

*Fraction 4* is 3,7-nonanedione, m.p. 51–53°, no depression on admixture with an authentic sample. An additional 0.2 g. of dione was recovered from *Fraction 5* by crystallization from ether–petroleum ether. The infrared spectra of the remainder of this fraction and of *Fractions 6 and 7* indicated a mixture of lactone and unsaturated acid.

*Fraction 8* crystallized on standing, m.p. 48.0–48.5° after precipitation from ether–petroleum ether, no depression of melting point on admixture with an authentic sample of  $\delta$ -ketoanthic acid.

BERKELEY, CALIF.

[COMMUNICATION NO. 1748 FROM THE KODAK RESEARCH LABORATORIES]

## Derivatives of Benzoylresorcinol

J. A. VANALLAN

Received May 22, 1958

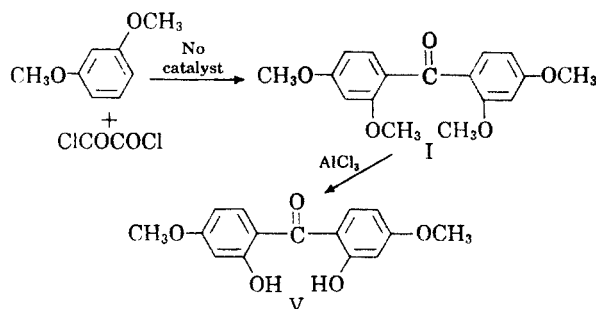
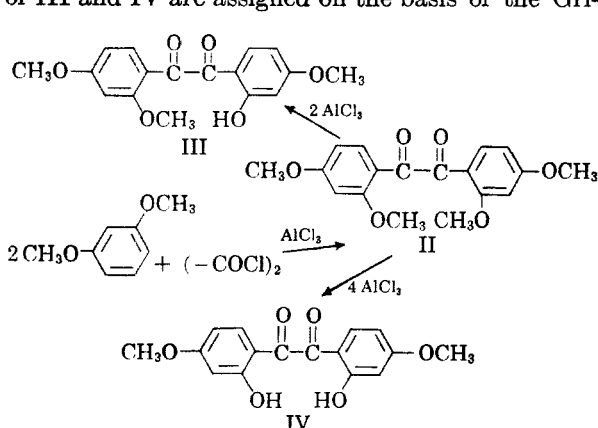
A new synthesis of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone is described. The substance stated by Staudinger to be 2,2',4,4'-tetramethoxybenzophenone has been shown to be 2,2',4,4'-tetramethoxybenzil. The ultraviolet absorption spectra of these materials are discussed.

In extending the investigation of derivatives of benzoylresorcinol,<sup>1</sup> we had occasion to synthesize a compound described<sup>2</sup> as 2,2',4,4'-tetramethoxybenzophenone (I). The ultraviolet absorption spectrum of this latter substance was at variance with that expected from our earlier work, so it was decided to re-examine this substance.

When *m*-dimethoxybenzene was allowed to react with oxalyl chloride in carbon disulfide<sup>2</sup> or ethylene chloride, with aluminum chloride as a catalyst, a substance melting at 129–130° was obtained, confirming Staudinger's result. However, methoxyl determination, Grignard analysis, and elementary analyses led to the conclusion that the substance melting at 129–130° was 2,2',4,4'-tetramethoxybenzil (II). To test this hypothesis, II was oxidized with alkaline hydrogen peroxide to 2,4-dimethoxybenzoic acid, a reaction typical of benzils. Selective demethylation of II with two and four equivalents of aluminum chloride gave 2-hydroxy-2',4,4'-trimethoxybenzil (III) and 2,2'-dihydroxy-4,4'-dimethoxybenzil (IV), respectively. The structures of III and IV are assigned on the basis of the Gri-

gnard analysis, on the known propensity of *o*-methoxyl groups to be demethylated, and the similarity of their ultraviolet curves to II.

