tained by further recrystallization from n-hexane and gave m.p. 129–130°; ν_{max}^{KBr} 3311, 1038 cm.$^{-1}$; n.m.r., δ 0.73 (3), 0.97 (3), 2.18 (disappears on the addition of deuterium oxide), 2.98 (doublet, 1 proton), 3.36 (doublet, 1 proton).

Anal. Calcd. for $C_{19}H_{32}O$: C, 82.54; H, 11.66. Found: C, 82.93; H, 11.57.

A solution of 0.79 g. of XI in 10 cc. of anhydrous pyridine was added to a stirred mixture of 1 g. of chromic anhydride in 10 cc. of pyridine, and the entire mixture was then stirred at room temperature for 2 hr. After pouring into ice–water the solution was extracted with ether; the ether extract was washed successively with 5% hydrochloric acid and 5% sodium hydroxide, and then dried over anhydrous magnesium sulfate. The solvent was removed by evaporation and 0.7 g. of crude product was obtained. Crystallization from methanol gave the air-sensitive aldehyde (0.5 g.), m.p. 85–92°; ν_{max}^{KBr} 2680, 1724 cm.$^{-1}$. The aldehyde was reduced to III without further purification.

Potassium hydroxide (1.5 g.) was heated with 1.5 cc. of 95% hydrazine and 10 cc. of diethylene glycol until it dissolved. The aldehyde XII (400 mg.) was added to this solution and the reaction mixture was refluxed for 3 hr. Some of the product sublimed into the condenser during this period. Excess hydrazine and water were distilled until the temperature of the residue reached 240°. The distillate was saved and the sublimed material was washed out of the condenser with ether. Hydrazine (1.5 cc.) was again added to the residue and refluxing continued for an additional 12 hr. The reaction mixture, distillate, and ether washings were combined, added to water (150 cc.), and the entire mixture was extracted with ether. The ether extract was thoroughly washed with water and then dried over anhydrous magnesium sulfate. Evaporation of the ether gave 350 mg. of hydrocarbon III, m.p. 75–79°. Recrystallization from acetone gave 320 mg., m.p. 84–86°. The analytical sample was obtained by two recrystallizations from acetone and had m.p. 86–87°; $[\alpha]_D$ +38.7° (c 0.036 in CCl_4); ν_{max}^{KBr} 2941, 1460, 1390, 1370 cm.$^{-1}$; n.m.r., δ 0.82 (3), 0.85 (3), and 0.93 (3).

Anal. Calcd. for $C_{19}H_{32}$: C, 87.61; H, 12.38. Found: C, 87.96; H, 12.41.

Pyrolysis of Trityl Esters Possessing β-Hydrogen. II[1,2]

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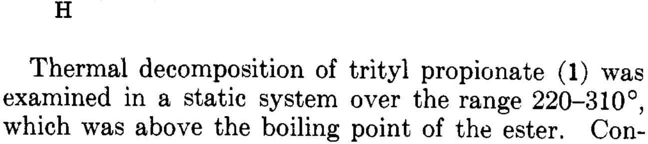
Pyrolysis of trityl propionate, trityl hydrocinnamate, and trityl pivalate has been examined over a temperature range of 225–430°. Nearly complete decomposition was observed in all examples whose reaction mixtures were analyzed meticulously by gas chromatography. Except in the case of trityl pivalate, the pyrolysates of the trityl esters were complex. The presence of tritan, tritanol, and benzophenone in the mixtures testified to the occurrence of both alkyl–oxygen and acyl–oxygen fission. Only with trityl pivalate was a degree of specificity observed, since isobutylene, carbon dioxide, and tritan were produced in high yields. Rather copious quantities of the respective acids were found in the other two pyrolysates, and only minor amounts of olefins were obtained. Mechanistic considerations involving radicals are proposed to explain the degradation results.

Trityl esters have been made readily accessible by a method described recently.[2] We now wish to report the pyrolysis studies of three trityl esters all of which possess at least one β-hydrogen atom in the acid portion of the molecule. Examination of the pyrolysate of trityl triphenylmethylacetate[5] appears to be the first recorded example in the area of trityl-substituted carbonyl compounds.[6] Tritan and carbon dioxide were the only components identified unequivocally in the reaction mixture.[5] Although stable at room temperature, trityl formate decomposed rapidly near 49° to give tritan and carbon dioxide.[7] Similarly, trityl fluoromethylacetate melted at 106° with decomposition but no details of a product analysis were presented.[8] In a study of the pyrolysis of several benzyl esters, Jones and Ritchie followed the thermal degradation of trityl benzoate.[9] The ester decomposed at 225° and 500° to give pyrolysates of nearly identical composition. The major pathway of cleavage involved aryl–acyl and alkyl–oxygen bond severance to give carbon dioxide and tetraphenylmethane. Minor products included benzoic acid, benzene, and triphenylmethane.[10]

Pyrolysis of acetates and xanthates has become a preferred method for preparation of olefins.[11] A decomposition process similar to that described in the acetate elimination reaction could be envisioned for the thermal collapse of a trityl ester whose structure is shown. Moreover, the absence of acidic products was an attractive possibility since a neutral medium at elevated temperatures would provide for minimum rearrangements.



