the product is very much like that of *p*-nitrophenylazotris-(*p*-anisyl)-methane.[2]

Anal.[3] Calcd. for $C_{26}H_{24}N_4O_7$: C, 63.6; H, 4.58; N, 10.6. Found: C, 63.63; H, 4.71; N, 10.24.

Decomposition of 2,4-Dinitrophenylazotris-(*p*-anisyl)-methane in Benzene at 75°.—The decomposition was carried out in degassed ampoules. The major product, obtained by adding petroleum ether to the benzene solution, was the hydrazo compound, identified by melting point and visible spectrum. By removing solvent from an aliquot of the benzene solution of the decomposition products and dissolving the residue in a mixture of acetic and perchloric acids the amount of hydrazo compound can be estimated spectrophotometrically as tris-*p*-anisylcarbonium ion. The yield on this basis was close to one-half of the theoretical (50.6%). Chromatography of the mother liquor from the isolation of the hydrazo compound on alumina failed to isolate additional pure products, but one fraction gave a color with acetone and sodium hydroxide in methanol, the spectrum of which closely resembles that produced by the action of the same reagents on *m*-dinitrobenzene. The hydrazo compound does not give such a color test.

Acknowledgment.—This work formed part of a program sponsored by the Office of Naval Research, whose support is gratefully acknowledged.

[2] M. D. Cohen, J. E. Leffler and L. M. Barbato, This Journal, **76**, 4169 (1954)

[3] Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA

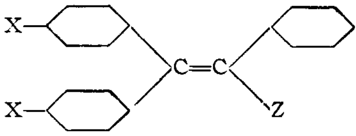
Triphenylethylene Derivatives. I

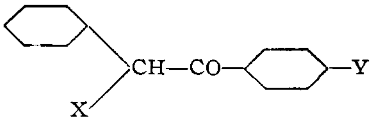
BY TOYOYUKI NAGANO

RECEIVED JULY 23, 1954

We have applied the Friedel–Crafts reaction to the preparation of estrogenic triphenylethylene derivatives with the thought that this method might be preferable to the Grignard synthesis.

4-Methoxydesoxybenzoin was converted to 4-methoxy-α′-chlorostilbene which reacted with anisole to give 1,1-dianisyl-2-phenylethylene (I), while α-chlorostilbene failed to react with benzene under these conditions. 4-Methoxydesyl bromide (II) condensed with benzene to give a mixture of 4-methoxy-α-phenyldesoxybenzoin (IV) and 4-hydroxy-α-phenyldesoxybenzoin (III), the extent of the demethylation depending on the conditions. When IV was heated with phosphorus pentachloride, 1,1-diphenyl-2-anisyl-2-chloroethylene (V) was formed. Attempts to condense II with anisole were unsuccessful.





	I	V		II	III	IV
X	OCH_3	H	X	Br	phenyl	phenyl
Y	H	OCH_3	Y	OCH_3	OH	OCH_3
Z	H	Cl				

Chloroacetyl chloride was treated with an excess of anisole in an attempt to prepared desoxyanisoin; the product, however, was *p*-methoxy-ω-chloroacetophenone and under more drastic conditions a dark resin was obtained.

Acknowledgment.—The author is indebted to Mr. Konomu Matsumura for his advice and encouragement.

Experimental

4-Methoxy-α′-chlorostilbene.—Phosphorus pentachloride (2.3 g., 0.011 mole) was added to a solution of 4-methoxydesoxybenzoin (2.3 g., 0.01 mole) in benzene (5 ml.) and the mixture allowed to stand for 15 hours at room temperature with occasional shaking. The resulting red solution was poured into ice-water and extracted with ether. On evaporation of the dried ether–benzene extract and washing of the residue with methanol (10 ml.), colorless crystals (1.8 g., 75%) were obtained, which were recrystallized from ethanol as colorless plates, m.p. 74–75°.

Anal. Calcd. for $C_{15}H_{13}OCl$: C, 73.62; H, 5.32; Cl, 14.52. Found: C, 73.56; H, 4.97; Cl, 14.18.

1,1-Dianisyl-2-phenylethylene (I).—Pulverized aluminum chloride (1.7 g., 0.013 mole) was added with shaking over a 15-minute period to a solution of 4-methoxy-α′-chlorostilbene (2.4 g., 0.01 mole) and anisole (1.3 g., 0.012 mole) in carbon disulfide (5 ml.). After standing for 4 hours at room temperature, the deep red solution was poured into crushed ice and extracted with ether (40 ml.). On evaporation of the dried extract, the residual oil yielded crystals which were treated with ethanol (10 ml.); yield 2.7 g. (85.4%), m.p. 63–64° with preliminary softening around 60°. For analytical purposes, a portion (0.1 g.) was recrystallized from ethanol (10 ml.) giving colorless prisms, m.p. 64–65°, reported[1] m.p. 62–64°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.58; H, 6.30.

