##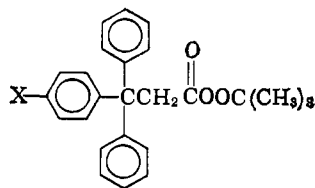 Thermal Decomposition of t-Butyl 3,3,3-Triarylperpropionates. Evidence for the Intramolecular Rearrangement and Cyclization of Aliphatic Acyloxy Radicals

Sir:
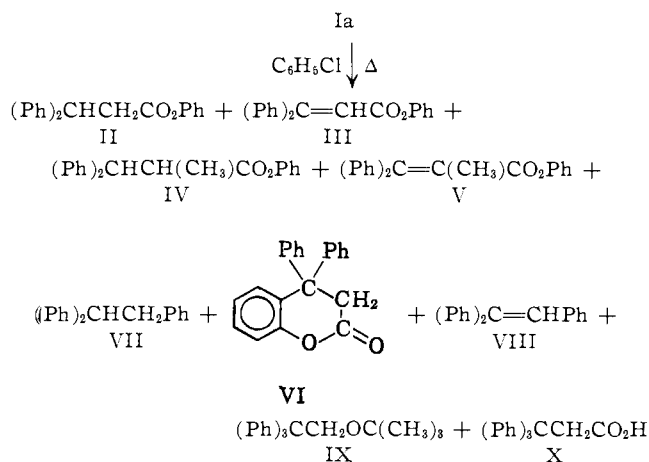
The low thermodyoamic stability of aliphatic acyloxy radicals has been well documented,[1] and the question of whether normal free-radical reactions of these species can be made competitive with their decomposition is still under debate.[2] Of particular interest in this context are certain anomalous cyclizations and rearrangements which have been reported to occur under conditions normally used for the Hunsdiecker reaction[3] and for the Kolbe electrolysis,[4] and which can be interpreted as involving entrapment of aliphatic acyloxy radicals by intramolecular processes. However, definitive evidence as to the intermediacy of free acyloxy radicals in these reactions is lacking, since the abnormal Hunsdiecker products could have been formed by way of polar intermediates, and the electrolytic rearrangements might have involved radicals which were not truly "free." Concerted mechanisms would also appear to be possible in all of these cases.

The present work represents an attempt to obtain more information relating to the question of intramolecular reactions of free aliphatic acyloxy radicals from a study of the thermal decompositions of t-butyl 3,3,3-triphenylperpropionate (Ia), t-butyl 3,3-diphenyl-3-p-methoxyphenylperpropionate (Ib), and t-butyl 3,3-diphenyl-3-p-nitrophenylperpropionate (Ic).[5]

Ia, X = —H
b, X = —OCH₃
c, X = —NO₂

Ia

$$C_6H_5Cl \downarrow \Delta$$

(Ph)₂CHCH₂CO₂Ph + (Ph)₂C=CHCO₂Ph +
     II   III

(Ph)₂CHCH(CH₃)CO₂Ph + (Ph)₂C=C(CH₃)CO₂Ph +
     IV   V

(Ph)₂CHCH₂Ph +   + (Ph)₂C=CHPh +
    VII   VIII

VI

(Ph)₃CCH₂OC(CH₃)₃ + (Ph)₃CCH₂CO₂H
     IX   X

TABLE I

PRODUCTS FROM DECOMPOSITION OF Ia IN CHLOROBENZENE[a]

Compound[b]	Moles/mole Ia[d]
Phenyl 3,3-diphenylpropionate (II)	0.218 ± 0.005
Phenyl 3,3-diphenylacrylate (III)	.186 ± .011
Phenyl 3,3-diphenyl-2-methylpropionate (IV)	.051 ± .010
Phenyl 3,3-diphenyl-2-methylacrylate (V)	.041 ± .005
4,4-Diphenyl-3,4-dihydrocoumarin (VI)	.051 ± .009
1,1,2-Triphenylethane (VII)	.077 ± .011
Triphenylethylene (VIII)	.121 ± .003
t-Butyl 2,2,2-triphenylethyl ether (IX)	.039 ± .006
3,3,3-Triphenylpropionic acid (X)	.229 ± .008
Benzophenone[c]	.005 ± .001
Phenol[c]	.007 ± .001
Carbon dioxide	.223 ± .043

