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THE CONDENSATION OF FURAN AND SYLVAN WITH SOME CARBONYL COMPOUNDS[1]

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ABSTRACT

Furan and sylvan condense with aldehydes, chlorinated aldehydes and ketones, and keto acids, in the presence of hydrochloric acid. In most cases, the corresponding difurylalkane or difuryl-substituted acid is formed. In special cases the reaction stops at the furylcarbinol stage.

Difurylalkanes have been accessible, in the past, only through a variety of indirect approaches. Thus, for example, difurylmethane (V) has been prepared by Reichstein, Grussner, and Zschokke (7) by the reduction of difuryl ketone. Gilman and Wright (5) synthesized the same substance by the interaction of 2-chloromercurifuran and furfuryl chloride. Dinelli and Marini (3) treated ethyl furoate with trioxane in the presence of sulphuric acid. By subsequent saponification, hydrolysis, and decarboxylation they obtained difurylmethane. This compound has also been isolated as a product during the acid-catalyzed resinification of furfuryl alcohol (4, p. 222).

Recently, Ackman, Brown, and Wright (1) have reported the formation of 2,2-difurylpropane by the condensation of furan with acetone in the presence of hydrochloric acid. Other methyl ketones gave analogous products.

In the present investigation, it has been found that furan also condenses with aldehydes, chlorinated aldehydes and ketones, and keto acids. The condensation products are difurylalkanes in the case of aldehydes and ketones. With keto acids, the corresponding difuryl-substituted acids result. Chlorinated aldehydes and ketones, when condensed with furan, yield chlorinated difurylalkanes in some cases, while in others, unstable products, thought to be chlorinated furylcarbinols, are formed. Willard and Hamilton (8) have already reported the condensation of furan (I) with chloral (VIII) to form 1-furyl-2,2,2-trichloroethanol (IX).

The investigation also includes the reaction of sylvan (2-methylfuran) (II) with the carbonyl compounds previously cited. Analogous products are obtained.

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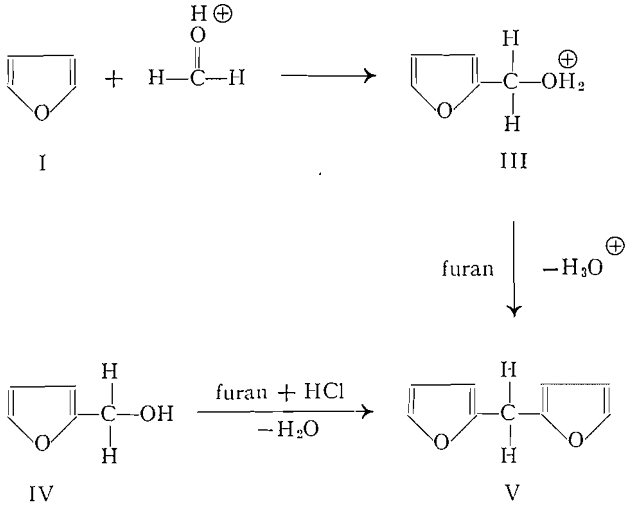
Tables I, II, and III show the specific carbonyl compounds concerned and data on the products formed.

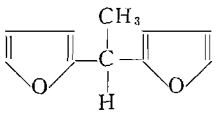
When furan (I) is treated with aqueous formaldehyde solution in the presence of hydrochloric acid, difurylmethane (V) is formed in low (1.7%) yield. The identity of the product was established by mercuration according to the method of Gilman and Wright (5). A mixture melting point of this mercurial with the mercurial of difurylmethane, the latter prepared by the procedure of Dinelli and Marini (3), showed no depression.

The proposed mechanism for the reaction is as follows:

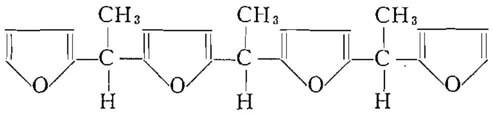


It seems likely that protonated furfuryl alcohol (III) is an intermediate in the reaction, since furfuryl alcohol (IV), when treated with furan in the presence of hydrochloric acid, forms difurylmethane (V) in increased (15%) yield. No apparent reaction occurs between furfuryl alcohol and furan in the absence of acid. Other acidic compounds might also serve as catalysts (8).