It was noted that, on mixing oxalyl chloride and *m*-dimethoxybenzene, the solution became reddish yellow and hydrogen chloride was slowly evolved; heating accelerated this evolution of gas. In order to determine the nature of this reaction, the components were heated for a few hours, and the reaction mixture was distilled. The distillate was recrystallized from ethanol to give a substance having a melting point of 135–136° which, from its elementary analysis, methoxyl determination, and Grignard analysis, is 2,2',4,4'-tetramethoxybenzophenone (I). Its mixed melting point with II is 110–113°, and its 2,4-dinitrophenylhydrazone (m.p. 150°) differs from that of II (m.p. 185°). Moreover, demethylation of I with aluminum chloride gives 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (V), identical with that obtained from *m*-dimethoxybenzene and phosgene in the presence of aluminum chloride.<sup>3</sup>



The melting point of I has been reported as 130°<sup>4</sup> and as 137.2–139°.<sup>5</sup> It is evident, therefore, that the substance Staudinger describes as 2,2',4,4'-

(1) J. A. VanAllan and J. F. Tinker, *J. Org. Chem.*, **19**, 1243 (1954).

(2) H. Staudinger, E. Schlenker, and H. Goldstein, *Helv. Chim. Acta*, **4**, 334 (1921).

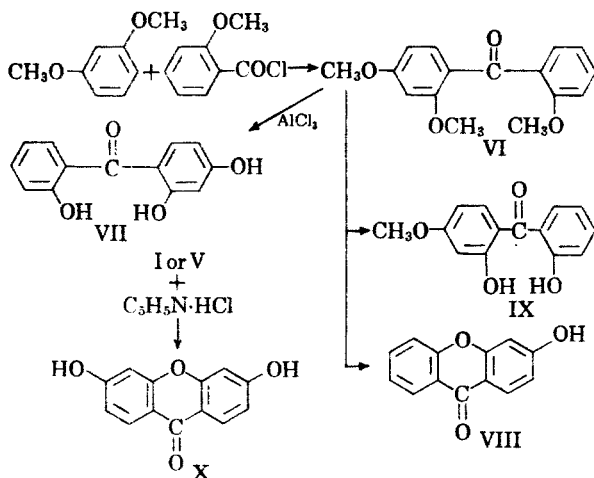
(3) General Aniline and Film Corp., Brit. Patent 706,151 (1954).

(4) J. Tambor, *Ber.*, **43**, 1882 (1910).

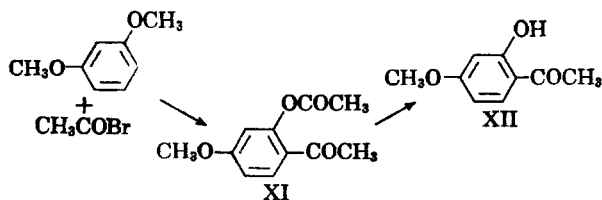
(5) G. Wittig and V. Pockels, *Ber.*, **72**, 89 (1939).

tetramethoxybenzophenone is most certainly 2,2',4,4'-tetramethoxybenzil.

To determine the generality of the reaction of organic acid halides with *m*-dimethoxybenzene, *o*-methoxybenzoyl chloride was allowed to react with *m*-dimethoxybenzene. The reaction proceeded smoothly, with the evolution of hydrogen chloride, to give a 91% yield of 2,2',4-trimethoxybenzophenone (VI), which was demethylated with aluminum chloride in benzene to 2,2',4-trihydroxybenzophenone (VII). If VI was demethylated using pyridine hydrochloride, the major portion of the product was 3-hydroxyxanthone (VIII), together with some 2,2'-dihydroxy-4-methoxybenzophenone (IX). Similarly, if V is demethylated using pyridine hydrochloride, the major portion of the product is 2,7-dihydroxyxanthone (X). The identities of VIII and X were confirmed by making their known acetyl derivatives. The formation of X from I is further confirmatory evidence for the structure of I.



Heating acetyl bromide and *m*-dimethoxybenzene for 3 hours at the boiling point of the mixture results in the formation of 2-acetoxy-4-methoxybenzophenone (XI) in 38% yield. The structure of the latter was established by hydrolyzing it to 2-hydroxy-4-methoxyacetophenone (XII), the identity of which was confirmed by comparison of its phenylhydrazone and 2,4-dinitrophenylhydrazone with those of authentic samples. Acetyl chloride failed to react with *m*-dimethoxybenzene under the same conditions.



