An examination of the dry, solid residues remaining after the reaction of ethyl acetate and ethyl isobutyrate with sodium ethoxide has been made and from the results obtained the conclusion is drawn that the so-called "primary reaction product" postulated by Scheibler as the intermediate in the acetoacetic ester condensation and ketene acetal formation does not exist.

MADISON, WISCONSIN

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Notes

Aryl *p*-Bromobenzenesulfonates as Derivatives for the Identification of Phenols

BY VLADIMIR C. SEKERA

In connection with the work on the higher alkyl sulfonates[1] one or two aryl esters were prepared. These beautifully crystalline compounds were so readily prepared and so easily purified that further examples were characterized in order to show their value as derivatives for identification of phenols.

The general method of preparation consisted of mixing equimolecular quantities of the phenol and *p*-bromobenzenesulfonyl chloride with about four equivalents of pyridine and stirring the mixture for about three hours at 15° or lower. With small quantities, less time was needed for the reaction. The reaction mixture was decomposed with ice water containing enough dilute hydrochloric acid to combine with the pyridine. The aryl sulfonate was collected on a Buchner funnel and air dried. One recrystal-

TABLE I

SOME ARYL *p*-BROMOBENZENESULFONATES

Phenol	Yield, %	M. p., °C.	Anal., % Br Calcd.	Anal., % Br Found
Phenol	86	115.5	25.5	25.5
α-Naphthol	81	104	22.0	21.9
β-Naphthol	69	151–152	22.0	22.4
o-Cresol	75	78–79	24.4	24.6
m-Cresol	74	69–70	24.4	24.3
p-Cresol	76	100	24.4	24.5
o-Nitrophenol	70	97–98	22.3	22.6
m-Nitrophenol	70	108–109	22.3	22.4
p-Nitrophenol	69	112	22.3	22.6
o-Bromophenol	57	125	40.8	41.0
Thymol	71	103.5	21.6	21.5
Guaiacol	61	103–104	23.3	23.6
2,4,6-Tribromophenol	85	139–140	58.1	58.4

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[1] Sekera and Marvel, THIS JOURNAL, 55, 345 (1933).

lization from alcohol using a little decolorizing carbon usually gave a pure product. Table I contains a description of these compounds.

Contribution from the
Chemical Laboratory of the
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Note on the Occurrence of Dehydrodeguelin and Dehydrotoxicarol in Some Samples of Derris Root

By E. P. Clark and George L. Keenan

On several occasions during the past two years, specimens of derris root were encountered which yielded no rotenone, but gave instead mixtures of yellow crystals whose melting points ranged from 200 to 225°. After purification by recrystallization from various solvents, these materials gave mixtures of dehydrodeguelin and dehydrotoxicarol. The identity of the substances was proved by the optical immersion method. In two instances, dehydrotoxicarol predominated so that it was possible by fractional crystallization to isolate this substance in an analytically pure condition and identify it by comparison with an authentic sample as to melting point, mixed melting point and optical properties. The materials remaining in the mother liquors were recovered and after recrystallization were shown to consist of mixtures which were impossible to resolve but which when examined by the optical method referred to above were conclusively shown to be essentially dehydrodeguelin and dehydrotoxicarol.

Recently there was obtained from a manufacturer of rotenone an interesting sample of yellow crystals derived from derris root which yielded no rotenone. Upon recrystallization this material yielded a beautiful yellow preparation which melted sharply at 217°. Repeated recrystallizations from various solvents failed to alter the melting point, and it was thought that possibly it was a dehydro derivative of an isomer of deguelin or rotenone. Upon subjecting the material to hydrolysis with alcoholic alkali, an acid corresponding to derrisic acid was readily obtained but it melted at 178° (derrisic acid melts at 158° while deguelic acid melts at 186°). The melting point of this acid did not change after several recrystallizations, which was in harmony with the assumption stated above, especially since analysis of the acid showed its molecular formula to be the same as that of derrisic acid. In the meantime, oxidation of the dehydro derivative (m. p. 217°) with permanganate in acetone and in alkaline aqueous solutions, and also with alkaline hydrogen peroxide, yielded 2-hydroxy-4,5-dimethoxybenzoic, nicouic, risic and derric acids.[1] These facts, especially the isolation of nicouic acid in essentially the same yield as is obtained from dehydrodeguelin, proved that at least the greater part of the original

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[1] Clark, This Journal, **54**, 3000 (1932).

preparation was dehydrodeguelin. Repeated recrystallization from toluene of the acid which melted at 178° was then undertaken, and its melting point was finally raised to 186°. It was then shown by its melting point, mixed melting point and optical properties to be deguelic acid.