In the reaction of acetaldehyde with furan, two products, 1,1-difurylethane (VI) and 1,1-*bis*[5-(methylfurfuryl)-furyl]ethane (VII), can be isolated.



VI



VII

Here, again, the protonated furylcarbinol appears to be the intermediate, since 1,1-difurylethane (VI) is formed when methyl-furylcarbinol is treated with furan in the presence of hydrochloric acid.

Inspection of Table I shows that the yields of 1,1-disubstituted alkanes are

TABLE I

Condensation products of aldehydes with furan and sylvan

Reactants	Yield, %	B.p., ° C./mm.	$\eta_D^{t°}$	$d^{20°}_{4°}$	Molecular formula	Analysis	
						Calc.	Found
Furan and:							
Formaldehyde	1.7	79–81/12	1.4991/16	1.098	$C_9H_8O_2$		
Acetaldehyde	58	86–87/15	1.4993/20	1.073	$C_{10}H_{10}O_2$	C, 74.1; H, 6.21	C, 74.0; H, 6.05
	9.7	136–137/4	1.5218/20	1.105	$C_{22}H_{22}O_4$	C, 75.4; H, 6.33	C, 75.3; H, 6.44
Propionaldehyde	24	88–93/15	1.4930/20	1.047	$C_{11}H_{12}O_2$	C, 75.0; H, 6.87	C, 75.2; H, 7.33
Butyraldehyde	38	108/14	1.4890/20	1.015	$C_{12}H_{14}O_2$	C, 75.8; H, 7.42	C, 76.1; H, 7.58
Benzaldehyde	No reaction						
Furfural	No reaction						
Glyoxal	No reaction						
Sylvan and:							
Formaldehyde	34	114/15	1.5017/20	1.042	$C_{11}H_{12}O_2$	C, 75.0; H, 6.87	C, 75.6; H, 6.88
Acetaldehyde	61	113/12	1.4993/20	1.027	$C_{12}H_{14}O_2$	C, 75.7; H, 7.42	C, 75.8; H, 7.42
Propionaldehyde	63	118/14	1.4949/20	1.008	$C_{13}H_{16}O_2$	C, 76.4; H, 7.96	C, 76.8; H, 7.87
Butyraldehyde	73	132/15	1.4935/20	0.989	$C_{14}H_{18}O_2$	C, 77.0; H, 8.32	C, 77.0; H, 8.11

higher from sylvan than from furan. This points up the activating influence at the 2-position of an electron-donating group located on the 5-position of the furan nucleus (4, p. 27).

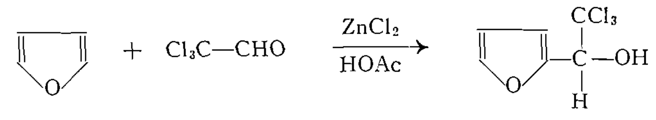
In Table II it may be seen that the presence of halogen in the carbonyl compound reduces the yield of the halogenated difurylalkane. The presence of an electron-donating group, such as methyl, either on the furan ring or in the carbonyl compound partially offsets the deactivating effect of chlorine in the carbonyl compound.

TABLE II

Condensation products of chlorinated aldehydes and ketones with furan and sylvan

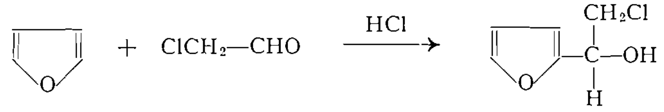
Reactants	Yield, %	B.p., °C./mm.	$\eta_D^{20°}$	$d^{20°}_{4°}$	Molecular formula	Analysis	
						Calc.	Found
Furan and:							
Chloroacetaldehyde		Decomposes			$C_6H_7O_2Cl$	Cl, 24.2	Cl, 22.3
Monochloroacetone	19	127–131/15	1.5208	1.170	$C_{11}H_{11}O_2Cl$	Cl, 16.9	Cl, 16.6
1,3-Dichloroacetone		Decomposes					
Sylvan and:							
Chloroacetaldehyde	11	142–144/14	1.5176	1.143	$C_{12}H_{13}O_2Cl$	Cl, 15.8	Cl, 15.7
Dichloroacetaldehyde		Decomposes					
Monochloroacetone	23	138–142/14	1.5160	1.115	$C_{13}H_{15}O_2Cl$	Cl, 14.9	Cl, 14.9
1,3-Dichloroacetone	5.2	175–179/14	1.5308	1.159	$C_{13}H_{14}O_2Cl$	Cl, 26.0	Cl, 26.0