[a] 100°, 0.500 g. of Ia, 10.0 ml. of solvent (triply degassed), helium atmosphere. [b] Other products are chlorotoluenes, acetone, t-butyl alcohol, methane, isobutylene, ethane (trace), propane (trace), and methyl chloride (trace). Compound X was isolated by extraction with sodium carbonate; all other compounds were determined by g.c. techniques. [c] Possible mechanisms for formation of this product will be discussed in a subsequent report. [d] Deviations are for duplicate runs. Material balances are carbon dioxide, 99.5 ± 6.5%; triphenylethyl fragment (excluding benzophenone and phenol), 101 ± 4%.

The major products resulting from decomposition of Ia in chlorobenzene solution are shown, and quantitative analytical data are given in Table I.

All products except IV and V were identified by comparing their g.c. retention times and infrared, n.m.r., and mass spectra with those of authentic samples. The structural assignments for IV and V are based on mass and infrared spectral data and are regarded as tentative. An unusual dehydrogenative cyclization resulting from treatment of X with chromic acid in refluxing aqueous acetic acid afforded 19% of the previously unreported lactone, VI, m.p. 150–151°.[5,6] Sulfuric acid-catalyzed alkylation of 2,2,2-triphenylethanol with isobutylene at room temperature in methylene chloride solution gave an essentially quantitative yield of the ether, IX, m.p. 106–107°.[5] Compounds II, III, VII, VIII, and X are described in the literature.

Preliminary kinetic studies of the decompositions were made by following the rates of gas evolution from chlorobenzene solutions approximately 0.1 M in perester. At 100° the apparent first-order rate constants obtained for decomposition of Ia, Ib, and Ic were 2.2×10^{-5} sec.$^{-1}$, 2.9×10^{-5} sec.$^{-1}$, and 1.5×10^{-5} sec.$^{-1}$, respectively. These values probably are higher than the true k values for the monomolecular reaction, since they are not corrected for induced decomposition. They are of the order of magnitude expected for decomposition of ordinary straight-chain aliphatic peresters under these conditions,[7] and they indicate, therefore, that the rate-determining step in the decomposition of Ia, Ib, and Ic is a simple homolytic cleavage of the oxygen–oxygen bond involving no aryl participation.[8] Rapid rearrangement, cyclization, or decarboxylation of the acyloxy radicals thus formed accounts for the observed variety of products.

(1) L. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

(2) For recent discussions containing leading references, see (a) H. J. Shine and D. M. Hoffman, *J. Am. Chem. Soc.*, **83**, 2782 (1961); (b) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 3004 (1961).

(3) (a) J. W. Wilt and J. L. Finnerty, *J. Org. Chem.*, **26**, 2173 (1961) and references therein; (b) U. K. Pandit and I. P. Dirk, *Tetrahedron Letters*, 891 (1963); (c) A. Roedig, G. Märkl, and M. Schlosser, *Chem. Ber.*, **95**, 2243 (1962); (d) A. W. Burgstahler and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **85**, 173 (1963).

(4) H. Breederveld and E. C. Kooyman, *Rec. trav. chim.*, **76**, 297 (1957).

(5) The structures of all new compounds were established by elemental analyses and the usual variety of spectroscopic techniques. Structure proofs and methods of synthesis will be described in detail in a later report.

(6) A similar cyclization of biphenyl-2-carboxylic acids has been described by G. W. Kenner, M. A. Murray, and C. M. B. Tylor, *Tetrahedron*, **1**, 259 (1957).