**Discussion of ultraviolet spectra.** In Fig. 1 (also Table I) it is shown that these hydroxylated benzophenones have spectra characteristics of the

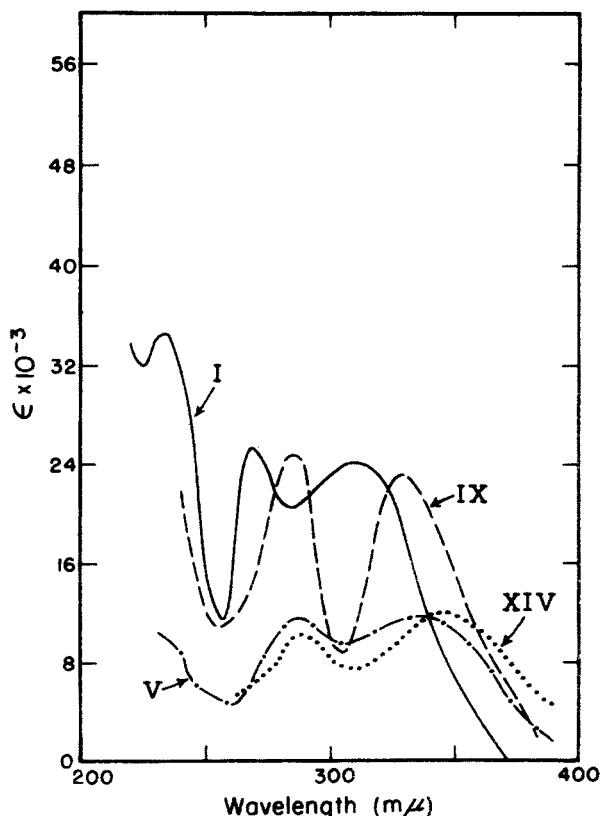
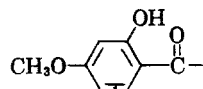


Fig. 1. Ultraviolet absorption spectra in methanol of: 2,2',4,4'-tetramethoxybenzophenone (I) —; 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (V) - · - · -; 2,2'-dihydroxy-4-methoxybenzophenone (IX) - - - -; 2,2',4,4'-tetrahydroxybenzophenone (XIV) · · · · ·

benzoylresorcinols, as shown by comparison with the known 2,2',4,4'-tetrahydroxybenzophenone (XIV). In Fig. 2, the spectra of the benzils just described are shown. The similarity of these two series is apparent at once, which is interpreted to mean that there is little resonance coupling through the *o*-diketo group. The intensity of absorption of the benzils is significantly higher than the benzophenones, which is consonant with the concept that the groupings,



in the benzils are acting, to some extent, additively.

A large decrease in intensity and a slight shift to longer wave lengths are observed in both series when 2,2'-methoxy groups are demethylated to the corresponding hydroxy groups. This is believed to be a consequence of conjugate chelation<sup>1</sup> which is possible between the carbonyl and hydroxy groups in both systems.

#### EXPERIMENTAL

**2,2',4,4'-Tetramethoxybenzophenone (I).** A mixture of 75 g. (70 ml., 0.55 mole) of *m*-dimethoxybenzene and 33 g.

TABLE I  
 PROPERTIES OF BENZOPHENONE AND BENZIL DERIVATIVES

Compound No.	$\lambda$	Log $\epsilon$	$\lambda$	Log $\epsilon$	Empirical Formula	Calcd.				Found					
						C	H	H <sup>b</sup>	Addn. <sup>b</sup> CH <sub>2</sub> O	C	H	H <sup>b</sup>	Addn. <sup>b</sup> CH <sub>2</sub> O		
VI	279	4.43	312	4.40	C <sub>16</sub> H <sub>16</sub> O <sub>4</sub>	70.6	5.9	—	—	34.2	71.0	5.9	—	—	31.7
I	278	4.45	312	4.42	C <sub>17</sub> H <sub>18</sub> O <sub>5</sub>	67.6	6.0	0.0	1.0	41.2	67.7	5.8	0.1	0.9	41.3
IX	285	4.40	329	4.36	C <sub>14</sub> H <sub>12</sub> O <sub>4</sub>	68.9	4.9	—	—	—	68.5	4.9	—	—	—
V	284	4.12	340	4.12	C <sub>15</sub> H <sub>14</sub> O <sub>5</sub>	65.8	5.1	2.0	1.0	22.6	65.5	5.2	2.0	1.3	22.6
VII	288	4.40	329	4.38	C <sub>15</sub> H <sub>16</sub> O <sub>4</sub>	67.5	4.3	—	—	—	67.7	4.1	—	—	—
XIV	287	4.01	348	4.17	Ref. 1	—	—	—	—	—	—	—	—	—	—
II	272	4.57	312	4.49	C <sub>18</sub> H <sub>18</sub> O <sub>5</sub>	65.5	5.4	—	2.0	37.5	65.6	5.3	—	1.6	36.9
III	284	4.60	325	4.53	C <sub>17</sub> H <sub>16</sub> O <sub>5</sub>	64.6	5.2	—	—	—	64.5	5.1	0.2	2.5	—
IV	284	4.32	328	4.25	C <sub>16</sub> H <sub>14</sub> O <sub>6</sub>	63.6	4.6	—	—	20.5	64.1	4.5	2.1	1.8	21.1
Ie <sup>a</sup>	—	—	—	—	C <sub>22</sub> H <sub>22</sub> O <sub>5</sub> N <sub>4</sub>	57.5	4.6	—	—	—	57.5	4.6	—	—	—
IIe	—	—	—	—	C <sub>24</sub> H <sub>22</sub> O <sub>5</sub> N <sub>4</sub>	56.4	4.3	—	—	—	56.9	4.7	—	—	—
XIIe	—	—	—	—	C <sub>16</sub> H <sub>14</sub> O <sub>6</sub> N <sub>4</sub>	52.2	4.1	—	—	9.0	52.0	3.9	8.8	—	—

