

63–66°. No solvent was used. Cloke and Ayers using a nickel catalyst in a Burgess–Parr apparatus³ reported a yield of 80% using *n*-butyl alcohol as a solvent. The furan was obtained by the method described by Wagner and Simons.⁴ The water and carbon dioxide were removed by passing the effluent gases through a mixture of calcium chloride (30) and soda lime (70) instead of sodium hydroxide pellets to avoid clogging the apparatus. The yield was 96%.

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(3) Cloke and Ayers, *THIS JOURNAL*, **56**, 2144 (1934).

(4) Wagner and Simons, *J. Chem. Ed.*, **13**, 270 (1933).

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The Constitution of the So-called "Phenoldiphenin"

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An analyzed condensation product (m. p. 134°) of diphenic anhydride with phenol was first reported by Dutt.¹ After demonstrating that his product contained two phenolic hydroxyls and that it dissolved in alkali with a reddish-pink color, he assumed for it a structure analogous to phenolphthalein and therefore named it phenoldiphenin. About the same time Underwood and Kochmann² prepared in this Laboratory by the same process a different but isomeric product (m. p. 250–251°) which unlike Dutt's material gave yellow (not pink) alkaline solutions. In view of its method of preparation and its analysis (C₂₆H₁₈O₄) Underwood also named his product "phenoldiphenin" and declared: "The statements made by Dutt . . . as to the constitution and properties of phenoldiphenin . . . appear to be in error."

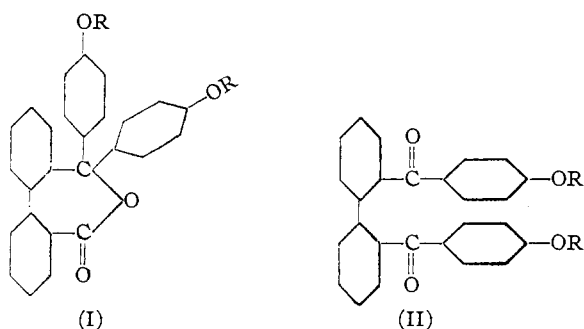
In their second paper Underwood and Kochmann³ wavered between the unsymmetrical (I) and symmetrical (II) formulations for their product (R = H) but because they were unable to obtain any reaction with hydroxylamine and because strong heating above its melting point decomposed their product with some loss of carbon dioxide, they favored the former. Underwood and Barker⁴ later showed that upon alkali fusion of their "phenoldiphenin" evidence could be

(1) Dutt, *J. Chem. Soc.*, **123**, 226 (1923).

(2) Underwood and Kochmann, *THIS JOURNAL*, **45**, 3073 (1923).

(3) Underwood and Kochmann, *ibid.*, **46**, 2070 (1924).

(4) Underwood and Barker, *ibid.*, **52**, 4082 (1930).



obtained for the formation of *o*-phenylbenzoic acid, phenol and carbon dioxide. Moreover, their compound yielded a potassium salt containing two atoms of metal, and on treatment with methyl iodide and powdered potassium hydroxide gave a product C₂₃H₂₂O₄ (m. p. 150–151°) which they designated as "phenoldiphenin lactone dimethyl ether." The latter was also obtained in 11% yield from the reaction of diphenic anhydride with anisole in the presence of aluminum chloride. Instead of recognizing that these facts were in complete accord with either formulation (I) or (II) but did not constitute distinguishing proof, they elected to construe the *analogy* to phenolphthalein formation as evidence and made the definite statement that "the structure of phenoldiphenin is similar to that of phenolphthalein." From this point of view Underwood and his collaborators have never receded. Subsequent to the death of the senior author various substitution products of "phenoldiphenin" and of "*o*-cresoldiphenin" were reported⁵ and although their absorption spectra⁶ proved to be quite unlike those to be expected from analogs of phenolphthalein, the name "diphenins" was retained throughout these papers.

In the meantime Bachmann⁷ reported the preparation of 2,2'-dianisoylbiphenyl as the result of Ullmann coupling of two molecules of 2-bromo-4'-methoxybenzophenone, obtained from *o*-bromobenzonitrile and *p*-methoxyphenylmagnesium bromide. The structure of his diketone is thus unimpeachable. Neither Bachmann nor Underwood, however, recognized that this 2,2'-dianisoylbiphenyl would be identical with the latter's "phenoldiphenin lactone dimethyl ether" if phenoldiphenin has the symmetrical structure of type (II).

Work on this problem has been in progress in

(5) Underwood and Barker, *ibid.*, **58**, 642 (1936).

(6) Underwood, Harris and Barker, *ibid.*, **58**, 643 (1936).

