Registry No.—Fluorene-9-carboxylic acid, 1989-33-9.

Acknowledgment.—We wish to thank the Petroleum Research Fund for their generous support of our programs. We are indebted to Dr. William Sheppard for a generous gift of pentafluorophenylcopper.

The Friedel–Crafts Reaction with 1-Bromo-1-phenyl-2-propanone

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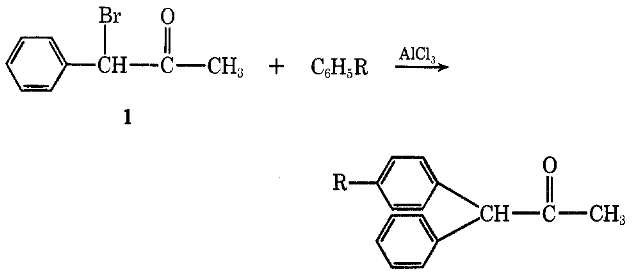
Under Friedel–Crafts reaction conditions, 1-bromo-1-phenyl-2-propanone (**1**) reacts with benzene to give 1,1-diphenyl-2-propanone (**2a**) in good yield.[1] As an extension of this method, Cragoe, *et al.*,[2] reacted **1** with substituted benzene to prepare substituted diphenyl-2-propanones (**2**). However, when they reacted **1** with anisole, they isolated 1,2-bis(*p*-methoxyphenyl)-1-phenylpropene (**3**) in good yield.

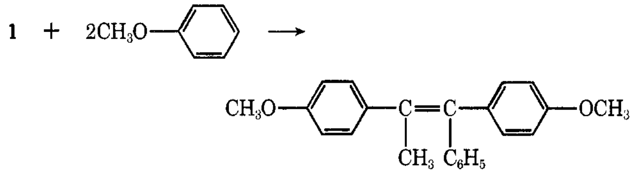


1

2a, R = H

b, R = CH_3

c, R = Cl

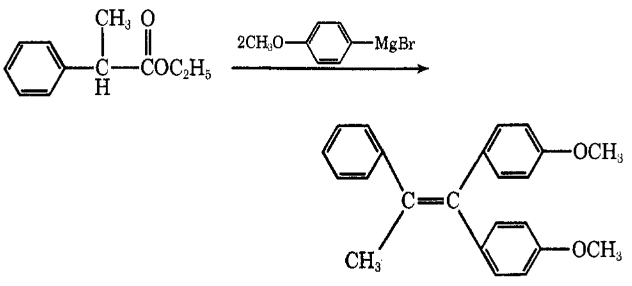


3

The structure assignment was based on elemental analysis and infrared data. Similar reaction[3,4] has been reported for acetyl chloride and anisole with aluminum chloride which gave 1,1-bis(*p*-methoxyphenyl)ethylene.

In our synthetic program, we had the occasion to prepare 1,1-bis(*p*-methoxyphenyl)-2-phenylpropene (**4**) by treating ethyl 2-phenylpropionate with *p*-methoxyphenylmagnesium bromide.

The melting point and boiling point of **4** were identical with those of **3** as reported by Cragoe.[2] It seemed unusual that two isomeric compounds should have the same melting point and boiling point. The preparation of **3** was repeated according to the literature procedure.[2]



4

The product was found to be identical in every respect (mixture melting point, ir, uv, nmr, and tlc) with **4**.

It remained to be determined which structure was correct. Ozonolysis of **3** would give 4-methoxyacetophenone and 4-methoxybenzophenone, while ozonolysis of **4** would give acetophenone and 4,4′-dimethoxybenzophenone. Ozonolysis and characterization of the reaction products of 1-bromo-1-phenyl-2-propanone (**1**) with anisole and ethyl 2-phenylpropionate with *p*-methoxyphenylmagnesium bromide confirmed that in both cases the end products are 4,4′-dimethoxybenzophenone and acetophenone, thus proving that **4** is the correct structure.

Ketones are known to rearrange under acidic conditions[5–7] and this may partly explain the formation of **4** from **1** under Friedel–Crafts reaction conditions.

Experimental Section[8]

Ethyl 2-Phenylpropionate.—To a solution of 34 g (0.13 mol) of 2-phenylpropionic acid in 100 ml of ethyl iodide cooled in an ice bath was added 26 g (0.07 mol) of Ag_2O in small portions with stirring. Stirring was continued at room temperature for 2 hr. The AgI was filtered and the filtrate was dried and concentrated. The ester was distilled to give 28.2 g of colorless liquid: bp 112–115° (15 mm); n^{22}_D 1.4932; ir 1730 cm^{-1} (ester); nmr δ 7.30 (s, 5, aromatic), 4.10 (q, 2, CH_2 next to CH_3), 3.70 (q, 1, CH), 1.5 (d, 3, CH_3), and 1.17 (t, 3, CH_3).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.92; H, 7.79.