(7) (a) M. Trachtman and J. G. Miller, *J. Am. Chem. Soc.*, **84**, 4828 (1962); (b) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

(8) This conclusion is supported by a rate constant for decomposition of Ia at 120° reported by C. Rüchardt and R. Hecht, *Tetrahedron Letters*, 1957 (1962). However, it should be emphasized that a rigorous proof requires the determination of thermodynamic activation parameters.

Compounds VII and VIII are the products expected from the 2,2,2-triphenylethyl radical, which rearranges with great ease,[9] while IX probably results from a rapid secondary cage recombination involving the unrearranged species and the t-butoxy radical. The probable precursor of IV and V is the radical formed by addition of a methyl radical (from β-scission of the t-butoxy fragment) to III. The origin of X is not clear; an interesting possibility is that it results from induced decomposition of Ia by one or more radicals capable of donating hydrogen.[10]

Reaction mixtures from the decomposition of Ib and Ic in chlorobenzene at 100° were saponified and then acidified to give mixtures of phenols which were examined by gas chromatography. Perester Ib yielded only phenol and p-methoxyphenol, while Ic gave exclusively phenol and p-nitrophenol; thus the transition state for the aryl migration is of the Ar_1–5 type rather than Ar_2–6.[11] From quantitative analyses of the phenolic products, the relative migratory aptitudes of phenyl (corrected by a statistical factor of two), p-methoxyphenyl, and p-nitrophenyl were determined to be 1.0:4.0:0.25.[12] A Hammett plot of these data using σ^+ constants gives an excellent correlation with ρ equal to -0.78. Although the general applicability of this correlation remains to be demonstrated, the electrophilic nature of the postulated acyloxy radical intermediate is clearly implied by the results already in hand.[13]

Acknowledgment.—The author thanks Mr. H. J. Tarski, Mr. V. H. Rushing, and various other members of the Research and Development Division for excellent technical assistance, and he also wishes to acknowledge helpful discussions of analytical problems with Dr. Thomas Aczel and Dr. K. W. Bartz and to thank Dr. R. H. Perry, Jr., for his continued support of this work.

(9) (a) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960); (b) D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).

(10) W. R. Foster and G. H. Williams, *J. Chem. Soc.*, 2862 (1962) have cited evidence for the formation of benzoic acid in the induced decomposition of benzoyl peroxide by phenylcyclohexadienyl radicals.

(11) R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3105 (1957).

(12) These numbers do not necessarily represent *intrinsic* migratory aptitudes, since there is no guarantee that the phenyl reference group migrates at the same rate in both cases.

(13) A study of the thermal decomposition of 3,3,3-triphenylpropanoyl peroxide has recently been carried out by H. M. Weiss, Ph. D. thesis, Rutgers University, 1962. The mechanism proposed is quite different from that suggested here for decomposition of the related t-butyl peresters.

RESEARCH AND DEVELOPMENT DIVISION
HUMBLE OIL & REFINING COMPANY　　　　W. H. STARNES, JR.
BAYTOWN, TEXAS

A New Noncyclic Butadiene Oligomer:
trans-3-Methylhepta-1,4,6-triene

Sir:

Wilke has opened a new field of cyclic diene oligomers such as cyclododecatriene.[1]

In the course of study on the mechanism of stereospecific high polymerization of butadiene, we have found that cobalt-containing catalysts can yield a new noncyclic butadiene oligomer in high yield.

Oligomerization of butadiene was effected in the absence or presence of an inert solvent at slightly above room temperature using dicobalt octacarbonyl–triethylaluminum catalyst. A new triene (I) of b.p. 117° (760 mm.), $n^{20}D$ 1.4657, d^{20}_4 0.7570, was obtained in 90% yield.

(1) G. Wilke, *Angew. Chem.*, **69**, 397 (1957); *ibid.*, **71**, 574 (1959); G. Wilke, *J. Polymer Sci.*, **38**, 45 (1959); G. Wilke, *Angew. Chem.*, **72**, 581 (1960); G. Wilke, *ibid.*, **73**, 33, 755, 756 (1961).

