methanol were added to a solution of 19 g. of the aldehyde III in 150 ml. of anhydrous acetone. The temperature rose to 0°. When the temperature had fallen again to $-10°$, the balance of the sodium methoxide solution was added and the stirring continued for 30 min. at $-10°$ and for 1 hr. at 25°. The mixture was neutralized with dilute sulfuric acid, diluted with water, and extracted with benzene to yield 17 g. (74%), b.p. 175–177° (1 mm.); $\lambda_{\max}^{\mathrm{EtOH}}$ 292 mμ (log ε 3.40); $\bar{\nu}_{\max}^{\mathrm{liq.}}$ 1675 cm.$^{-1}$ (carbonyl).

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.9; H, 8.0. Found: C, 84.3; H, 8.2.

The 2,4-dinitrophenylhydrazone precipitated as an oil which crystallized on trituration with butyl alcohol. From the same solvent or from ethanol, orange-red crystals, m.p. 112–114°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 385 mμ (log ε 4.45).

1-Butadienyl-2-phenylcyclohex-4-ene (XVI). The ketone IX (14 g.) was reduced in the usual manner with 14 g. of aluminum isopropoxide and 100 ml. of isopropyl alcohol. The product, which boiled at 150–153° (2 mm.) (yield, 8 g., 57%) showed in the infrared no residual carbonyl absorption and the hydroxyl band at 3400 cm.$^{-1}$ It was heated with 1.5 g. of freshly fused potassium hydrogen sulfate at 140° *in vacuo.* The desired diene distilled at 130–132° (3 mm.); yield, 4.2 g. (52%). $\lambda_{\max}^{\mathrm{EtOH}}$ 230 mμ (log ε 4.06); 292 mμ (log ε 2.72). $\bar{\nu}_{\max}^{\mathrm{liq}}$ (cm.$^{-1}$) 1600; 1650 (substituted butadiene);[19] 660 (terminal=CH_2).[20]

Anal. Calcd. for $C_{16}H_{18}$: C, 91.4; H, 8.6. Found: C, 91.4; H, 8.4.

JERUSALEM, ISRAEL

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(19) W. Bruegel, *Einfuehrung in die Ultrarotspektroskopie* Steinkopff, Darmstadt, 1954, p. 272.

(20) R. S. Rasmussen, R. R. Brattain, and P. S. Zucco, *J. Chem. Phys.*, **15**, 135 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Attempts to Prepare Pyracylene. 1,2-Dihydropyracylene[1,2]

ARTHUR G. ANDERSON, JR., AND ROBERT G. ANDERSON

Received August 5, 1957

The preparation of pyracene derivatives having eliminable functional groups on the five-membered rings and the attempted conversion of these to pyracylene is described. 1,2-Dihydropyracylene has been prepared by reaction of pyracene with chloranil or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Since the initiation of the work on the synthesis of pyracene[3] one of the objectives has been to obtain the conjugate-unsaturated nonalternant hydrocarbon pyracylene (I).[4] Our interest in this compound arose from two considerations. First, it would have a total of 14 π-electrons associated with a cyclocondensed ring structure in which 12 of the electrons could be viewed as being in the planar perimeter and 2 in the ethylene core of the molecule.[5] The molecule would thus be an important addition to the type exemplified by pleiadiene (II) and acepleiadylene (III)[6] and provide a further test for the various theories of electronic structure of complex molecules.[7] Further, Brown[8] has calculated the resonance energy of pyracylene to be about 88 kcal./mole as compared to values of 61 and 36 for naphthalene and benzene obtained by the same method. The value for pyracylene is probably incorrect because of the neglect of strain considerations in the calculations (herewith).

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(1) From the Ph.D. thesis of Robert G. Anderson.

(2) Support for a part of this work by contract DA-04-200-ORD-235 with the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

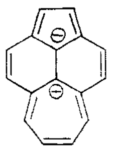
(3) A. G. Anderson, Jr. and R. H. Wade, *J. Am. Chem. Soc.*, **74**, 2274 (1952).