As shown by Willard and Hamilton (8), when furan (I) reacts with chloral (VIII) in the presence of zinc chloride and glacial acetic acid, the product is 1-furyl-2,2,2-trichloroethanol (IX) in fair yield. The inductive effect of the halogens decreases the basicity of the oxygen and to some extent increases the C—O bond strength by forcing participation of the unshared electrons of oxygen in this bonding. Hence the OH becomes less likely to be protonated and thus less labile than in the unsubstituted cases.



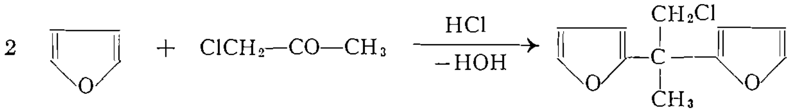
I VIII IX

In the case of some of the halogenated carbonyl compounds, the reaction with furan appears to have stopped at the carbinol stage. Thus, for example, furan (I) reacts with chloroacetaldehyde (X) to yield 1-furyl-2-chloroethanol (XI).



I X XI

However, when furan (I) and monochloroacetone (XII) are treated with hydrochloric acid the product of the reaction is 1-chloro-2,2-difurylpropane (XIII). Here the methyl group is able to overcome the inhibiting action of the chlorine atom.



I XII XIII

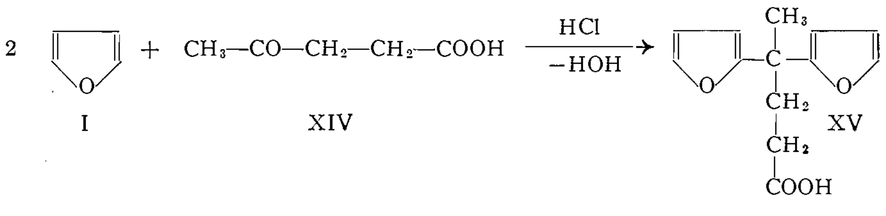
In the reaction of furan and sylvan with keto acids (Table III), some of the products are those which one would expect on the basis of normal reaction.

TABLE III

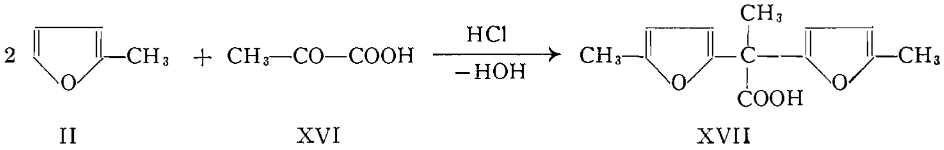
CONDENSATION PRODUCTS OF KETO ACIDS AND ESTERS WITH FURAN AND SYLVAN

Reactants	M.p., ° C.	B.p., ° C./mm.	Yield, %	Molecular formula	Analysis	
					Calc.	Found
Furan and:						
Levulinic acid	68.5–69.5	180–220/17	29	$C_{13}H_{14}O_4$	N.E., 234	N.E., 232
Pyruvic acid	Gave only resins					
Ethyl acetoacetate		140–170/17	11 wt. %			
Sylvan and:						
Levulinic acid	84–85	207–230/16	33	$C_{15}H_{18}O_4$	C, 68.7; H, 6.91 N.E., 262	C, 69.1; H, 6.76 N.E., 261
Pyruvic acid	110.5–111.5		68	$C_{13}H_{14}O_4$	C, 66.6; H, 6.02 N.E., 234	C, 66.8; H, 6.11 N.E., 231
Acetoacetic acid		135–210/3	36 wt. %			
Ethyl acetoacetate		170–220/16	43 wt. %			

Thus, for example, furan (I) reacts with levulinic acid (XIV) to form γ-*bis*(furyl)-valeric acid (XV).