A portion of the crude material (m.p. 63–64°) was brominated in carbon tetrachloride to give colorless prisms, m.p. 114–115°, reported[1] m.p. 114–115°.

4-Methoxydesyl Bromide.—This compound was obtained in 80% yield by brominating 4-methoxydesoxybenzoin with bromine in carbon tetrachloride. A poorer yield was obtained by bromination with phosphorus pentabromide in boiling benzene.

4-Hydroxy-α-phenyldesoxybenzoin (III).—Pulverized aluminum chloride (3 g., 0.022 mole) was added to a solution of 4-methoxydesyl bromide (3 g., 0.01 mole) in benzene (30 ml.) and the mixture gently refluxed for 3 hours. After standing overnight at room temperature, the reaction mixture was treated with ice and hydrochloric acid and extracted with benzene. After removal of the solvent, the residue was treated with sodium hydroxide solution (1%, 20 ml.). The alkali-insoluble portion (0.2 g.) was washed with ethanol and recrystallized to give IV, m.p. 128–130°. When the alkaline solution was acidified with hydrochloric acid, a light brown solid (2.6 g.) separated which crystallized from benzene as colorless plates, m.p. 181–182°. The ethanol solution of this material gave an orange color with ferric chloride.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.26; H, 5.59. Found: C, 83.32; H, 5.75.

The acetyl derivative separated as colorless prismatic needles from glacial acetic acid, m.p. 114–116°. The cold ethanol solution of the acetylated compound gave no color reaction with ferric chloride, but developed an orange color instantly on warming.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.97; H, 5.36.

4-Methoxy-α-phenyldesoxybenzoin (IV).—4-Methoxydesyl bromide (3 g.) and aluminum chloride (2 g., 0.015 mole) in benzene were heated at 70° for an hour. After standing for about 20 hours at room temperature, the solution was treated with ice and hydrochloric acid and extracted with ether (30 ml.). The ether–benzene layer was shaken with sodium hydroxide solution (1%, 20 ml.). When the alkaline layer was acidified, 0.9 g. of the 4-hydroxy compound III was obtained which after two recrystallizations from benzene melted at 181–182°. The residue obtained by evaporation of the ether–benzene solution was recrystallized twice from ethanol to give colorless needles; yield 1.7 g., m.p.

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[1] R. S. Shelton, This Journal, **75**, 5493 (1953).

128–130°, reported m.p. 130–131°[2] and 129–130°.[3]

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.37; H, 5.91.

1,1-Diphenyl-2-anisyl-2-chloroethylene (V).—4-Methoxy-α-phenyldesoxybenzoin (IV) (0.30 g.) and phosphorus pentachloride (0.25 g.) in benzene (1 ml.) were refluxed for 3 hours. The crude product (0.2 g.) was crystallized from ethanol as colorless prisms, m.p. 123–124°.

Anal. Calcd. for $C_{21}H_{17}OCl$: C, 78.62; H, 5.03; Cl, 11.05. Found: C, 78.42; H, 5.30; Cl, 11.22.

***p*-Methoxy-ω-chloroacetophenone.**—Anisole (0.4 g.), chloroacetyl chloride (0.1 g.) and aluminum chloride (0.4 g.) in carbon disulfide (5 ml.) were kept for 20 hours at room temperature. Colorless needles were isolated which gave a positive Beilstein test for chlorine; m.p. 102–104°, reported[4] m.p. for *p*-methoxy-ω-chloroacetophenone 102°. When the above chlorides and anisole were heated in nitrobenzene on a water-bath, a dark resin was obtained.

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(2) A. McKenzie and A. K. Mills, *Ber.*, **62**, 1792 (1929).

(3) R. Lagrave, *Ann. chim. phys.*, [10] **8**, 363 (1927).

(4) F. Kunckell and F. Johannssen, *Ber.*, **31**, 170 (1898).

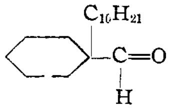
CHEMICAL LABORATORY
KITASATO INSTITUTE
TOKYO, JAPAN

Ketone Formation by the Decarboxylation of α-*n*-Decyl Substituted Glycidic Acids

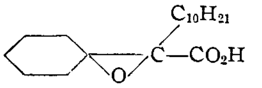
BY HORTON H. MORRIS AND CAROL JEAN ST. LAWRENCE[1]

RECEIVED AUGUST 30, 1954

A recent report[2] has shown that Darzens[3] was mistaken in stating that α-*n*-decylcyclohexanecarboxaldehyde (I) is produced by the decarboxylation

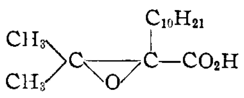


I

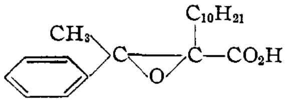


II

of α-*n*-decyl-α,β-epoxycyclohexylidene acetic acid (II). Since he also reported that the decarboxylation of α-*n*-decyl-β,β-dimethylglycidic acid (III)



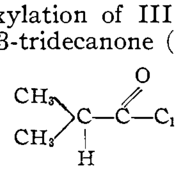
III



IV

and of α-*n*-decyl-β-methyl-β-phenylglycidic acid (IV) yielded aldehydes through a migration of the *n*-decyl radical, it seemed advisable to repeat the work.

