d	0.189^d
Phenyl migration in VI, %	6.9^e	16.4^e	11.9^f	12.2^f	15.7^f
Ph$_2$CO from VII, mc./mole			0.141	0.147	
Phenyl migration in VII, %			11.7^f	12.2^f	

^{a} ±0.010 to 0.015. ^{b} ±0.006 to 0.008. ^{c} ±0.05. ^{d} ±0.0007 to 0.0015. ^{e} Not to be compared with figures in columns 3 and 5, respectively, due to differences in the experimental conditions of the decarbonylation and degradation. ^{f} Including rearrangement caused by oxidative degradation.

rearrangement). That from the experiment conducted at 178–184° had a specific activity of 0.0159 mc./mole (2.46% rearrangement).

Decarbonylation of 2,3,3-Triphenylpropionaldehyde-2-C^{14}.— The previous labeled aldehyde was decarbonylated in *o*-dichlorobenzene solvent in the manner described for the unlabeled analog, each reaction mixture being divided into several equal portions

for decarbonylations at different temperatures. The decarbonylation products were isolated as before, assayed, and then degraded by either permanganate or chromic oxide oxidation. The final benzophenone 2,4-dinitrophenylhydrazone from each experiment was assayed to determine the extent of phenyl migration during each decarbonylation. The results of these experiments are summarized in Table III.

Nitrogen Analogs of Ketenes. VI.[1] Dehydration of Amides

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A novel method for the preparation of nitrogen analogs of ketenes has been developed which involves direct linear dehydration of the corresponding amides.

Ketenimines were first prepared in 1921 by Staudinger in unspecified yield by the interaction of a phosphinimine and a ketene,[3] and more recently Backer has successfully prepared several ketenimines by the reaction of diazomethane with negatively substituted nitriles.[4] Over the past decade this laboratory has sought more general and convenient methods for the synthesis of these interesting compounds. Two methods were developed which involved (1) the dechlorination of α-chloroimino chlorides with sodium iodide in acetone,[5a] and (2) the dehydrochlorination of imino chlorides with a tertiary amine.[5b] This paper reports a third new and general method for the facile preparation of ketenimines by the direct linear dehydration of N-monosubstituted amides.

Although the linear dehydration of N-monosubstituted amides for the preparation of nitrogen analogs of ketenes is not known, dehydration of amides to form nitriles is well known.[6] Some of the common dehy-

drating agents are phosphorus pentoxide, phosphorus oxychloride, phosphorus pentachloride, thionyl chloride, polyphosphoric acid, and phthalic anhydride. Phosphorus pentoxide is preferred for the dehydration of unsaturated amides where the use of dehydrating agents such as phosphorus pentachloride may give halogen-containing products.

Scheibler and co-workers[7] used phosphorus pentoxide in combination with a tertiary amine to dehydrate an acid-sensitive amide. From diethoxy acetamide they obtained diethoxyacetonitrile in 30% yield with phosphorus pentoxide and quinoline. In the same reaction, McElvain and co-workers[8] employed N-hexylpiperidine and triethylamine as tertiary bases with phosphorus pentoxide and obtained yields of 45% and 80%, respectively, of diethoxyacetonitrile. In the case of N-substituted amides, cyclic dehydration is the basis of the Bischler–Napieralski reaction.[9] Thus, β-phenethylamides on cyclic dehydration lead to 3,4-dihydroisoquinolines and Itoh and Sugasawa[10] used phosphorus pentoxide mixed with dry sand and pyridine to obtain isoquinoline derivatives in excellent yields.

In the present work, exploration of the dehydration of N-monosubstituted amides was initiated using various tertiary amines in combination with a five- to

(1) The previous paper of this series was by C. L. Stevens and M. E. Munk, *J. Am. Chem. Soc.*, **80**, 4069 (1958).

(2) Abstracted in part from the dissertation of Gopal H. Singhal in partial fulfillment of the requirement for the degree of Doctor of Philosophy, Wayne State University, 1962. This work was supported by Grant No. CY3772 from the National Institutes of Health.

(3) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 887 (1921).

(4) R. Dijkstra and H. J. Backer, *Rec. trav. chim.*, **73**, 575, 695 (1954).

(5) (a) C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **75**, 657 (1953); (b) **76**, 4398 (1954).

(6) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 596–598; see also R. E. Kent and S. M. McElvain, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 493.

(7) H. Scheibler, *et al.*, *Ber.*, **67**, 1513 (1934).

(8) S. M. McElvain and Robert L. Clarke, *J. Am. Chem. Soc.*, **69**, 2659 (1947).

(9) W. M. Whaley and T. R. Govindachari, *Org. Reactions*, **6**, 99 (1951).

(10) N. Itoh and S. Sugasawa, *Tetrahedron*, **1**, 45 (1957).