(4) The only report indicating the existence of pyracylene is that of S. H. Hastings, B. H. Johnson, and H. E. Lumpkin, *Anal. Chem.* **28**, 1243 (1956), who found that mass spectral data on a minor component of the aromatic fraction of virgin gas oil fit the molecular formula. Dibenzo[*a,g*]pyracylene and several of its derivatives are known; *cf.* E. Clar, *Ber.* **64**, 2199 (1931); B. P. Federov, *Bull. Acad. Sci., U. S. S. R. Classe Sci. Chem.*, 397 (1947); C. Dufraisse and R. Girard, *Bull. soc. chim., France* (5) **1**, 1359 (1934); C. Dufraisse, (5) **3**, 1857 (1936); C. Dufraisse and R. Horelois, (5) **3**, 1894 (1936); H. W. D. Stubbs and S. H. Tucker, *J. Chem. Soc.*, 2936 (1951).

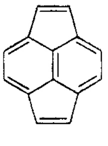
(5) J. R. Platt, *J. Chem. Phys.*, **22**, 1448 (1954); W. T. Simpson, *J. Chem. Phys.*, **17**, 1218 (1949).

(6) V. Boekelheide, W. E. Langeland, and C.-T. Liu, *J. Am. Chem. Soc.*, **73**, 2432 (1951); V. Boekelheide and G. K. Vick, *J. Am. Chem. Soc.*, **78**, 653 (1956).

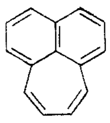
(7) For a theoretical interpretation of the pleiadienes see J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 1261, 4217 (1956). Profs. H. J. Dauben and W. T. Simpson have suggested (private communication) that an explanation based on the valence bond method which is consistent with the observed chemical and spectral properties and with the molecular orbital description may be advanced. This derives from a qualitative consideration of the reasonable valence bond structures with the inclusion of the dipolar sesquifulvalenoid structure shown. Since calculations [B. Pullman, A. Pullman, E. D. Bergman, H. Berthod, E. Fischer, Y. Hirschberg, D. Lavie, and May Mayot, *Bull soc. chim. France*, **73** (1952)] indicate that the resonance stabilization of sesquifulvalene would be almost the same as that of naphthalene, the sesquifulvalenoid and naphthalenoid structures would be expected to contribute almost equally to the hybrid (strain will be the same in both types of structure).



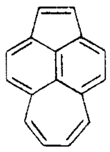
(8) R. D. Brown, *J. Chem. Soc.*, 2391 (1951). The molecular orbital method with overlap was used.



I



II



III

From the molecular orbital treatment[8,9] the π-electron densities, free valencies and mobile bond orders and, consequently, the most probable positions for electrophilic, nucleophilic and homolytic attack have been predicted.

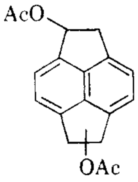
Second, the structure of pyracylene would classically be expected to have considerable strain[10] and a correlative study of its physical and chemical properties would be of importance in this respect. The existence of dibenz[*a,g*]pyracylene[4] shows that the strain is not prohibitive for a 1,2- and 5,6-bond distance of approximately 1.4 Å. Since these bonds are of the order of 1.64 Å as single bonds in pyracene,[11] perhaps pyracylene could exist with double bonds of about 1.4 Å. The enhancement of reactivity might, however, be much greater with the lengthening of double bonds and polymerization, for example, might occur very readily.

In the earlier work it was observed that liquid phase, catalytic (Pd-C) dehydrogenation of tetrahydropyracene at *ca.* 300° only gave pyracene.[3] Also, it has been observed by many workers that acenaphthylene polymerizes at temperatures above 200°. Accordingly, the usual catalytic reagents and conditions seemed unpromising and attention was directed to the introduction of unsaturation through elimination processes involving groups other than hydrogen. Any such scheme must involve the preparation of a pyracene (or hydropyracene) derivative having eliminable groups, preferably identical, in both *peri*-rings. Two approaches of this type were investigated.