Thermal decomposition of trityl propionate (1) was examined in a static system over the range 220–310°, which was above the boiling point of the ester. Contents of the pyrolysate were virtually unaltered at temperatures studied within the preceding range. Neither a bromine trap nor direct infrared analysis of the gaseous products from 1 indicated more than a trace of ethylene formed.

Clearly a concerted, intramolecular decomposition is not operative here as is known in acetate pyrolysis.[11] Table I contains pertinent data of a typical run on the type and weight of components in the pyrolysate from

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[1] (a) We gratefully acknowledge the support of the National Science Foundation, grant G-19733. Partial support by the Oklahoma State University Research Foundation is acknowledged. (b) Presented at the Southwest Regional Meeting of the American Chemical Society, Dallas, Tex., December 6–8, 1962.

[2] For paper I in the series, see *J. Org. Chem.*, **27**, 3595 (1962).

[3] To whom inquiries should be addressed.

[4] National Science Foundation teacher training participant, summer, 1962; on leave from the Department of Chemistry, Augustana College, Rock Island, Ill.

[5] R. Anschutz, *Ann.*, **359**, 196 (1908).

[6] For a review of pyrolysis reactions of trityl ketones, see R. C. Fuson and K. D. Berlin, *J. Am. Chem. Soc.*, **81**, 2130 (1959).

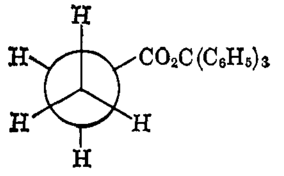
[7] S. T. Bowden and T. F. Watkins, *J. Chem. Soc.*, 1333 (1940).

[8] P. W. Sharp and N. Shephard, *ibid.*, 674 (1957).

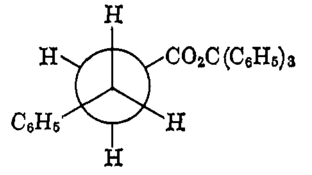
[9] E. Jones and P. D. Ritchie, *ibid.*, 4141 (1960).

[10] The use of vapor phase chromatography was not referenced as an analytical tool in this research.

[11] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).



1



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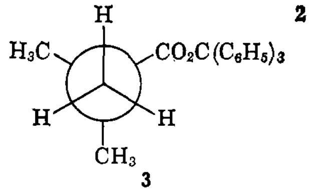


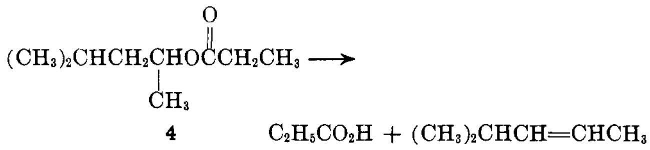
3

1. Below 220° little decomposition of **1** occurred after four hours since analysis of the residue by infrared spectroscopy and gas chromatography indicated nearly pure starting material. Noteworthy is the substantial amount of propionic acid isolated. This is reminiscent

$$1 \longrightarrow CH_3CH_2CO_2\cdot + (C_6H_5)_3C\cdot$$

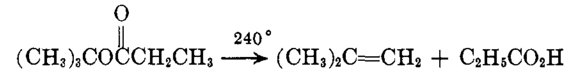
of the behavior of other simple aliphatic propionates. For example, pyrolysis of **4** gave 4-methyl-2-butene and propionic acid in good yields.[12]

Similarly, *t*-butyl propionate (**5**) was converted to



$$(CH_3)_2CHCH_2\underset{CH_3}{CH}O\overset{O}{\overset{\|}{C}}CH_2CH_3 \longrightarrow C_2H_5CO_2H + (CH_3)_2CHCH{=}CHCH_3$$

4



$$(CH_3)_3CO\overset{O}{\overset{\|}{C}}CH_2CH_3 \xrightarrow{240^\circ} (CH_3)_2C{=}CH_2 + C_2H_5CO_2H$$

5

isobutylene and propionic acid at 240°.[13] Since decomposition was heterogeneous and not reproducible in clean glass vessels and some polymerization of isobutylene was implied, the reaction may be radical in nature.

Analysis of the pyrolysate from **1** revealed tritan, tritanol, benzophenone, benzene, styrene, ethylbenzene, ethane, ethylene, and butane as the major components in addition to propionic acid. However, some polymeric material also could be obtained and it was carefully isolated and characterized. The weight of products separated by column chromatography totaled more than 90% of the initial weight of ester. Such complexity in the pyrolysate has been reported when esters of triphenylacetic acid were thermally decomposed.[14] Tritan, carbon dioxide, and a mixture of saturated and unsaturated hydrocarbons were obtained, and an intermediate trityl radical was postulated.