<sup>a</sup> 2,4-Dinitrophenylhydrazone derivative of compound is signified by "e" following the Roman numeral. <sup>b</sup> These data were obtained by Grignard analysis, the "H" indicating the number of moles of active hydrogen generated by one mole of compound and the addition the number of moles of Grignard reagent consumed by addition to the carbonyl groups of the compound.

(24 ml., 0.24 mole) of oxalyl chloride was slowly heated to 170–180°. Vigorous evolution of hydrogen chloride ensued, and the mixture became bright red. After refluxing 1.5 hr., the reaction mixture was distilled to give 25 ml. of *m*-dimethoxybenzene, b.p. 98–100°/6 mm., 30 ml. of a fraction 200–210°/0.4 mm. which was recrystallized from alcohol to give 28 g. (38%) of I, m.p. 135–136°. 2,4-Dinitrophenylhydrazone of I, m.p. 150°, was recrystallized from a mixture of butanol and methanol. See Table I for analytical results. The distillation residue was boiled with alcohol and the yellow insoluble portion was recrystallized first from butanol and then from xylene to give bright yellow crystals of a substance, m.p. 193–195°, having the same empirical formula as I.

Anal. Found: C, 67.4; H, 5.4.

This latter substance was not investigated further.

*2,2',4,4'*-Tetramethoxybenzil (II). A well-stirred mixture of 35 ml. of *m*-dimethoxybenzene, 12.9 g. (9.0 ml.) of oxalyl chloride, and 200 ml. of ethylene chloride was cooled to 0° and 30 g. of aluminum chloride slowly added, the temperature being kept below 15°; the mixture became highly colored. Stirring was continued for 1 hr. at 15–20°; the temperature was then raised to 60° for 0.5 hr. After cooling, the aluminum chloride complex was decomposed with cold, dilute hydrochloric acid. The organic layer was separated, washed with water and dilute sodium hydroxide, dried, and distilled. A forerun of 5 ml. of *m*-dimethoxybenzene was recovered. The product distilled between 240–260°/1 mm. and was twice recrystallized from ethanol to give 19 g. of white, platelike crystals of II, m.p. 129–130°. The 2,4-dinitrophenylhydrazone, m.p. 185°, was crystallized from benzene-methanol.

*2,2'*-Dihydroxy-4,4'-dimethoxybenzil (IV). A solution of 6.0 g. (0.02 mole) of II in 80 ml. of ethylene chloride was treated with 11 g. (4+ equivalents) of aluminum chloride. The mixture was heated on the steam bath for 2 hr. and decomposed with cold, dilute hydrochloric acid. The organic layer was separated and extracted with 10% sodium hydroxide solution. Acidification of the alkaline phase produced a white precipitate which was collected on a filter and dried; the yield was 6.0 g., m.p. 136–139°. One recrystallization from butanol gave 4 g. and raised the m.p. to 149–150°.

*2-Hydroxy-2',4',4'*-trimethoxybenzil (III). If the amount of aluminum chloride is reduced to 5.32 g. (2 equivalents) in the preparation just described, a 14% yield of III (m.p. 145–146°) is obtained.