A careful examination of the original dehydro compound by the optical immersion method then revealed that it consisted of dehydrodeguelin and dehydrotoxicarol. This observation is of interest in that the mixture of the two substances was such that it could not be resolved by repeated recrystallization, and it possessed a sharp melting point. It may be possible that such conditions as here presented were responsible for the recording by the earlier workers upon derris root of various yellow compounds which melted in the range between 200 and 230°.[2,3,4] It is of further interest that dehydrotoxicarol has not hitherto been reported as a natural plant constituent, and it was only recently that Merz[5] reported for the first time the natural occurrence of dehydrodeguelin in the seeds of *Tephrosia vogelii*.

(2) Sillevoldt, *Ned. Tijd. Pharm.*, **11**, 246 (1899); *Arch. Pharm.*, **237**, 595 (1899).

(3) Tattersfield and Roach, *Ann. Appl. Biol.*, **10**, 1 (1923).

(4) Power, *Proc. Am. Pharm. Assoc.*, **50**, 296 (1902); *Pharm. Arch.*, **5**, 145 (1902); **6**, 1 (1903).

(5) Merz, *Arch. Pharm.*, **270**, 362 (1932).

CONTRIBUTION FROM THE INSECTICIDE DIVISION
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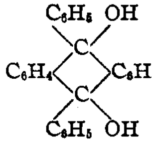
Furan Reactions. V. Derivatives of Furfuryl Alcohol

BY CHARLES D. HURD AND CHARLES L. THOMAS[1]

Furfuryl triphenylmethyl ether, $C_4H_3O\text{-}CH_2\text{-}O\text{-}C(C_6H_5)_3$, was prepared and found to be a convenient derivative for the identification of furfuryl alcohol. Similarly, the furfuryl ether of 9,10-diphenyl-9,10-dihydroanthracenediol was studied.

Nine grams of triphenylchloromethane was added to a cold (0°) mixture of 3.3 g. of furfuryl alcohol and 40 cc. of pyridine. It was left for one and a half days at room temperature. Then it was diluted with 10 cc. of water and the resulting precipitate crystallized from alcohol. The white plates which formed melted at 137–139°; yield, 4 g.

Anal. Subs., 0.1892: CO_2, 0.5837; H_2O, 0.1041. Calcd. for $C_{24}H_{20}O_2$: C, 84.7; H, 5.92. Found: C, 84.2; H, 6.12.



Diphenyldihydroanthroanthracenediol was prepared by the method of Haller and Guyot[2] from phenylmagnesium bromide and anthraquinone. Then 4.4 g. of it was refluxed for one hour with 2.2 g. of furfuryl alcohol and 20 cc. of acetic anhydride.

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[1] Quaker Oats Fellow, 1929–1930.

[2] Haller and Guyot, *Compt. rend.*, **138**, 327 (1904).

On cooling, needle crystals separated which, after recrystallization from alcohol, gave 0.5 g. of light cream-colored needles which melted at 223°. The analytical data were satisfactory for the monofurfuryl ether of the diol.

Anal. Subs., 0.1886: CO_2, 0.5763; H_2O, 0.0928. Calcd. for $C_{31}H_{24}O_3$: C, 83.8; H, 5.41. Found: C, 83.4; H, 5.47.