Initial homolytic fission of the alkyl–oxygen bond to give trityl and propionoyloxy radicals seems probable for several reasons: (1) the low yield of ethylene detected precludes a concerted intramolecular abstraction of hydrogen by the trityl radical; (2) the high yields of tritan and propionic acid; (3) a probable low O–C bond dissociation energy[15]; and (4) the presence of benzophonone in the pyrolysate.[16] In addition, an effort was made to trap trityl radicals by conducting a stream of molecular oxygen through the melt of **1** at 300°. Discoloration of the liqiud in this experiment was essentially the same as when the pyrolysis was performed under nitrogen, namely from clear to yellow to red to brown. A marked increase in the amount of benzophenone was observed along with propionic acid in high yield. The interpretation here is that trityl radicals are oxidized to triphenylmethylperoxy radicals which might be expected to couple with trityl radicals to give trityl peroxide. However, trityl peroxide is known to decompose in solution below 150°[17] and thus it is reasonable that a similar reaction could occur in the melt to give phenyl radicals and benzophenone. Tritan also was formed, but the yield was reduced, as expected, by approximately 50%. Therefore, this observation lends credence to the postulate that initial homolytic cleavage occurs in pyrolysis of **1**, to give trityl and propionyloxy radicals.

Pertinent to this discussion are the results of Rembaum and Szwarc who investigated the degradation of propionyl peroxide in the gas phase near 245°.[18] In spite of the low, comparable O–O bond dissociation energy (*ca.* 30 kcal./mole) and the similar over-all rate of decomposition of acetyl peroxide and propionyl peroxide, it was suggested that the efficiency at which the corresponding acyloxy radicals decay must differ markedly. Loss of carbon dioxide from the propyl derivative and formation of butane was rationalized on the supposition that ethyl radicals were created; this was supported further by the detection of ethane and ethylene.[19] These same three hydrocarbons were isolated from the decomposition of **1** in addition to styrene and ethylbenzene. The data suggest that propionyloxy radicals from **1** decay by a route similar to that shown in the decomposition of propionyl peroxide. Formation of the latter two compounds may well be dependent upon the presence of phenyl radical whose evolution from collapse of triphenylmethoxy radical is well documented.[16] A general scheme for the pyrolysis under nitrogen is provided.

Propionic acid is formed early in the decomposition as it could be isolated from a static pyrolysis after one hour at 250°. The acid is reported to be stable to 460° and decomposes near 600°.[20] Stability of the alkyl radical, which results from loss of carbon dioxide, may

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(12) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

(13) E. Warrich and P. Fugassi, *J. Phys. Colloid Chem.*, **52**, 1314 (1948).

(14) J. F. Norris and A. Cresswell, *J. Am. Chem. Soc.*, **56**, 423 (1934).

(15) The low bond dissociation energy of trityl compounds has been determined in a few cases: see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chap. 18; C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; M. Szwarc, *Proc. Soc.* (London), **A207**, 5 (1951); and W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, New York, N. Y., 1946.

Attempts were made to assemble a molecular model of **1** from Courtauld models. The system could only be made when the normal 0.5-Å. brass link was extended to 0.6 Å. The van der Waals envelope of each atom causes molecular crowding between the trityl group and the oxygen atoms of the carboxyl function with the normal brass links. It is implied that perhaps the O–C bond may be stretched somewhat. For example, this is the apparent situation in $(C_6H_5)_3CBr$ where the C–Br distance is 1.99 Å. as compared to C–Br value of 1.91 ± 0.06 in CH_3Br; see L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," S.P. 11, The Chemical Society, London, England, 1958.

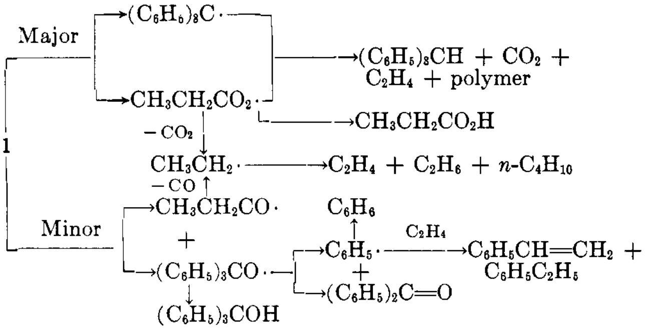
(16) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959); on p. 274 the simultaneous formation of phenyl radical is discussed in regard to the decomposition of triphenylmethoxy radicals.

(17) M. Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900); see also ref. 16.

(18) A. Rembaum and M. Szwarc, *J. Chem. Phys.*, **23**, 909 (1955); for a general review of this type of decomposition, see J. O. Edwards, Ed., "Peroxide Reaction Mechanisms," Interscience Publishers, Inc., New York, N. Y., 1962.

(19) For a recent review on the degradation of ethyl radicals, see M. Matsuoka, P. S. Dixon, A. P. Stefani, and M. Szwarc, *Proc. Chem. Soc.*, 304 (1962).

(20) C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, N. Y., 1929, Chap. 13.