*2,2'*-Dihydroxy-4,4'-dimethoxybenzophenone (V). Demethylation of I to V was accomplished in 59% yield by using the procedure described for IV.

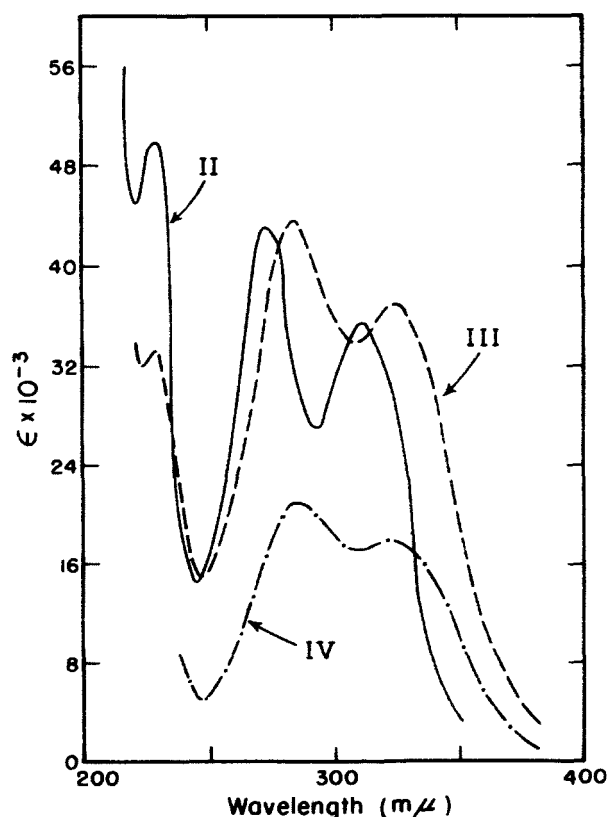


Fig. 2. Ultraviolet absorption spectra in methanol of: *2,2',4,4'*-tetramethoxybenzil (II) —; *2-hydroxy-2',2'*-dihydroxy 4,4'-dimethoxybenzil (IV) - - - -.

*2,2',4-Trimethoxybenzophenone* (VI). A solution of 28 g. (0.2 mole) of 2-methoxybenzoyl chloride in 40 ml. of *m*-dimethoxybenzene was heated to reflux temperature. A vigorous reaction ensued, and the heat source was removed until the reaction had subsided. The mixture was then heated until the evolution of hydrogen chloride had stopped (about 1 hr.) and then distilled; 18 ml. of *m*-dimethoxybenzene, b.p. 95–100°/5 mm., was recovered. The temperature then rose quickly and a fraction, b.p. 180–200°/15 mm., was collected; this fraction 47.5 g. (88.6%),  $n_D^{25}$  1.608, is essentially VI.

*2',2,4-Trihydroxybenzophenone* (VII). Thirteen and six-

tenths grams of VI was dissolved in 80 ml. of ethylene chloride and 20 g. of aluminum chloride was added. The mixture was heated on the steam bath for 2 hr., then decomposed with dilute hydrochloric acid. The aqueous layer was drawn off and the organic layer washed with water, then with dilute sodium hydroxide solution. The alkaline solution was acidified and extracted with ethylene chloride. The ethylene chloride was removed *in vacuo* and the residual oil crystallized from benzene to give 4.1 g. of VII, m.p. 128°.

*3-Hydroxyxanthone* (VIII) and *2,2'-dihydroxy-4-methoxybenzophenone* (IX). Pyridine hydrochloride (70 g.) and 21.0 g. of V were gently refluxed for 4 hr., then poured into water, and the precipitate, A, was collected on a filter. The solid, A, was added to 100 ml. of water and made alkaline with 50% sodium hydroxide solution; the solution was filtered and acidified; the precipitated solid amounts to 7.0 g. This crude material was suspended in 25 ml. of warm acetic anhydride and a drop of sulfuric acid added. Heating was continued until solution was complete. After cooling, the precipitate was collected and then recrystallized from benzene to give 7.0 g. of 3-acetoxyxanthone,<sup>6</sup> VIIIa, m.p. 160°. Saponification of 19.0 g. of VIIIa gave 15 g. of 3-hydroxyxanthone, m.p. 242°. 3,6-Diacetoxyxanthone,<sup>7</sup> m.p. 203–204°, from xylene was prepared from I in a manner similar to that just described.

