[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

Difuryl Tetra-arylethanes

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The purpose of the present study was to determine whether the furan nucleus is effective in causing dissociation of the hexa-substituted ethanes.

***sym*-Tetraphenyl-di-2-furylethane.**—The diphenyl-2-furylcarbinol was prepared from ethyl furoate and was converted into the chloride by the action of thionyl chloride in the presence of a slight excess of pyridine, a method which had been used with success by Kirner[2] for the preparation of α-furfuryl chloride. The chloride proved to be very unstable and all attempts to isolate the compound failed. That the desired chloride was actually present in the solution, and in good quantity, was shown by the behavior of the solution under various conditions. Thus, addition of water gave back the original carbinol. The chloride in solution was also converted into a series of alkyl ethers by treatment with various alcohols in the presence of pyridine. This reaction had been used previously in the preparation of triphenylmethyl alkyl ethers.[3] On the basis of the carbinol used, the yields of the alkyl ethers were as follows: methyl 95%, ethyl 89%, *n*-propyl 44%, *i*-propyl 75%, benzyl 79%. As a check on the structures of these ethers, they were also prepared by refluxing diphenyl-2-furylcarbinol with the aliphatic alcohols and *p*-toluenesulfonic acid. The ethyl ether was also obtained from the tertiary chloride by the action of ethoxymagnesium iodide, as well as by the use of sodium ethylate. In accordance with the ether structure, these compounds gave no evidence of active hydrogen in the Grignard machine. These results demonstrated the formation of diphenyl-2-furylchloromethane in good yield, and the ether solutions in which the chloride was prepared were therefore used in the preparation of the ethane. This reaction was carried out by the action of mercury and lead powder or by the use of mercury alone[4] after the removal of the pyridine hydrochloride. The product of this reaction was shown by analysis and determination of molecular weight to be the ethane. Attempts to form the peroxide by the action of air or to cleave the molecule by low pressure hydrogenation failed. The compound was also stable toward sodium–potassium alloy.

Attempted Synthesis of *sym*-Tetraphenyl-di-2-(3,4,5-triphenylfuryl)-ethane.—Diphenyl-2-(3,4,5-triphenylfuryl)-carbinol was prepared by the action of phenylmagnesium bromide on benzoyltriphenylfuran. Both the ketone and the carbinol had been prepared previously by Dilthey and Putter[5] though their preparation of the carbinol differed from the one used here. The chloride prepared in benzene solution, when treated with methyl alcohol, gave a substance which gave the correct analysis for the methyl ether. The chloride prepared in ether, when treated with methyl alcohol or when shaken with mercury, gave diphenyl-2-(3,4,5-triphenylfuryl)-methane, identical with the compound prepared by the reduction of the carbinol with red phosphorus and iodine. Presumably the chloride in the ether solution containing thionyl chloride was reduced to the methane in the same manner that triphenylchloromethane in ether solution is reduced to triphenylmethane by the action of various metallic chlorides.[6] The benzene solution of the chloride was shaken with merucry, but no isolable product was obtained.

Tetra-*p*-biphenylyl-2-di-furylethane.—As in the previous case the trisubstituted methyl chloride could not be isolated but was identified by its conversion into the methyl ether. This methyl ether was also synthesized from the two alcohols. The compound obtained by the action of mercury on the chloride in ether solution gave the correct analysis and molecular weight for the ethane. The attempt to form the peroxide by the action of atmospheric oxygen failed.

Experimental

Diphenyl-2-furylchloromethane.—Five grams (0.02 mole) of freshly prepared diphenyl-2-furylcarbinol was placed in a 125 cc., three-necked flask with 80 cc. of dry ether and 1.74 cc. (0.022 mole) of pyridine. The flask contents were cooled to 0° with a freezing mixture bath, and 1.44 cc. (0.02 mole) of thionyl chloride in 15 cc. of dry ether were added from a dropping funnel over a period of thirty minutes. Stirring was continued for an additional thirty minutes, when the ether solution was filtered (to remove the pyridine hydrochloride) into a separatory funnel for use in further reactions.

Preparation of the Ethers from the Chloride.—The chloride as prepared above was added to a mixture of 20 cc. of absolute alcohol and 6 cc. of pyridine, and the solution was refluxed for from eleven to fifteen hours (two hours in the case of benzyl alcohol). The two layers were separated, and the reaction mixture was washed with water and a dilute solution of base, dried over sodium sulfate, and the ether was evaporated. The ethers were crystallized from alcohol. Molecular weights were determined by the freezing point lowering of benzene. Yields are based on the carbinol used in the reaction.

These ethers were also prepared by refluxing the two alcohols in a soxhlet extractor, using *p*-toluenesulfonic acid as the condensing agent, and placing calcium carbide in the thimble in order to remove the water. The melting points of the ethers prepared by the two methods were identical, and mixed melting points of the ethers obtained by the two methods showed no depressions.

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[1] This paper represents part of the thesis material submitted by Mr. Smith at the University of Missouri.

[2] Kirner, THIS JOURNAL, **50**, 1955 (1928).

[3] Helfrich, Speidel and Toeldte, *Ber.*, **56**, 766 (1923).

[4] Gomberg and Schoepfle, THIS JOURNAL, **39**, 1652 (1917).

[5] Dilthey and Putter, *J. prakt. Chem.*, **149**, 183 (1937).

[6] Gomberg, THIS JOURNAL, **35**, 204 (1913).