SCHEME I

well govern the process. As will be seen later trityl pivalate undergoes thermal collapse rather specifically at 420° and pivalic acid is not isolated. For comparison, phenyl propionate is only slightly decomposed at 500° at short contact time but suffers complete degradation at 650°. Styrene, carbon dioxide, ethylene, ethane, phenol, and several other volatile products were recorded.[21] Although phenyl acrylate was suggested as the precursor of styrene,[20] the ester is known to yield acetylene, carbon monoxide, and phenol in a sealed tube at 320°.[22] However, the pyrolysate of phenyl propionate did contain some methyl ketene,[21] a product also possible from **1** if acyl–oxygen fission occurred and an α-hydrogen atom was removed. Tritanol was isolated from the reaction mixture, but a ketone or a ketene dimer was not detected in the evolved gases by infrared or gas chromatographic analysis with a hydrogen flame detection unit. Lifetime of the propionoyl radical is probably short and disintegration to carbon monoxide and ethyl radical would be predicted although trace quantities of ketenes may have been undetected.

$$CH_3CH_2CO\cdot + R\cdot \longrightarrow CH_3CH{=}C{=}O + RH$$

Styrene and ethylbenzene most likely arise from disproportionation of two β-phenethyl radicals[23] which could conceivably result from attack of phenyl radicals on ethylene. Direct coupling of phenyl radicals with ethyl radicals is also possible since ethane and ethylene are gaseous products. Szwarc and co-workers have noted also that ethyl radicals produced from propionyl peroxide can add to aromatic systems to form an unknown hydrogen donor.[24] Ethylbenzene may be formed *via* this route. Careful analysis of the amount of benzene recovered in the residue and traps from pyrolysis of **1** revealed the quantity was always less than the total benzophenone obtained. Thus it is attractive to consider that the origin of phenyl radical occurs primarily from collapse of triphenylmethoxy radical. Consequently, the yield of ethylbenzene and styrene should never exceed the benzophenone isolated as is actually observed.

Infrared analysis of the glassy, polymeric material (melting range 70–90°) isolated from the residue of **1** contains peaks for the hydroxyl group (3448 cm.$^{-1}$), a carbonyl group (1715 cm.$^{-1}$ broad), and monosubstituted benzene (701 cm.$^{-1}$). Attempted methanolysis of the polymer in pure methanol did not result in the formation of a trityl methyl ether which would be expected if a trityl ester was present.[25] Solution of the polymer occurred slowly in cold, aqueous sodium hydroxide and suggested a carboxyl function. Esterification of the acidic group was accomplished in ethanol with concentrated hydrochloric acid as catalyst. The new polyester exhibited bands for a carbonyl group (1730 cm.$^{-1}$) and monosubstituted benzene (699 cm.$^{-1}$), but the hydroxyl band had vanished. In view of the infrared absorption for a monosubstituted phenyl group in the polymer and the fact that styrene is a component of the pyrolysate, the obvious assumption is for a copolymer structure. The infrared spectrum and physical appearance of the polymer and polyester also suggest an acrylate repeating unit.[26] Support of the postulated copolymer structure was afforded by comparison of its infrared spectrum with that of a copolymer prepared from ethyl methacrylate and styrene. Except for a few peaks of low intensity the spectra were nearly superimposable. Acrylic acid and styrene polymerize readily with radical catalysts[27] and by thermal initiation.[28]

The unsaturation necessary in the pyrolysate to provide the stoichiometry for hydrogen balance in the formation of tritan and propionic acid is partially accounted for by the monomers required in the copolymerization. Assuming styrene was formed by disproportionation of β-phenyl radicals with another radical, one-half mole of hydrogen would be produced per mole of styrene. Likewise, assuming propionic acid furnished one mole of hydrogen when converted to acrylic acid, a total of 0.025 mole of hydrogen made available can be calculated from data in Table I. Certainly, if the ratio of acrylic acid to styrene was greater than one in the copolymer, the value for total moles of hydrogen available would be increased. From weights of tritan and propionic acid in Table I, a total of 0.037 mole of hydrogen is calculable as needed to convert trityl radicals and propionyloxy radicals to the hydrocarbon and acid, respectively. The approximately 30% hydrogen deficiency cannot be due entirely in the residual styrene, and we estimate it may be found in the 5–10% (by weight) of trace materials unidentified.

Trityl hydrocinnamate (**2**) should possess active benzylic hydrogen and, consequently, styrene, carbon dioxide, and tritan might be anticipated as major products. Unfortunately, the pyrolysis residue is much more complex as indicated in the scheme with many parallelisms to the decomposition of trityl propionate (**1**).

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(21) C. D. Hurd, P. Perletz, and S. S. Drake, *J. Org. Chem.*, **10**, 62 (1945).

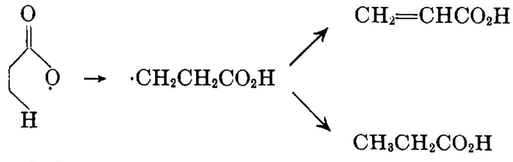
(22) See ref. 20, p. 532.

(23) W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, New York, N. Y., 1946, p. 212.

(24) J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 3322 (1956).