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 89.20; H, 11.20.

A typical procedure is as follows. All operation was carried out under pure nitrogen. In a stainless-steel autoclave of 12-l. capacity were placed 13.6 g. (80 mmoles) of crystalline dicobalt octacarbonyl and 4300 g. (80 moles) of dried "pure grade" butadiene. After the autoclave was chilled to 0°, 272 g. (2.4 moles) of triethylaluminum was added slowly under gentle stirring. The temperature was raised gradually to 40° and kept for 48 hr. with stirring. The reaction mixture was again chilled to 0° and the organometallic catalysts were destroyed by *tert*-butyl alcohol.

Gas chromatographic analysis of an aliquot from the reaction mixture indicated that 60% of butadiene was converted to dimers of which 90, 8, and 1% were I, 4-vinylcyclohexene-1 plus a n-octatriene, and 1,5-cyclooctadiene, respectively. Fractional distillation gave I as a main fraction, b.p. 69–73° (180 mm.).

Pure substance for analytical purpose was obtained by preparative gas chromatography. From the molecular weight found by the cryoscopic method in benzene and quantitative hydrogen absorption with platinum catalyst, the product was found to be a dimer which contains three double bonds. The infrared spectrum of the hydrogenated product was identical with that of 3-methylheptane. The ultraviolet absorption spectrum (λ_{max} 227 mμ (log ϵ 4.40)) indicated conjugation of two double bonds but not of three. The infrared spectrum (900 (s), 910 (s), 948 (m), 1000 (m), 1368 (m), 1410 (m), 1450 (s), 1603 (s), 1636 (s), 1800 (m); s, strong, m, medium) showed the presence of C—CH_3, =CH_2, and conjugated double bonds. Nuclear magnetic resonance data showed the presence of one CH_3—CH (doublet $\tau = 8.9$, $J = 7.0$) and two —CH_2— and four =CH— groups.

A maleic anhydride addition reaction gave further information. Thus, the infrared spectrum of the adduct (m.p. 61–62°) showed one terminal vinyl group was still retained.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.82; H, 6.90.

Moreover, the ease of the Diels–Alder reaction suggests that the inner —CH=CH— group probably has *trans* configuration, as shown in the *cis*- and *trans*-piperylene[2] and 1,3,5-hexatriene isomers.[3]

The structure of the triene is thus best formulated as 3-methylhepta-1,4,6-triene (I).

$$CH_2\!\!=\!\!CH—CH\!\!=\!\!CH—\underset{\underset{\displaystyle CH_3}{|}}{CH}—CH\!\!=\!\!CH_2$$

I
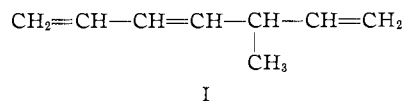
The absence of the geometrical and/or structural isomers, such as normal octatriene, in I was confirmed from the quantitative yield of the Diels–Alder reaction and from the gas chromatographic analysis.

The infrared absorption spectrum of the reaction between the cobalt carbonyl and triethylaluminum indicated complete disappearance of the CO stretching bands (terminal CO: 2028 (s), 2037 (m), 2050 (s), 2065 (m), 2077 (s), bridge CO: 1853 (s), 1862 (m)), irrespective of the presence or absence of butadiene monomer. The best catalytic activity, however, was obtained when the two components were admixed in the presence of the monomer, resulting in a homogeneous solution.

(2) E. H. Farmer and F. L. Marren, *J. Chem. Soc.*, 3221 (1931); R. F. Robey, C. E. Morrell, and H. K. Wiese, *J. Am. Chem. Soc.*, **63**, 627 (1941); J. A. Norton, *Chem. Rev.*, **31**, 349 (1942); D. Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943).

(3) J. C. H. Hwa, P. L. De Benneville, and H. J. Sims, *J. Am. Chem. Soc.*, **82**, 2537 (1960).