While sylvan (II) reacts normally with pyruvic acid (XVI) to form α-*bis*(sylvyl)-propionic acid (XVII), furan reacts violently to yield a resinous product.



Both furan and sylvan react vigorously with ethyl acetoacetate in the presence of hydrochloric acid. The product in each case is an oil which does not lend itself readily to purification. These oils have not been investigated further.

Ackman, Brown, and Wright (1) prepared substituted tetroxaquaterenes by condensing difurylalkanes with the parent methyl ketones. In view of this, difurylmethane would be expected to condense with formaldehyde to form the unsubstituted tetroxaquaterene. Attempts to produce such a compound failed. When 1,1-difurylethane (VI) and 1,1-*bis*[5-(methylfurfuryl)-furyl]ethane (VII) were treated with acetaldehyde in the presence of hydrochloric acid, resinous products were formed. No tetroxaquaterene formation occurred.

EXPERIMENTAL

All melting points have been corrected against reliable standards. Molecular weights were determined by Rast method. For the sake of brevity, only a few of the preparations are reported in operational detail. It may be assumed that the products listed in Tables I, II, and III may be obtained by following the procedure outlined for preparing a homologue.

Difurylmethane (V)

(*a*) *From Furan and Formaldehyde*

Into a 2-liter three-necked round-bottom flask fitted with a stirrer were introduced 50 ml. of 20% hydrochloric acid and 190 ml. (2.5 moles) of 36% aqueous formaldehyde solution. While cooling externally with tap water (14° C.), 170 gm. (2.5 moles) of furan was added dropwise over a period of 30 min. After five hours the reaction mixture was neutralized with solid sodium carbonate and then steam distilled. The distillate was extracted with ether, and the ether solution washed with 28% aqueous ammonia solution to remove formaldehyde and then with water to remove ammonia. The ether solution, after being dried over anhydrous magnesium sulphate, was evaporated. The residual oil was distilled under diminished pressure giving 3.10 gm. (1.7%) of a colorless oil, b.p. 79–81° C. (13 mm. Hg); $\eta_D^{16°}$ 1.4991; $d_{4°}^{20°}$ 1.098. Physical constants reported for difurylmethane (4, p. 78) are: b.p. 78° (12 mm. Hg); $\eta_D^{20°}$ 1.5049; $d_{4°}^{20°}$ 1.102.

(*b*) *From Furan and Furfuryl Alcohol*

In a 125 ml. Grignard-type flask, fitted with a stirrer, were placed 17 gm. (0.25 mole) of furan, 24.5 gm. (0.25 mole) of furfuryl alcohol, and 5 ml. of 37% hydrochloric acid. The mixture was cooled to 13° C. and stirred vigorously for four hours at this temperature. When the reaction mixture was worked up according to the procedure outlined in (*a*), 5.65 gm. (15%) of a colorless oil was obtained. This oil had identical physical constants with the oil described in (*a*).

Both oils were shown to be identical by mixture melting point of their mercurials, m.p. 149.5°, prepared by the method of Gilman and Wright (5). A mixture melting point of these mercurials with the mercurial of difurylmethane, m.p. 149.5°, the latter prepared by the procedure of Dinelli and Marini (3), showed no depression.

1,1-Difurylethane (VI)

(*a*) *From Furan and Methyl-furylcarbinol*

To 0.2 mole of methyl-furylcarbinol Grignard complex, prepared *in situ* by the method of Peters and Fischer (6), was added 17 gm. (0.25 mole) of furan. The ice-cold mixture was stirred while 100 ml. of water was added, and the resulting mixture treated with 37% hydrochloric acid until 5 ml. were in excess. After it had been stirred for two and one-half hours the reaction mixture was neutralized with solid sodium carbonate and steam distilled. The oil obtained by this procedure distilled at 84–87° C. (15 mm. Hg), and weighed 7.3 gm. (22%); $\eta_D^{20°}$ 1.5003; $d_{4°}^{20°}$ 1.072.