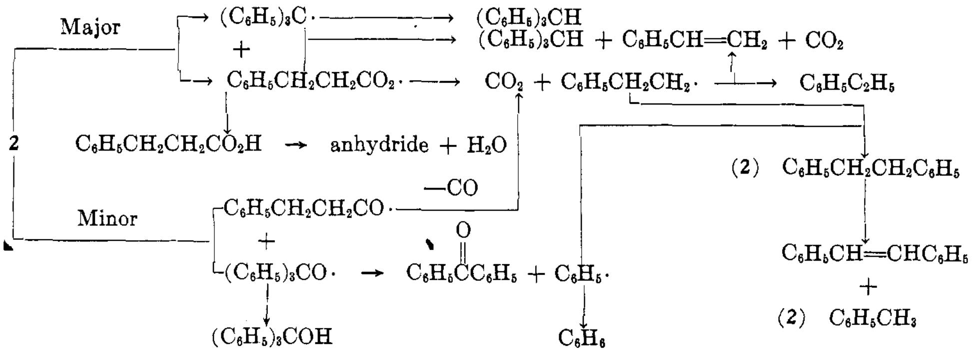
(25) See ref. 2 for a discussion of this reaction.

(26) A referee has suggested that the radicals produced in the initial homolytic bond cleavage process may never be free with special emphasis on the probable instability of the acyloxy radicals at the pyrolysis temperature. An intramolecular hydrogen transfer in the acyloxy radical *via* a five-membered cyclic transition state has been recorded; see W. Pritzkau and K. Dietzsch, *Ber.*, **93**, 1733 (1960). Disproportionation of the alkyl radical could lead to propionic acid and acrylic acid in the case of ester **1**. To be sure the alkylcarboxylate radical could be attacked by trityl radical to give acrylic acid also. In any event the intramolecular hydrogen shift is reasonable and would reduce the acyloxy radical population, but not exclusively. For a summary of transfer reactions in radical processes, see T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, **27**, 3067 (1962).



(27) F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

(28) C. Walling, "Free Radicals In Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 180.



SCHEME 2

TABLE I

PYROLYSIS OF TRITYL PROPIONATE IN A STATIC SYSTEM

(Temperature, 300–310°; time, 6 hr.)

Products	Wt., g.	Moles product/ mole ester
Carbon dioxide	0.3343	0.12
Carbon monoxide	.2053	
n-Butane		
Benzene	.047	.01
Water	.021	.01
Ethylbenzene	.103	.01
Styrene	.010	.001
Propionic acid	2.120	.60
Tritan	10.952	.77
Benzophenone	1.408	.13
Tritanol	0.299	.001
Copolymer	2.886	.27
Trace materials (mixture)	0.316	
Total weight of products	18.8016	
Initial weight of ester 1	18.960	

TABLE II

PYROLYSIS OF TRITYL HYDROCINNAMATE IN A STATIC SYSTEM

(Temperature, 290–310°; time, 6 hr.)

Products	Wt., g.	Moles product/ mole ester
Carbon dioxide	0.413	0.22
Carbon monoxide plus other volatiles	0.423	
Benzene	.053	.017
Toluene	.069	.018
Ethyl benzene	.021	.004
Styrene	.579	.13
Water	Trace	
Diphenylmethane	0.278	.04
1,2-Diphenylethane	.072	.009
trans-Stilbene	.830	.039
Hydrocinnamic acid Hydrocinnamic anhydride	2.874	
Tritan	8.340	.807
Benzophenone	1.036	.147
Traces of unknowns plus tritanol	0.090	
Total weight of products	15.078	
Initial weight of ester 2	15.680	

As in the propyl analog 1, components from the minor route probably decay in part to products which also arise from the major alkyl–oxygen cleavage process. Table II contains a summary of the quantities of components found in the pyrolysis of 2. Several compounds must serve as sources of hydrogen for the trityl radical since with the two main products, tritan and hydrocinnamic acid; the yield of acid did not exceed 50% although tritan was isolated in yield of 85–90%. Styrene could result from disproportionation of β-phenethyl radicals as described previously. In addition toluene and/or ethylbenzene are reported to yield small quantities of the olefin at high temperature.[29] Hydrocinnamic anhydride was found in the residue from 2, which is in agreement with the recorded preparation of the anhydride from the acid.[30] Confirmation of this dehydration process to form the anhydride was achieved in this laboratory. Hydrocinnamic acid is relatively stable being only slightly decomposed at 370° in a sealed tube.[31a]

trans-Stilbene, 1,2-diphenylethane, and toluene make appearances in the pyrolysate of 2, all of which probably originate from the acid portion of the ester.[31b] Related to this situation is the moderate yield of benzophenone found. The significance of this is that an equal amount of phenyl radical must have formed simultaneously. It was observed that in all runs the total yield of stilbene and toluene never exceeded the total return of benzophenone. The inference is that 1,2-diphenylethane may be created primarily *via* a coupling of β-phenethyl and phenyl radicals.