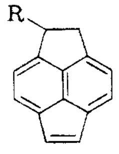
The conversion of acenaphthene to acynaphthylene by a bromination-debromination sequence and also by acetoxylation followed by pyrolytic elimination of acetic acid had been accomplished.[12] When pyracene was treated with either four moles or an excess of *N*-bromosuccinimide, however, a mixture of bromides was obtained from which the desired tetrabromide could not be separated. Reaction of the mixture with zinc in tetrahydrofuran yielded zinc bromide plus a yellow polymeric material and it was not possible to determine whether or not pyracylene had been formed as an intermediate.

A test with acenaphthene showed that acetoxylation with even a large excess of lead tetraacetate formed only the monoacetate. Thus the diacetoxypyracene obtained from the corresponding reaction with pyracene was most probably the 1,5- or 1,6-compound (IV) or a mixture of these. Either product would yield pyracylene on the elimination of two molecules of acetic acid.

The ultraviolet spectrum of the pyrolysate from the diacetoxypyracene was very similar to that of acenaphthylene. The substance in the pyrolysate polymerized on attempted isolation but the polymer showed a band at 5.75μ which corresponded to absorption by the diacetoxypyracene. These findings suggested that 1-acetoxy-1,2-dihydropyracylene (V) was the initial product.

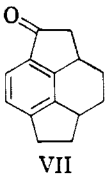


IV

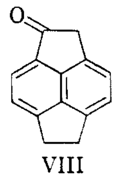


V, R = OAc
VI, R = H

It was felt that the properties of 1,2-dihydropyracylene (VI) would provide better evidence concerning the identity of the pyrolysate product as V. As 2a,3,4,4a-tetrahydro-1-pyracenone (VII), a possible intermediate for the preparation of VI, was at hand,[3,13] an attempt was made to carry out the conversion. Liquid phase dehydrogenation of VII with Pd-C catalyst or with a Rh-C catalyst plus benzene gave only polymeric material. Vapor phase dehydrogenation with a Pd-C catalyst gave low (≤4%) and erratic yields of pyracenone-1 (VIII).



VII



VIII

Although VIII was apparently reduced to the corresponding alcohol with lithium aluminum hydride, the poor yields of VIII forced abandonment of the sequence.

The report by Braude and coworkers[14] of the dehydrogenation of acenaphthene with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone led us to try this reagent and also chloranil with pyracene.

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[9] J. J. F. Alonso and J. Mira, *Anales real soc. españ. fís. y quím.*, **50B**, 146 (1954).

[10] The introduction of double bonds in the peri-rings of pyracene would be expected to result in shortening of the 1,2- and 5,6-bonds. Prof. H. J. Dauben (Abstracts of Papers, 130th Meeting of the American Chemical Society, New York, September, 1956, p. 37–0) has calculated the strain energy of pyracylene to be *ca.* 52 kcal./mole. If the resonance energy value of Brown (ref. 8) is considered to be the delocalization energy then correction of this for strain would give 36 kcal./mole as a perhaps more realistic value for the resonance energy.

[11] A. I. Kitaigardoski, *J. Phys. Chem.* (*U. S. S. R.*), **23**, 1036 (1949).

[12] A. G. Anderson, Jr. and R. G. Anderson, *J. Am. Chem. Soc.*, **77**, 6610 (1955).

[13] A. G. Anderson, Jr. and R. G. Anderson, *J. Org. Chem.*, **22**, 1197 (1957).

[14] E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954).

The reaction with chloranil gave a 51% yield of a yellow crystalline material which was stable in the cold under a nitrogen atmosphere but decomposed at room temperature. Microanalysis, quantitative (one mole) hydrogenation to pyracene, the close similarity of the ultraviolet spectrum to that of acenaphthylene, and the characteristic (double bond) absorption at 6.20μ in the infrared established this product as 1,2-dihydropyracylene (VI).