(*b*) *From Furan and Acetaldehyde*

In a 250 ml. Grignard-type flask, fitted with a stirrer, were placed 20 ml. of 37% hydrochloric acid, 20 ml. of water, and 136 gm. (2.0 mole) of furan. After the flask had been cooled externally with tap water at 15° C., 44 gm. (1.0 mole) of acetaldehyde was added dropwise over a period of 100 min. Stirring at 15° C. was continued for 17 hr. At the end of this time, 200 ml. of water was added to the mixture which was then made alkaline by the addition of saturated sodium bicarbonate solution. After it was extracted with 200 ml. of ether, the ether solution was separated, washed with 100 ml. of water, and dried over anhydrous sodium sulphate. After the ether was flashed off, the residual brown oil was fractionated in a column as described by Bower and Cooke (2). The first fraction was a colorless oil weighing 94.5 gm. (58%) and boiling at 86–87° C. (15 mm. Hg); $\eta_D^{20°}$ 1.4993; $d_{4°}^{20°}$ 1.073. Anal. Calc. for $C_{10}H_{10}O_2$ (162.18): C, 74.1; H, 6.21. Found: C, 74.0; H, 6.05.

It is important that the order of addition of reagents to the flask be as indicated. If the acetaldehyde is mixed with the acid, and furan added subsequently, paraldehyde is the chief product.

1,1-bis[5-(Methylfurfuryl)-furyl]ethane (VII)

A second fraction from the preceding distillation, a pale yellow oil, boiled at 136–137° C. (3–4 mm. Hg). It weighed 11.3 gm. (9.7%); $\eta_D^{20^\circ}$ 1.5218; $d^{20^\circ}_{4^\circ}$ 1.105. Anal. Calc. for $C_{22}H_{22}O_4$: C, 75.4; H, 6.33; mol. wt., 350. Found: C, 75.3; H, 6.44; mol. wt., 330.

1-Chloro-2,2-difurylpropane (XIII)

In a 250 ml. Grignard-type flask, fitted with a stirrer, were placed 34 gm. (0.5 mole) of furan, 23 gm. (0.25 mole) of monochloroacetone, and 10 ml. of 20% hydrochloric acid. The mixture was stirred for 55 hr. at 20° C. A greenish viscous mass formed. After it was neutralized with solid sodium carbonate the mixture was steam-distilled. The colorless oil obtained in this manner distilled at 127–128° C. (15 mm. Hg). It weighed 10.0 gm. (19%) and had $\eta_D^{20^\circ}$ 1.5208; $d^{20^\circ}_{4^\circ}$ 1.170. Anal. Calc. for $C_{11}H_{11}O_2$ Cl (210.60): Cl, 16.9. Found: Cl, 16.6.

α-bis(Sylvyl)-propionic acid (XVII)

In a 250 ml. Grignard-type flask, fitted with a stirrer, were placed 22 gm. (0.25 mole) of pyruvic acid, 41 gm. (0.50 mole) of sylvan, and 5 ml. of 37% hydrochloric acid. The mixture evolved heat and was cooled to 11° C. while stirring for two hours, at which time it was partially neutralized with sodium carbonate. A solid weighing 40 gm. (68%) formed.

The acid was difficult to purify, but repeated crystallization from acetone–hexane gave light brown cubes, m.p. 110.5–111.5° C. Anal. Calc. for $C_{13}H_{14}O_4$: C, 66.6; H, 6.02; N.E., 234. Found: C, 66.8; H, 6.11; N.E., 231.

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REFERENCES

1. Ackman, R. G., Brown, W. H., and Wright, G. F. J. Org. Chem. 20: 1147. 1955.
2. Bower, J. R. and Cooke, L. M. Ind. Eng. Chem. 15: 290. 1943.
3. Dinelli, D. and Marini, G. B. Gazz. chim. ital. 67: 312. 1937; Chem. Abstr. 32: 154. 1938.
4. Dunlop, A. P. and Peters, F. N. The furans. Reinhold Publishing Corporation, New York. 1953.
5. Gilman, H. and Wright, G. F. J. Am. Chem. Soc. 55: 3302. 1933.
6. Peters, F. N. and Fischer, R. J. Am. Chem. Soc. 52: 2079. 1930.
7. Reichstein, T., Grussner, A., and Zschokke, H. Helv. Chim. Acta, 15: 1066. 1932.
8. Willard, J. R. and Hamilton, C. S. J. Am. Chem. Soc. 73: 4805. 1951.