In view of the reported tendency of trityl peroxide to decompose in xylene,[16] an attempt was made to effect a decomposition of 2 in boiling *p*-xylene with ultraviolet light. A stream of dry oxygen was passed through a 50% solution of the ester which was irradiated with a 100-watt Hanovia lamp for seventy-two hours. As anticipated, hydrocinnamic acid and benzophenone were major constituents of the decomposition with more than 50% recovery of starting material.[32] The similarity of these results to those obtained from the oxidation of the melt of 1 is consistent with a radical mechanism for the decompositions.

Surprisingly, the exhaustive analyses of pyrolysates from 1 and 2 by gas chromatography did not divulge the presence of 1,1,1-triphenylpropane or 1,1,1,4-tetraphenylpropane, respectively. Two factors which must be considered as influential are the rate of hydrogen abstraction by the trityl group[33] and the availability of the alkyl radicals. Diffusion of radicals formed initially seems probable in view of the high yields of tritan and

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(29) See ref. 20, pp. 103–104.

(30) D. Davidson and P. Newman, *J. Am. Chem. Soc.*, **74**, 1515 (1952).

(31) (a) See ref. 20, p. 336; (b) see ref. 22, p. 98.

(32) Further results of the photolysis experiments will be reported at a later date.

(33) Rapid abstraction of hydrogen by trityl radical has been recorded on several occasions; see ref. 25, p. 52, and F. Benington, "Third Symposium on Combustion, Flame and Explosion Phenomena," Williams and Wilkens Co., Baltimore, Md., 1949, p. 448; also, D. Y. Curtin and T. C. Miller, *J. Org. Chem.*, **25**, 885 (1960).

respective acid in each case. Although trityl radical is known to add to aromatic systems,[34] no tetraphenylmethane was observed in pyrolysates of **1** and **2** is spite of the presence of benzene. All trace materials unidentified in each pyrolysate were extremely volatile and, therefore, probably of low molecular weight. Apparently the rate of hydrogen abstraction is great at pyrolysis temperatures. Moreover, loss of carbon monoxide and carbon dioxide is small which suggests a low population of alkyl radicals. Such an observation has been made recently with trityl benzoate in which presumably only aromatic hydrogen is available to trityl radical.[9] Considerable tritan was extracted from the pyrolysis residue.

Trityl pivalate as observed in Table III decomposed in a clean manner to give tritan, carbon dioxide, and isobutylene in high yields. Remarkably little decomposition occurred below 300° in a static system after three hours.[35] However, a smooth pyrolysis resulted at 430° in a rapid flow system (see Experimental). Since pivalic acid is known to be stable at 450°,[12] it probably does not form in the pyrolysis of **3**. The marked affinity of trityl radical to abstract hydrogen prompts an immediate postulation that the decomposition involves attack of this radical on pivaloyloxy radical. A particularly attractive feature of this theory is that it allows for a reasonable explanation for the high yields of all three products. Some charring does occur in the pyrolysis chamber, and the yields of products were influenced by the degree of charring. Courtauld molecular models imply a close proximity of the trityl moiety to a hydrogen atom on a methyl group. In view of the ease of formation of trityl radical in esters **1** and **2**, a completely concerted mechanism is unattractive. Whether or not carbon dioxide is lost with simultaneous abstraction of hydrogen to yield isobutylene cannot be stated definitively. It should be pointed out, however, that the *t*-butyl radical, if formed, could be expected to abstract hydrogen as has been shown in the photolysis of trimethylacetaldehyde.[36]

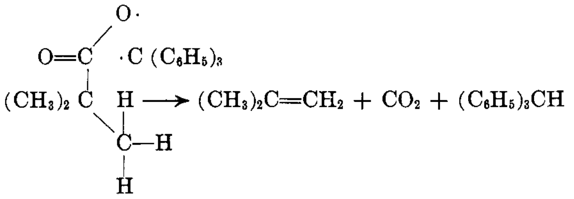

TABLE III

PYROLYSIS OF TRITYL PIVALATE IN A RAPID FLOW SYSTEM

(Temperature, 430 ± 10°.)

Products	Wt., g.	Moles product/ mole ester
Tritan	12.484	0.921
	2.6656	.858
Isobutylene	1.9639	.804
Carbon dioxide		
Tritanol	0.9114	.056
Benzophenone and biphenyl	Trace	
Initial weight of ester **3**	19.1165	

No isobutane was found in the gaseous products of **3**. Tritanol and benzophenone in the pyrolysate testify to a minor acyl-oxygen fission process.

Experimental[37]

Trityl Esters.—The esters were prepared as described previously.[2] Some improvements in yields were noted when anhydrous carbon tetrachloride was used as a solvent.

Pyrolysis of Trityl Propionate (1) and Trityl Hydrocinnamate (2) in a Static System.—The pyrolyses were conducted in a Pyrex system in a nitrogen atmosphere. All volatile components were swept into Dry Ice–acetone traps except for components gaseous at room temperature which were collected over salt water or in liquid nitrogen traps. Liquid components were analyzed directly on the hydrogen flame gas chromatographic unit. Gases were analyzed by gas chromatography and infrared spectrometry. Solution of the individual residues was essentially complete in ether–benzene. Extraction of the acid (and anhydride in **2**) was accomplished with a known quantity of standard aqueous base. Titration of the excess base and salt with standard hydrochloric acid afforded standard titration curves for propionic and hydrocinnamic acids, respectively. This was checked with the known acids in this laboratory. In the pyrolysate of **1** the copolymer also dissolved in aqueous base, but was precipitated by the addition of acid.