TABLE I

DIPHENYL-2-FURYLMETHYL ALKYL ETHERS

R	Yield, %	M. p., °C.	Molecular wt. Calcd.	Molecular wt. Found	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
CH_3—	95	108–108.5	264	260	81.81	6.06	81.50	6.14
C_2H_5—	89	107–108	278	277	82.01	6.47	81.70	6.59
n-C_3H_7—	44	106–107	292	288	82.19	6.85	82.09	6.90
i-C_3H_7—	75	85–86	292	287	82.19	6.85	81.95	6.96
$C_6H_5CH_2$—	79	89–90	340	336	84.70	5.88	84.73	6.08

The ethers were nearly white (slightly cream colored) crystalline solids and, when pure, were stable for several months.

The ethyl ether was also prepared by treating the ether solutions of the chloride with ethoxymagnesium iodide, and with sodium ethylate.

***sym*-Tetraphenyl-di-2-furylethane.**—An ether solution of diphenyl-2-furylchloromethane was placed in a dry flask previously filled with dry nitrogen, and containing 20 g. of mercury and 0.5 g. of lead powder. The flask was repeatedly evacuated and filled with pure nitrogen, then placed on the shaking machine for five hours. The solution was filtered, washed with dilute base and then with water. The ether solution was then evaporated, and the ethane crystallized from acetone. The yield, calculated from the carbinol used, was 75%; m. p. 149–150°.

Anal. Calcd. for $C_{34}H_{26}O_2$: C, 87.55; H, 5.58. Found: C, 87.65; H, 5.88. Mol. wt. by freezing point lowering of benzene: calcd. for the ethane 466; found 456.

Dry air was passed for several hours through a boiling benzene solution of the ethane. The ethane was recovered unchanged. Hydrogen at room temperature and at 3 atmospheres, using platinum oxide catalyst, was without effect, and the ethane was recovered.

3,4,5-Triphenyl-2-benzoylfuran was prepared by the method of Dilthey and Putter.[5]

Diphenyl-2-(3,4,5-triphenylfuryl)-carbinol.—This compound was prepared by the action of an ether solution of 3,4,5-triphenyl-2-benzoylfuran on phenylmagnesium bromide. The solution was refluxed for three hours, then hydrolyzed with ice and ammonium chloride. The carbinol was crystallized from acetone; white crystals, m. p. 179°; yield 70%.

Diphenyl-2-(3,4,5-triphenylfuryl)-chloromethane and Methyl Ether.—The chloride was prepared as described above, using benzene instead of ether as the solvent. Treatment with methyl alcohol and pyridine and refluxing for six hours gave the methyl ether. The yield, 10%, gave crystals from acetone–alcohol mixture, m. p. 204°.

Anal. Calcd. for $C_{36}H_{28}O_2$: C, 87.80; H, 5.69. Found: C, 87.62; H, 5.47.

Attempts to prepare the methyl ether from the two alcohols failed.

The preparation of the chloride was also attempted in ether solution. These ether solutions were shaken with mercury in the usual way, and others were treated with methyl alcohol. From all such reactions diphenyl-2-(3,4,5-triphenylfuryl)-methane was obtained in yields up to 90%: m. p. 183–184°.

Anal. Calcd. for $C_{35}H_{26}O$: C, 90.91; H, 5.63. Found: C, 90.91; H, 5.69.

The same compound was obtained by the reduction of the carbinol as follows. A mixture of 150 cc. of glacial acetic acid, 2.5 g. of red phosphorus, and 1.5 g. of iodine was permitted to stand for twenty minutes, when 5 cc. of water and 5 g. of diphenyl-2-(3,4,5-triphenylfuryl)-carbinol were added. After eight hours of boiling the hot solution was poured into a cold, well-stirred sodium bisulfite solution. The product was crystallized from acetone and chloroform mixture: m. p. 183–184°, yield 80%.

Di-*p*-biphenylyl-2-furylcarbinol.—To the Grignard solution from 23.3 g. (0.1 mole) of *p*-bromobiphenyl was slowly added 7 g. of ethyl furoate. After three hours of boiling the solution was hydrolyzed with ice and ammonium chloride. The carbinol was crystallized from petroleum ether (b. p. 60–70°): yield 70%; m. p. 149–150°.

Anal. Calcd. for $C_{29}H_{22}O_2$: C, 86.56; H, 5.47. Found: C, 86.26; H, 5.57.

Di-*p*-biphenylyl-2-furylchloromethane and Methyl Ether.—The chloride was prepared as described above, except that room temperature was used, and the solvent was a mixture of ether and benzene. The ether–benzene solution of the chloride was treated with methyl alcohol and pyridine in the usual manner: yield of the methyl ether 80%; m. p. 94–95°.

Anal. Calcd. for $C_{30}H_{24}O_2$: C, 86.54; H, 5.76. Found: C, 86.34; H, 6.01.

This ether was also prepared by refluxing the two alcohols, as described above.

***sym*-Tetra-*p*-biphenylyl-di-2-furylethane.**—The chloride in ether–benzene solution was shaken with mercury for seven hours. The solution was filtered and the solvent evaporated at room temperature. Acetone was added to precipitate the solid which was recrystallized from a mixture of benzene and petroleum ether: yield 80%; m. p. 203–204°. Molecular weight determined by freezing point lowering of benzene: calcd. for ethane 770; found 754. Dry air was passed through a boiling benzene solution of the ethane for several hours. The ethane was recovered unchanged.

Anal. Calcd. for $C_{58}H_{42}O_2$: C, 90.38; H, 5.46. Found: C, 90.10; H, 5.76.

Summary

1. *sym*-Tetraphenyl-di-2-furylethane and *sym*-tetra-*p*-biphenylyl-di-2-furylethane have been synthesized.

2. Determinations of molecular weight and the stability toward oxygen show these compounds to be undissociated.

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