1,1-Bis(*p*-methoxyphenyl)-2-phenylpropene. Method A.— To a mixture of *p*-methoxyphenyl Grignard reagent [formed by reacting 41.1 g (0.22 mol) of *p*-bromoanisole and 5.76 g (0.24 g-atom) of Mg in 100 ml of ether] was added slowly 17.8 g (0.1 mol) of ethyl 2-phenylpropionate dissolved in 50 ml of ether. The mixture was refluxed with stirring for 1 hr and then was poured into ice water. The mixture was acidified with concentrated HCl, extracted with ether, and dried. Removal of ether gave a viscous brown residue. The crude product was dissolved in hot hexane to give a pale yellow solution. The hexane was removed under reduced pressure and the residue was distilled to give 25 g of colorless product that solidified immediately, bp 190–195° (0.08 mm). The product was recrystallized from hexane and then from methanol to give 18 g of colorless crystals: mp 93–94.5°; ir 1602 cm^{-1} (C=C conjugated); uv λ_{max} (isooctane) 285 mμ (ε 14,736) and 247 (21,530); nmr δ 7.13 (s, 5, aromatic), 7.3 (q, 4, aromatic, J_{AB} = 9 Hz), 6.68 (q, 4, aromatic, J_{AB} = 9 Hz), 3.8 (s, 3, OCH_3), 3.66 (s, 3, OCH_3), and 2.13 (s, 3, CH_3).

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.29; H, 6.63.

Method B[2].—To a stirring solution of 55.5 g (0.41 mol) of 1-phenyl-2-propanone in 250 g of CS_2 was added 67 g (0.42 mol)

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(1) E. M. Schultz, *Org. Syn.*, **29**, 38 (1949).

(2) E. J. Cragoe, Jr., A. M. Pietruskiewiez, and C. M. Robb, *J. Org. Chem.*, **23**, 973 (1958).

(3) L. Gattermann, *Ber.*, **22**, 1129 (1889).

(4) L. Gattermann, R. Ehrhardt, and H. Maisch, *ibid.*, **23**, 1199 (1890).

(5) S. Barton and C. R. Porter, *J. Chem. Soc.*, 2483 (1956).

(6) H. D. Zook and S. C. Paviak, *J. Amer. Chem. Soc.*, **77**, 2501 (1955).

(7) H. D. Zook, W. E. Smith, and J. C. Green, *ibid.*, **79**, 4436 (1957).

(8) Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian A-60A spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer using spectral grade solvents. Microanalyses were performed by Chemical Analytical Services, University of California, Berkeley, Calif. 94701.

of bromine dropwise. This bromination solution was added to a mixture of 340 ml of anisole and 113 g (0.84 mol) of $AlCl_3$ in a 1-l. three-necked flask equipped with mechanical stirrer. The mixture was heated to 80–90° for 1 hr with stirring and then was stirred at room temperature for 2 hr. The mixture was poured into 500 g of ice and acidified with 75 ml of concentrated HCl. The organic layer was separated and the aqueous layer was extracted with 1 l. of ether. The combined organic layers were washed with water, dilute NaOH, and water. The dried solution was concentrated under reduced pressure. The residue was distilled to give 80 g of product bp 180–190° (0.08 mm). Recrystallization of the product from methanol twice gave 54 g of colorless crystals: mp 93–94.5°; ir 1602 cm^{-1} (C=C conjugated); uv λ_{max} (isooctane) 285 mμ (ε 14,840) and 247 (21,653); nmr δ 7.13 (s, 5, aromatic), 7.3 (q, 4, aromatic, J_{AB} = 9 Hz), 6.68 (q, 4, aromatic, J_{AB} = 9 Hz), 3.8 (s, 3, OCH_3), 3.66 (s, 3, OCH_3), and 2.13 (s, 3, CH_3). A mixture melting point with the product obtained from method A showed no depression.

Ozonolysis of 1,1-Bis(*p*-methoxyphenyl)-2-phenylpropene (4).—A solution of 3 g of the olefin **4** in 200 ml of ethyl acetate was cooled in a Dry Ice–acetone bath. A stream of ozone was passed into the solution. After about 20 min, the solution became light blue. Ozone was passed into the solution for another 30 min. The ozone generator was switched off and oxygen was passed through the solution for 20 min. The flask was removed from the Dry Ice–acetone bath and dry nitrogen was passed through the solution for 20 min. The solvent was removed under reduced pressure to give a yellow mixture of solid and oil. The residue was stirred in 25 ml of acetic acid and 1 g of Zn dust for 1 hr at room temperature. The mixture was diluted with 300 ml of ether and was filtered through Celite. The clear filtrate was washed with 2 × 200 ml of water and dilute $NaHCO_3$ solution until neutral. The ether solution was dried and concentrated to give a semisolid. Recrystallization from alcohol gave 1.5 g of product, mp 141–143°. Recrystallization again from hexane gave tiny needles, mp 142–143°. Dimethoxybenzophenone from Aldrich, recrystallized twice, melted at 142–144°. A mixture melting point showed no depression. Both materials showed the same spot on tlc (20% ethyl acetate in benzene). The ir, uv, and nmr spectra of both materials were also identical.