Analysis of the extracted residue was completed by gas chromatography. Columns which proved superior were 10% SE-30 on Chromosorb W, 20% Apiezon L on Chromosorb W, and Lac-32-728 on Chromosorb W. Gaseous products could be analyzed reasonably well with a 10% di-*n*-butyl phthalate on Fluoropak 90. Pure samples of all components were injected to verify all retention times under a particular set of conditions with a column. The weights given in Table I and II for products obtained from **1** and **2** were typical of more than a dozen runs in each case. Some fluctuation of individual yields of products was noted over the range 225–330° but no other compounds were detected by the methods employed. Carbon dioxide was absorbed in an Ascarite trap and weighed. Carbon monoxide was detected by means of infrared analysis as mentioned and by reaction with palladium chloride.[38] Chromatography of the residues was most convenient on alumina with a cyclohexane–benzene–petroleum ether system.

Interestingly, the liquid β-form of benzophenone was obtained directly from the pyrolysates of **1** and **2** rather than the more common α-modification which melts at 48°.[39] Since the α-form can be distilled at 190° (15 mm.),[40] it is possible that the β-form is produced specifically although the temperature differential may be significant here.[39] Cristol and Leffler have noted the decomposition of trityl nitrate in a sealed tube at 110° gave the α-form of benzophenone from the collapse of triphenylmethoxy radicals.[41]

Pyrolysis of Trityl Pivalate (3).—Since little decomposition of **3** occurred below 300° in 3 hr. in a static system, a rapid flow apparatus was utilized. It consisted of a Vycor tube mounted vertically in heavy-duty hinged, electric, combustion tube furnace; i.d., 2.375 in.; length, 12 in. An addition funnel with gas inlet tube was placed on top of the combustion tube which was packed with Pyrex helices; o.d., 0.094 in. Ice, Dry Ice–acetone traps, an Ascarite absorber, and a liquid nitrogen trap were used to capture all products. A calibrated pyrometer controller[42] maintained the pyrolysis temperature of 430 ± 10° during the runs. A 10% solution of the ester in benzene was added dropwise (*ca.* 1.5 ml. per minute) over a 5-hr. period to a helium-purged system.

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[34] R. A. Benkeser and W. Schroeder, *J. Am. Chem. Soc.*, **80**, 3314 (1958).

[35] Traces of pivalic acid and tritan were isolated but infrared analysis of the residue indicated nearly pure starting material **3**.

[36] J. B. Conant, C. N. Webb, and W. C. Mendum, *J. Am. Chem. Soc.*, **51**, 1246 (1929).

[37] All melting points are corrected. All boiling points are uncorrected. All infrared spectra were recorded on a Beckman IR-5 and/or IR-7 instrument. All gas chromatographic analyses were performed with a Wilkens Model A-550 Hy Fi hydrogen flame unit and a Wilkens Model A-350 with a dual column system and linear temperature programmer.

[38] V. J. Altieri, "Gas Analysis," American Gas Association, Inc., New York, N. Y., 1945, p. 257.

[39] Isomerization of the α-form to the β-form was observed on a silicone column at 210° in a gas chromatograph. When heated at 220°, the α-form is converted to the β-compound (80%); see K. Schaum, K. Schaeling, and F. Klausing, *Ann.*, **441**, 161 (1916).

[40] C. S. Marvel and W. M. Sperry, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 95.

[41] S. J. Cristol and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 4468 (1954).

[42] Model 478 is available from the Bristol Co., Waterbury 20, Conn.

Tritan, tritanol, benzophenone, and biphenyl were caught in the ice trap, but isobutylene was found in all containers including the liquid nitrogen trap. After rinsing the column with dry benzene, the solution of pyrolysate in the ice trap was made up to a total volume of 500 ml. The solid products caught in the ice trap were chromatographed on alumina as described previously, and were analyzed by gas chromatography with columns cited earlier. The remaining cold traps were warmed and purged with helium through a gas scrubber to dissolve residual isobutylene in benzene. All solutions were combined and made up to a volume of 500 ml. with benzene. Isobutylene proved more difficult to determine, but with meticulous effort a modification of the Fritz and Hammond method[43] was developed which gave reproducible results. Bromine was generated in an evacuated system by introducing 5 ml. of 6 N sulfuric acid into the bromination flask containing a known quantity of standardized potassium bromate solution (*ca.* 15% excess). After 3 min. a sample (20-ml. aliquot) from the ice trap solution was introduced into the dark bromination flask. Enough benzene was added to bring the volume to 40 ml. and an additional 20 ml. of acetic acid was introduced. The mixture was stirred and shaken vigorously for 9 min. and 15 ml. of 20% potassium iodide solution was added. After another minute, vacuum was alleviated in the system, and the excess free iodine was titrated at once with standard sodium thiosulfate solution to a starch end point. Triplicate runs were performed on aliquots from both the ice traps and the combined contents of the other cold traps. In several determinations an average yield of 86% was obtained for isobutylene. Duplicate blanks were also run in benzene to check the fading end point and to establish the small correction factor for the end point observed in titration of the aliquot from the ice trap solution. Moreover, to ascertain the reliability of the method a sample of 1-heptene (98% pure by gas chromatography) served as a test substrate. An average recovery of 97% was realized. To complete the determination, a sample of the pyrolysate was treated with bromine and 1,2-dibromo-2-methylpropane was actually isolated from the mixture. Comparison of the dihalide with the bromination product from pure isobutylene showed them to be identical.