(7) Bachmann, *ibid.*, **54**, 1972 (1932).

this Laboratory⁸ since the death of Professor Underwood. We have repeated and checked the preparation and properties of "phenoldiphenin" and its dimethyl ether, m. p. 150.5–151.5° uncorr. (according to Underwood) and the preparation of 2,2'-dianisoylbiphenyl, m. p. 150–151.4° uncorr. (according to Bachmann). We have also made a direct comparison of the so-called "phenoldiphenin lactone dimethyl ether" and the 2,2'-dianisoylbiphenyl by the method of mixed melting points and find that no depression occurs (mixed m. p. 150–151°). In view of the fact that all the positive experimental evidence brought forward to support the unsymmetrical formulation is equally applicable to the symmetrical type and particularly in view of the insolubility of the "lactone" in alkali, the yellow color of alkaline solutions of "phenoldiphenin," and the great dissimilarity of their absorption spectra from those of phenolphthalein, the results of the direct comparison reported here for the first time appear to assure the validity of the symmetrical or diketone formulation (II).

While our work was in progress Bell and Briggs⁹ also confirmed Underwood's preparation of "phenoldiphenin" and its dimethyl ether. In addition they prepared 2,2'-dianisoylbiphenyl by interaction of diphenic acid chloride with anisole in the presence of aluminum chloride. Bell and Briggs, however, gave no indication that they were aware of Bachmann's previous synthesis of this compound. Moreover, since their method did not eliminate the possibility that the aluminum chloride might have caused rearrangement of the symmetrical diphenic acid chloride to an unsymmetrical form analogous to that well known for phthalyl chloride,¹⁰ their preparation may not by itself be regarded as *proof* of the symmetrical structure. Furthermore, they reported no direct comparison of their "phenoldiphenin dimethyl ether" and their 2,2'-dianisoylbiphenyl. In other words, Bell and Briggs' statement that these two compounds are identical is correct, but the evidence for it is contained solely in the combination of Bachmann's work with our own direct comparison of the Underwood and Bachmann products. Bell and Briggs' report now, however, becomes evidence that in the Friedel-Crafts

condensation with anisole diphenic acid chloride does react in the symmetrical form.

With Underwood's "phenoldiphenin lactone dimethyl ether" thus established as in fact 2,2'-dianisoylbiphenyl, the question arises whether Dutt's compound may not have been the true phenoldiphenin. We are continuing our experiments on the preparation of the latter by an independent method.

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Non-Reaction of Ethylene Oxide and Methanol

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In an effort to obtain an example of a gaseous bimolecular association reaction, the writer studied the possible reaction between ethylene oxide and methanol to form monomethyl ether of ethylene glycol. Purified and dried samples of the gases were mixed under the usual conditions for the study of reaction kinetics. There was no evidence of an association reaction (resulting in pressure decrease) for temperatures up to 350° and over a period of four hours. An ethylene oxide pressure of 125 mm. and 200 mm. of methanol were typical of the concentrations employed. In order to determine whether a comparatively rapid reaction was occurring, 112 mm. of ethylene oxide and 154 mm. of methanol were mixed at 183° and the temperature of the thermostat gradually raised to 342°; the final pressure was within one mm. of the calculated pressure based upon no reaction. A similar experiment was tried at 181° employing 163 mm. of ethylene oxide and 142 mm. of purified *t*-butyl alcohol and heated for ninety minutes. No pressure change was detected. There was no evidence of acetaldehyde or acetone in the reaction products of the methanol experiments, thus excluding, respectively, the isomerization of ethylene oxide or the formation of a hemi-acetal. There was a definite increase in the pressure of pure ethylene oxide on standing at 342° for 10.5 hours (from 100 to 131 mm.).¹

Fletcher and Rollefson reported that ethylene oxide catalyzed the decomposition of methanol at 465° (pure methanol is stable at 465°). Heckert and Mack reported a rapid reaction between gaseous ammonia and ethylene oxide at room tempera-

(8) Carten, S.B. Thesis, 1936; Moos, M.S. Thesis, 1937; Moos, Ph.D. Thesis, in progress.

(9) Bell and Briggs, *J. Chem. Soc.*, 1561 (1938).

(10) Ott, *Ann.*, **392**, 273 (1912); "Organic Syntheses," **11**, 88 (1931).

(1) Heckert and Mack, *THIS JOURNAL*, **51**, 2706 (1929); Fletcher and Rollefson, *ibid.*, **58**, 2135 (1936); Thompson and Meissner, *Trans. Faraday Soc.*, **32**, 1451 (1936).