The decarboxylation of III has been found to yield 2-methyl-3-tridecanone (V) as proved by alternate synthesis and the determination of mixed melting points of derivatives. As in the case of I, Darzens apparently was misled in his identification by traces of an easily oxidized contaminant in the decarboxylation product.



$(CH_3)_2CH-C(=O)-C_{10}H_{21}$

V

The melting point of the semicarbazone of V does not agree with the melting point of the semicarbazone of the product reported by Darzens and several variations of reaction conditions have been made in an attempt to duplicate the reported results. In every case only the ketone was formed upon decarboxylation of the glycidic acid. Since some glycidic esters have been reported[4,5] to rearrange to α-keto esters because of high distillation temperatures, and since the corresponding α-keto acid might be expected to yield I upon decarboxylation, a sample of ethyl α-*n*-decyl-β,β-dimethylglycidate was heated to 280–290° for two hours. Examination of the product after this treatment showed only unchanged glycidic ester.

Although numerous attempts have been made, no product which can be identified conclusively as ethyl α-*n*-decyl-β-methyl-β-phenylglycidate has been obtained in this Laboratory. The method of preparation reported by Darzens has been repeated, using the α-bromo ester in place of the α-chloro ester, but no glycidic ester could be isolated. The use of a method recently reported by Johnson, *et al.*,[6] which has given excellent results in the preparation of other glycidic esters gave an unidentified product having the correct analysis for the desired ester but which had properties differing greatly from those of the product reported by Darzens and which gave other tests indicating that it was not a glycidic ester.

Claisen's method[7] for the saponification of glycidic esters, involving the use of sodium ethoxide followed by exactly one equivalent of water, has proved more satisfactory than the usual methods.

The thermal decarboxylation of glycidic acids often gives low yields of decarboxylation product. In the case of III, however, the method proved to be satisfactory since it gave yields as high as that obtained by the modification of the method of Yarnall and Wallis reported by Johnson, *et al.*[6]

Experimental

Preparation of Intermediates.—The acetone was of C.P. grade and was carefully purified by fractional distillation before use. Matheson Company best grade acetophenone was used without further purification. Ethyl α-bromolaurate was prepared by the Hell–Volhard–Zelinsky reaction and was purified carefully by fractionation through a suitable column. The *t*-butyl alcohol was purified by repeated partial crystallization. Sodium ethoxide, when used as condensing agent, was prepared from a sodium dispersion and absolute ethanol by the method previously reported.[2]

Preparation of Ethyl α-*n*-Decyl-β,β-dimethylglycidate.—This ester was prepared from one mole (307 g.) of ethyl α-bromolaurate and one mole (58 g.) of acetone, using 1.6 moles of sodium ethoxide as the condensing agent according to the method given in an earlier report.[2] Fractionation through a Todd precise fractionation assembly gave 102 g. (36%) of a product with b.p. 169° (4 mm.), $n^{20}{}_D$ 1.4430, $d^{20}{}_4$ 0.9128, $d^0{}_4$ 0.9276. Darzens[3] reports b.p. 162–165° (5 mm.), $n^{20}{}_D$ 1.4612, $d^0{}_0$ 0.993.

Anal. Calcd. for $C_{17}H_{32}O_3$: C, 71.77; H, 11.34; *MR*, 82.82; sapn. equiv., 284. Found: C, 71.74; H, 11.39; *MR*, 82.42; sapn. equiv., 281 ± 3.

As in previously reported cases,[2] a large amount (127 g.) of crude glycidic acid was obtained by acidifying the combined water and bicarbonate washes. Apparently the excess of condensing agent causes saponification when water is added at the conclusion of the reaction period.

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(1) From the thesis submitted by C. J. St. Lawrence in partial fulfillment of the requirements of the degree of Master of Science in Chemistry, August, 1954.

(2) H. H. Morris and M. L. Lusth, THIS JOURNAL, **76**, 1237 (1954).

(3) G. Darzens, *Compt. rend.*, **195**, 884 (1932).

(4) E. Troell, *Ber.*, **61**, 2498 (1928).

(5) R. Pointet, *Compt. rend.*, **148**, 417 (1909).

(6) W. S. Johnson, J. Belew, L. Chinn and R. Hunt, THIS JOURNAL, **75**,4995 (1953).

(7) L. Claisen, *Ber.*, **38**, 693 (1905).