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[43] J. L. Fritz and G. S. Hammond, "Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 275.

Polarographic Reduction of Some Alkyl-, Alkylene-, and Polymethylnaphthalenes[1]

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Polarography was conducted on naphthalene and twenty-seven substituted naphthalenes (bearing monoalkyl, dimethyl, trimethyl, allyl, and alkylene substituents) in 0.1 M tetra-*n*-butylammonium iodide in 75% dioxane–water. Using naphthalene as a standard of comparison the change in the half-wave reduction potential, $-\Delta E_{1/2}$, for the single wave obtained for each of the derivatives is positive, consistent with a decrease in ease of electroreduction due to the substituent(s). For the monoalkyl derivatives plots of $-\Delta E_{1/2}$ *vs.* σ^*, the polar substituent constant, for the 1- and for the 2-series are linear. There is no indication of a steric effect due to the bulkiness of the alkyl group. For dimethylnaphthalenes approximate additivity in $-\Delta E_{1/2}$ exists, except for the cases of the 1,8- and 2,3-isomers, where an enhancement potential must be included in order to retain additivity. For trimethylnaphthalenes, acenaphthene, and hexahydropyrene, $-\Delta E_{1/2}$ is an additive function of the effects of the individual substituents and the over-all geometric pattern of substitution.

In a previous paper[3] data were reported on the polarographic reduction of some alkyl- and polymethylanthracenes in 0.1 M tetra-*n*-butylammonium iodide in 75% dioxane–25% water as solvent–electrolyte. The present paper concerns an extension of this study to polarographic reduction of alkyl-, allyl-, alkylene-, and polymethylnaphthalenes.

Used in these studies were the parent naphthalene itself, as well as nine monoalkyl, the two allyl, all of the ten possible dimethyl, four trimethyl, and two alkylene derivatives. Six of these compounds were synthesized by new or modified procedures. Thus, the allylnaphthalenes were obtained by coupling the naphthylmagnesium bromides with allyl bromide (62% crude yield for 1-isomer). Catalytic hydrogenation of the allyl substituents occurred readily using glacial acetic acid and platinum to form the *n*-propylnaphthalenes. 1-*t*-Butylnaphthalene resulted in 13% yield from dehydration (with alumina at 380°) and subsequent dehydrogenation of the carbinol obtained by interaction of α-tetralone and *t*-butylmagnesium bromide. Chloromethylation of 1,8-dimethylnaphthalene produced 1-chloromethyl-4,5-dimethylnaphthalene, hydrogenolyzable to 1,4,5-trimethylnaphthalene in good yield.

Polarography was conducted in the same manner as employed for the anthracenes. Polarograms, obtained for three different concentrations of each hydrocarbon, showed the presence of only one wave out to a cathode potential of *ca.* −2.8 v. (*vs.* the saturated calomel electrode), where the solvent–electrolyte undergoes reduction. In contrast to the regular waves found for the anthracenes the upper portions of the sigmoid-shaped waves for the naphthalenes increased linearly with increasing E, the applied cathode potential, instead of levelling off or paralleling the slightly rising line for the residual current. Onset of electrolysis of the solvent–electrolyte prevented checking this upper linear portion over a sufficiently extensive range in E so as to allow determination of the true asymptotic diffusion current, i_d. Under these circumstances an approximate diffusion current, i_d' (where $i_d' < i_d$), was measured (*cf.* Experimental) and used in calculations. Polarographic diffusion current constants, I_d', average values (reproducible to ±3 mv.) of $-E_{1/2}$, and values of $-\Delta E_{1/2}$ (the difference between $-E_{1/2}$ for a substituted naphthalene and that for naphthalene itself as a standard of comparison) are presented in Table I. On the basis of the fact that values of I_d' do not vary markedly from one compound to another it is presumed that all of the waves correspond to the uptake of two electrons (as found by coulometry for naphthalene)[4] to produce 1,4-dihydronaphthalenes, compounds which should not be

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[2] Research Associate, 1959–1962.

[3] L. H. Klemm, A. J. Kohlik, and K. B. Desai, *J. Org. Chem.*, **28**, 625 (1963).

[4] L. H. Klemm, C. D. Lind, and J. T. Spence, *ibid.*, **25**, 611 (1960).