A comparison of the spectra of VI and of the pyrolysate showed that the latter was not the acetoxy derivative (V). Thus the pyrolysis of the diacetoxypyracene must give a dimer, trimer, or some such species which can polymerize further; or pyracylene may be the unstable intermediate. Attempts to prepare pyracylene by altering the ratio of pyracene to chloranil, by treating the 1,2-dihydropyracylene with chloranil separately, or by the use of the dichlorodicyanoquinone were unsuccessful. The latter reagent gave a 42% yield of VI.

Efforts to achieve 1,6-disubstituted pyracene derivatives *via* the cyclization of 1-keto-2a,3,4,5-tetrahydroacenaphtheneacetic acid,[13] its oxime, or the acetate ester of the corresponding alcohol were unsuccessful with a variety of reagents and conditions. The ketal of the keto acid could not be formed by either direct or exchange reaction methods. The oxime resisted catalytic reduction with Raney nickel and treatment with sodium and alcohol.

EXPERIMENTAL[15,16]

Bromination—debromination of pyracene. A mixture of pyracene (0.196 g., 0.001 mole), *N*-bromosuccinimide (0.775 g., 0.0044 mole), 45 ml. of anhydrous carbon tetrachloride and a few crystals of benzoyl chloride was heated under reflux for 25 min. The product (0.31 g.) isolated as described elsewhere[12] and recrystallized three times from benzene, melted at 130–135° (dec.) and analyzed (C, 38.02; H, 2.86) as a mixture of bromides. Reaction of the mixture with zinc (2 equivalents based on tetrabromide) in tetrahydrofuran gave only a yellow polymeric material which was not characterized.

The use of an excess of *N*-bromosuccinimide in the procedure gave similar results.

1,5(1,6)-Diacetoxypyracene (IV). To a warm (60°) solution of pyracene[3,13] (0.43 g., 0.0024 mole) in 42 ml. of glacial acetic acid was added 4.0 g. (0.0058 mole) of red lead in 1 g. portions with stirring. The orange color produced by the red lead was allowed to disappear before the next portion was added. The mixture was stirred and kept at 60° until it no longer oxidized starch iodide paper and then poured into water (85 ml.). The aqueous solution was extracted with ether and the combined extracts washed with water, saturated sodium chloride solution, and finally dried (sodium sulfate). Removal of the solvent left a gummy residue which crystallized from methanol to give 0.53 g. (75%) of crude product, m.p. 162–180°. Sublimation and two further recrystallizations left 0.18 g. (25%) of pure material, m.p. 190–192°.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.90; H, 5.45. Found: C, 72.60; H, 5.47.

Pyracenone-1 (VIII). 2a,3,4,4a-Tetrahydro-1-pyracenone[3,13] (0.47 g., 0.0023 mole) was sublimed in an oxygen-free nitrogen atmosphere through a column packed with a 5% Pd-C catalyst and maintained at 350–400° and a pressure of 20 mm.[17] over a period of 8 hr. The yellow solid in the receiver was washed out with acetone and when purified by crystallization from ethanol, sublimation, and recrystallization amounted to 0.018 g. (4%), m.p. 182–183°. The ultraviolet spectrum displayed maxima at 258mμ (log ϵ_{max} 1.75) and 346mμ (log ϵ_{max} 0.49).

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.48; H, 5.43.

1,2-Dihydropyracylene (VI). A solution of pyracene (0.210 g., 0.0012 mole) and chloranil (0.30 g., 0.0012 mole) in 10 ml. of xylene was refluxed under a nitrogen atmosphere for 24 hr. The brown reaction mixture was cooled to 0° and washed with 10% potassium hydroxide until the washings were colorless. The red organic layer was dried over magnesium sulfate and passed through a column (10 × 100 mm.) of activated, basic alumina. Removal of the solvent from the yellow effluent gave 0.108 g. (51%) of product, m.p. 145–150°. A portion recrystallized twice from hexane and sublimed at 80° and 0.3 mm. melted at 155–156°. The infrared spectrum showed a peak at 6.20μ. The ultraviolet absorption spectrum had maxima in mμ at 240 (log ε 4.28), 320 (log ε 4.00), 342 (log ε 3.78) and 357 (log ε 3.25). The substance was stable in the cold under nitrogen but decomposed at room temperature.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.13; H, 5.62.