DEPARTMENT OF CHEMISTRY
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Note on the Preparation of Trialkyl Phosphates and their Use as Alkylating Agents

BY C. R. NOLLER AND G. R. DUTTON

Alkyl halides, sulfates, sulfites and sulfonates appear to be the best general alkylating agents known but because none of these classes of compounds is entirely satisfactory, it was considered desirable to investigate the use of other esters for this purpose. Preliminary experiments indicated that the alkyl borates, carbonates, nitrites and phosphites would be of no value, but the trialkyl phosphates showed some promise and were further investigated.

None of the various methods for preparing alkyl phosphates reported in the literature[1] proved as convenient as the reaction of phosphorus oxychloride with the alcohol in the presence of pyridine. This method is an adaptation of that used by Milobendski and Sachnovski[2] for the preparation of alkyl phosphites, in which benzene has been used as a solvent instead of ether and in which the pyridine hydrochloride is removed by adding water and removing the water layer instead of filtering off the solid pyridine hydrochloride.

In order to compare the various esters as alkylating agents a standard procedure was developed using one equivalent of alkylating agent per mole of phenol. This method was not devised for producing the maximum yiel

TABLE I

YIELDS OF PHOSPHATES AND PHENOL ETHERS

	Phosphates		Phenol Ethers	
Ester	% Yield	B. p., °C.	% Yield	B. p., °C.
Ethyl sulfate	..	....	73.0	168–170
Ethyl phosphate	51.7	104–107 (16 mm.)	21.6	167–170
n-Propyl phosphate	63.5	128–134 (15 mm.)	Not run	
n-Butyl phosphate	74.0	160–162 (15 mm.)	39.0	204–211
Sec.-butyl phosphate	44.0	119–129 (8–12 mm.)	18.7	188–198
n-Amyl phosphate	63.7	158–163 (6 mm.)	15.0	125–128 (25 mm.)

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[1] (a) Evans, Davis and Jones, *J. Chem. Soc.*, 1310 (1930); (b) Bannister, U. S. Patent 1,799,349 (1931); (c) Johnson, British Patent 330,228 (1930).

[2] Milobendski and Sachnovski, *Chemik Polski*, **15**, 34 (1917), [*Chem. Abs.*, **13**, 2865 (1919)].

of ether but for ease of controlling conditions so that the results would be comparable. This accounts for the fact that the yield of phenetole using ethyl sulfate is not as high as that reported by Cade.[3] The yields of phosphates and phenol ethers are given in Table I.

It should be noted that while the yields of phenol ethers from phosphates are low compared with that from the sulfate, they are based on the amount of alkyl radical available. Many of the higher yields from other esters reported in the literature are based on the substance being alkylated, using a large excess of alkylating agent.

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[3] Cade, *Chem. Met. Eng.*, **29**, 319 (1923).

CONTRIBUTION FROM THE
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COMMUNICATIONS TO THE EDITOR

PREPARATION OF KETENE DIETHYL ACETAL

Sir:

According to the communication of Snell and McElvain [THIS JOURNAL, **55**, 416 (1933)] these authors were unable to duplicate the preparation of ketene diethyl acetal described by me [Scheibler, Marhenkel and Nikolic, *Ann.*, **458**, 28 (1927)]. This preparation, however, has often been accomplished in my laboratory by several young chemists. The above failure may have been due to two causes. (1) The residue obtained from sodium ethoxide and ethyl acetate after removal of the volatile substances, containing the so-called "primary reaction product of the acetoacetic ester synthesis," may have lost alcohol during the treatment and been transformed into the sodium derivative of acetoacetic ester which, treated with water, of course did not give ketene acetal [Scheibler and Marhenkel, *Ann.*, **458**, 6, 18 (1927)].

The evaporation of ether and the excess ester must be performed quickly at low temperature under diminished pressure. It is not surprising that Snell and McElvain, who dried the residue in a vacuum desiccator over sulfuric acid until it attained a constant weight, only obtained sodioacetoacetic ester. The weight of the dry residue obtained by them from 23 g. of sodium was only 90–100 g. instead of 125 g. A small amount of ethyl acetate may remain in the residue and be quickly saponified when it is treated with water, in contrast with ketene acetal, which does not undergo any decomposition in aqueous alkaline solution.

(2) The authors may have used too much calcium chloride in shaking