(6) St. v. Kostanecki and R. Rutishauer, *Ber.*, **25**, 1648 (1892).

(7) R. Meyer and A. Conzetti, *Ber.*, **32**, 2103 (1899).

*2-Acetoxy-4-methoxyacetophenone* (XI). *m*-Dimethoxybenzene (57 g., 0.54 mole) and 60 ml. of acetyl bromide were refluxed for 3 hr. and distilled. A fraction (32 g., 38% yield) was collected, b.p. 155–160°/5 mm., which is essentially XI,  $n_D^{20}$  1.550.

*Anal.* for C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>. Calcd.: C, 63.3; H, 5.8. Found: C, 63.8; H, 5.8.

The 2,4-dinitrophenylhydrazone of XI was prepared in the usual manner, but in the process, the acetyl group is lost, m.p. 230°, from dioxanebutanol.

*2-Hydroxy-4-methoxyacetophenone* (XII). 2,4-Dimethoxyacetophenone (18 g.) in 70 ml. of benzene was treated with 29 g. of aluminum chloride. A vigorous reaction ensued. After the reaction had subsided, the mixture was heated on the steam bath for 0.5 hr., then decomposed with iced hydrochloric acid. The benzene layer was extracted with dilute alkali, and the alkaline layer was acidified to give an oil. This, on distillation, gave 8 g. of XII, b.p. 145–147°/5 mm., which solidified, m.p. 46–48°, phenylhydrazone, m.p. 107–108°. Saponification of XI with alcoholic potassium hydroxide also gave XII, as proved by the identity of its phenylhydrazone, m.p. 107–108°, with that prepared above. The 2,4-dinitrophenylhydrazone (m.p. 230°) of XII is identical to that of XI.

*Acknowledgment.* We are indebted to D. W. Stewart of these Laboratories for the ultraviolet spectra reported.

ROCHESTER 4, N. Y.

[CONTRIBUTION FROM THE EDGAR C. BRITTON RESEARCH LABORATORY OF THE DOW CHEMICAL Co.]

## Aromatic Phosphorodichloridites and Phosphorodichloridothioates.

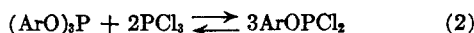
### I. Aryl Phosphorodichloridites

HENRY TOLKMITH

Received April 22, 1958

A series of aryl phosphorodichloridites were prepared in yields of 84 to 98% by treating phenols with PCl<sub>3</sub> at a mole ratio of about 1:6 at reflux under atmospheric pressure and then completing this reaction by addition of catalytic amounts of anhydrous magnesium chloride.

For the preparation of the aryl phosphorodichloridites no satisfactory method was known at the outset of this investigation, although the first member of this series of compounds was described in 1883.<sup>1</sup> There were two synthetic methods mentioned in the literature:<sup>1,2</sup>



Phenol and its homologs were reported to react readily with phosphorus trichloride in equimolar proportions in the absence of catalysts or hydrochloric acid acceptors, at about 20–60°. However, during the actual course of reaction 1 substantial

amounts of bis- and tris-esters were regularly produced.<sup>1,3–6</sup>

The reaction involving *p*-chlorophenol was reported to require a large excess of phosphorus trichloride in order to produce even small yields of *p*-chlorophenyl phosphorodichloridite.<sup>4</sup>

Even recently the yields for aryl phosphorodichloridites were reported to be not better than 25–50% of theory.<sup>6,7</sup>

Reaction 2 was reported to require a reaction temperature of 150° and to give only a 47% yield of phenyl phosphorodichloridite.<sup>2</sup> All previous in-

(3) R. Anschutz and W. O. Emery, *Ann.*, **239**, 309 (1887).

(4) W. Strecker and Ch. Grossmann, *Ber.*, **49**, 85 (1916).

(5) W. Broecker, *J. prakt. Chem.* (2) **118**, 287 (1928).

(6) G. R. Cebrian, *Arch. inst. farmacol. expl. (Madrid)*, **8**, 61 (1956).

(7) J. C. Bill and B. A. Hunter, U. S. Patent 2,732,365 (1956).

(1) E. Noack, *Ann.*, **218**, 87 (1883).

(2) J. B. Conant, V. H. Wallingford, and S. S. Gandbeker, *J. Am. Chem. Soc.*, **45**, 764 (1923).