The above procedure was also carried out with a 2:1 molar ratio of chloranil to pyracene and a 1:1 molar ratio of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The yields of VI were 45% and 42% respectively.

Treatment of VI with one molar equivalent of chloranil as above resulted in the recovery of the starting material (27%) as the only product which could be identified.

A solution of pure VI (0.053 g., 0.0003 mole) in ethanol took up 7.3 cc. (0.0003 mole) of hydrogen over a platinum catalyst at one atmosphere pressure and room temperature to give 0.052 g. (96%) of pyracene, m.p. 211–215°.[3]

1-Keto-2a,3,4,5-tetrahydro-5-acenaphtheneacetic acid oxime. A solution of the keto acid[13] (5.0 g., 0.022 mole) in 70 ml. of 10% potassium hydroxide was added to 30 ml. of an aqueous hydroxylamine hydrochloride solution and the mixture warmed on a steam bath for 30 min. Acidification of the cooled (0°) reaction mixture gave a precipitate which was washed with water and dried to yield 4.4 g. (82%) of tan product. A portion recrystallized several times from ethanol melted at 225–230°.

Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16. Found: C, 68.67; H, 6.06.

1-Hydroxy-2a,3,4,5-tetrahydro-5-acenaphtheneacetic acid. A solution of 1-keto-2a,3,4,5-tetrahydroacenaphtheneacetic acid (7.6 g., 0.033 mole) in 25 ml. of 10% potassium hydroxide and 100 ml. of methanol was added in 20-ml. portions with shaking over a period of 30 min. to a solution of sodium borohydride (5.8 g., 0.152 mole) in 150 ml. of methanol. After about 10 hr. the mixture was acidified slowly with 10% hydrochloric acid and most of the methanol removed with a stream of air while the solution was warmed on a steam bath. The precipitate which formed was collected and dried to give 7.6 g. (99%) of crude product. A portion recrystallized three times from ethanol melted at 215–220° and had a

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(15) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Ultraviolet spectra were taken on a Cary Model 11S Recording Spectrophotometer or (ε values) on a Beckmann Model DU Spectrophotometer in ethanol. Infrared spectra were obtained with a Perkin Elmer Recording Spectrophotometer with sodium chloride cells.

(16) Microanalyses were performed by B. Nist and C. H. Ludwig.

(17 A. G. Anderson, J. A. Nelson, and J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953); H. L. Pan, M. S. Thesis, Univ. of Wash., 1953.

neutral equivalent of 232 (calcd. N.E. 232). The ultraviolet spectrum displayed maxima in mμ at 267 (log ε 2.92) and 274 (log ε 2.90).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C 72.11; H, 7.12.

1-Acetoxy-2a,3,4,5-tetrahydroacenaphtheneacetic acid. To a solution of the above hydroxy acid (2 g., 0.0086 mole) in 20 ml. of anhydrous pyridine was added with shaking 8 ml. of acetic anhydride. The mixture was heated under reflux for 15 min., cooled, and poured into 100 ml. of ether. The resulting solution was washed with 10% hydrochloric acid, then water, and finally with saturated sodium chloride solution. The organic layer was dried (magnesium sulfate) and the solvent removed to give an orange solid which melted at 172–186° and amounted to 2.1 g. (79%) after crystallization from ethanol. A portion recrystallized twice more from ethanol melted at 179–188° and showed absorption maxima in mμ at 274 (log ε 2.96) and 267 (log ε 2.95).

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.01; H, 6.79.