Acetophenone was detected by tlc in the alcoholic mother liquor, but no attempt was made to isolate it.

Registry No.—**1**, 23022-83-5; **4**, 33835-17-5; ethyl 2-phenylpropionate, 2510-99-8.

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Glyoxal Derivatives. IV. 2-Dimethoxymethyl-4,5-dimethoxy-1,3-dioxolane and 2,2′-Bis(4,5-dimethoxy-1,3-dioxolane)

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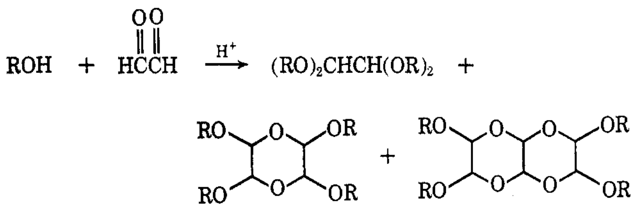
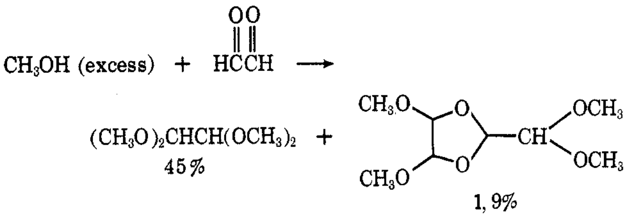
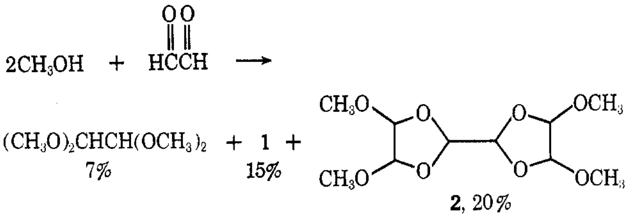
The reaction of aqueous glyoxal with alcohols to give bisacetals is well known and has been the subject of two basic patents.[2] General descriptions of the preparation of tetraalkoxyethanes, tetraalkoxydioxanes, and tetraalkoxynaphthodioxanes from aqueous glyoxal and



butanol or isopropyl alcohol have also been published.[3] The reaction of glyoxal with methyl alcohol, or glyoxal sulfate with methyl alcohol in the presence of calcium chloride, has also been reported.[4,5] In those cases the only product isolated was 1,1,2,2-tetrakis(methoxy)ethane. In this paper we report the isolation and identification of two totally new acetal derivatives of glyoxal based upon the dimeric and trimeric forms of glyoxal.

We have found that 80% glyoxal reacts with methyl alcohol under acid conditions to give, as previously reported, 1,1,2,2-tetrakis(methoxy)ethane and a new compound, 2-dimethoxymethyl-4,5-dimethoxy-1,3-dioxolane (**1**), in 45 and 9% yields, respectively. If the reaction is run with only 2 mol of methyl alcohol/mol of glyoxal the higher molecular weight dimer and a trimer, **2**, predominate. In both of these reactions substantial amounts of intractable residues were produced.





The structures of compounds **1** and **2** were deduced from their molecular weights, carbon and hydrogen analyses, and proton magnetic resonance spectra. In the case of compound **2**, no reasonable alternative to the assigned structure exists, apart from diastereoisomerism. The final choice between two possible structures for compound **1** is based upon interpolation between the rigorously assigned structure of glyoxal dimer[6] and compound **2**.

The elemental analysis and molecular weight of compound **2** are supportive for a trimer of glyoxal with four methoxyl groups. The pmr spectrum in deuteriochloroform at 60 MHz shows one strong line at 3.41 ppm (downfield from tetramethylsilane) representing the four methoxyl groups and three equally intense

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(1) (a) Tarrytown; (b) South Charleston.

(2) (a) C. B. Purves, U. S. Patent 2,194,405 (March 19, 1940); (b) L. G. MacDowell and R. W. McNamee, British Patent 559,362 (Feb 16, 1944).

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(5) D. H. Graangard and C. B. Purves, *J. Amer. Chem. Soc.*, **61**, 755 (1939); *ibid*, **61**, 428 (1939).

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