SEATTLE 5, WASH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Aromatization of the Diels-Alder Adduct of Tetraphenylcyclopentadienone and Fumaronitrile[1]

ROBERT F. DOERING,[2] ROBERT S. MINER, JR.,[2] LEONARD ROTHMAN,[2]
AND ERNEST I. BECKER[3]

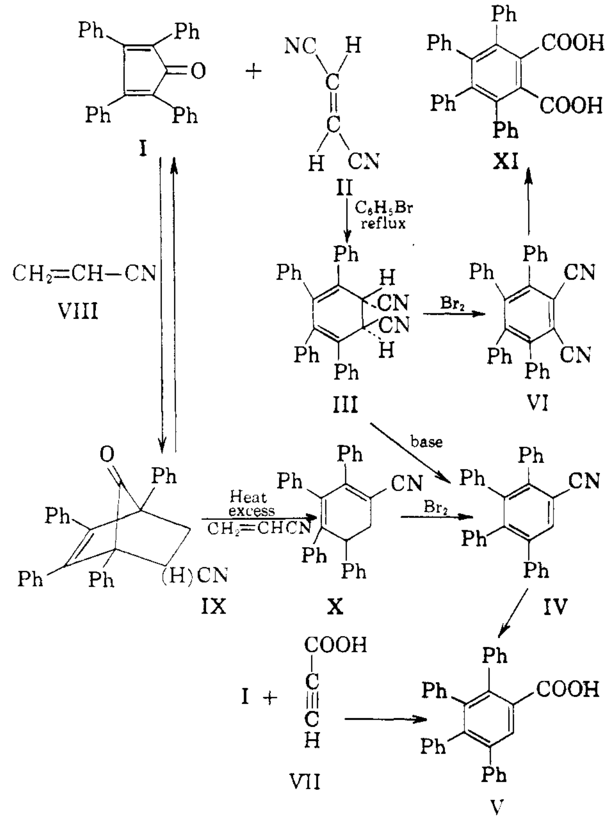
Received September 19, 1957

The reaction of tetraphenylcyclopentadienone (I) and fumaronitrile (II) in bromobenzene gave *trans*-1,2-dihydrotetraphenyl-*o*-phthalonitrile (III). Bromine converted III to tetraphenyl-*o*-phthalonitrile (VI). Alkali dehydrocyanates III to give 2,3,4,5-tetraphenylbenzonitrile (IV).

When tetracyclone (tetraphenylcyclopentadienone) (I) was refluxed with fumaronitrile (II) in bromobenzene, *trans*-1,2-dihydro-3,4,5,6-tetraphenyl-*o*-phthalonitrile (III) was formed. The trans configuration is assumed by analogy with other Diels-Alder reactions. Bromine aromatized III to tetraphenyl-*o*-phthalonitrile (VI). In turn VI was hydrolyzed to tetraphenylphthalic acid (XI), a known compound. Somewhat unexpected was the thermal behavior of III.

Heating III above its melting point gave a poor yield of a colorless compound whose analysis corresponded to that of 2,3,4,5-tetraphenylbenzonitrile (IV). Thus, the central ring of III had been aromatized by elimination of hydrogen cyanide, an infrequently observed reaction.[4] The same dehydrocyanation was effected by means of an alkaline alumina during an attempted chromatographic purification of III in 89% yield and by refluxing III in bromobenzene with diethylenetriamine in over 90% yield.

The structures of these compounds were proved by alternate syntheses. The synthesis of V via the reaction of I with propiolic acid went smoothly in 62% yield.[5] An attempt to prepare tetraphenylbenzoic acid (V) by hydrolysis of IV gave only a small quantity of V. The two acids agreed in their physical properties but the poor yield in the hydrolysis prompted a search for a more elegant proof for the structure of IV.



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[1] Presented in part at the Meeting-in-Miniature of the Metropolitan-Long Island Subsection of the American Chemical Society, February 20, 1953.

[2] Taken from the B.S. thesis of R.F.D. (1951), the M.S. thesis of R.S.M., Jr., (1953) and from a portion of the Ph.D. dissertation of L.R.

[3] To whom inquiries should be sent.

[4] For a recent reference see A. Treibs and R. Derra, *Ann.*, **589**, 176 (1954).

[5] It is interesting to note the difference in the behavior of phenylpropiolic acid with tetracyclone. Dilthey, *et al.*,[6,7] have pointed out that decarboxylation occurs when phenylpropiolic acid reacts with tetracyclone to give pentaphenyl-