formed V, which was then recrystallized from methanol m.p. 175–176°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3. Found: C, 73.3; H, 5.4.

2-Amino-6-methoxybiphenyl, VI. Schmidt degradation of V was carried out according to the directions of Briggs and Lyttleton.[9] Concentrated sulfuric acid (0.15 ml.) was added to a mixture of 0.4 mmoles of V, 0.5 ml. of about 1*N* HN_3 in $CHCl_3$, and 1 ml. of $CHCl_3$ and the mixture was stirred until the evolution of gas had ceased. By treating the reaction mixture as described above a yellow oil was isolated being 2-amino-6-methoxybiphenyl, VI. It showed a positive reaction with Duke's reagent for primary amines. It was benzoylated by means of benzoyl chloride and pyridine to form a benzoate m.p. 106–107°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: N, 4.6. Found: N, 4.5.

2,6-Dihydroxybiphenyl, VII. 2-Amino-6-methoxybiphenyl, VI, was diazotized and the diazonium salt decomposed in the usual way. By distillation 2-hydroxy-6-methoxybiphenyl could be isolated in the form of a yellowish oil which was cleaved by refluxing with a mixture of HBr (d = 1.38) and glacial acetic acid for 3 hr. to give white crystals of 2,6-dihydroxybiphenyl, VII, which recrystallized from a mixture of ether and ligroin. M.p. 118.5–119.5°, undepressed on admixture with the saponified rearrangement product. Identity was further proved by paper chromatography.

Acknowledgment. The authors wish to thank Prof. Dr. F. Wessely for his interest and helpful suggestions.

II. CHEMISCHES INSTITUT
UNIVERSITÄT WIEN
VIENNA, AUSTRIA

---

[9] L. H. Briggs and J. W. Lyttleton, *J. Chem. Soc.* 421 (1943).

Reactions of Several 4-Pyrones Catalyzed by Potassium Acetate and Trifluoroacetic Acid

L. L. WOODS[1] AND P. A. DIX

Received January 13, 1959

In a previous communication[2] the reaction of aryl aldehydes with 2,6-dimethyl-4-pyrone in the presence of potassium hydroxide was described. The product in each of the cases reported was a vinyl derivative.

This Note is, in part, the description of the reaction of aryl aldehydes with 4-pyrones, some of which are methylated at positions 2 and 6, whereas others have these positions open or blocked with other groups. The only common denominator in the pyrones used in these experiments is that position 3 is unoccupied.

Since none of the various pyrones failed to react with the aryl aldehydes under the influence of fused potassium acetate, the point of ring attachment to form a secondary alcohol was probably position 3. The infrared absorption spectrum of the simplest compound of the I series (I_G), gives an absorption band at 3502 cm.$^{-1}$ indicating the presence of a hydroxyl radical. Chromanone formed unsaturated derivatives due to the presence of an extra ring hydrogen in position 3, which made possible the elimination of water. The compounds formed by the reaction of 4-pyrones with aldehydes under the catalytic influence of potassium acetate are given as I_{A-I} series of Table I.

A part of the study of the effect of certain catalysts on the reactive nature of 4-pyrones was the examination of the use of trifluoroacetic acid with acylating compounds on such substances.

It was found that the use of trifluoroacetic acid as a solvent would permit acyl halides to react with 4-pyrones in a clean reaction giving good yields in a short reaction time. The product was not contaminated with large amounts of polymeric substances as was encountered in some of the preparations by the zinc chloride method.[2,3]

Benzoylation of kojic acid diacetate gave the compound II_B which was quite different in its physical constants from 2-acetoxymethyl-5-acetoxy-6-benzoyl-4-pyrone which had been prepared earlier.[4] The fact that these two compounds are different means that the point of the attachment of the benzoyl group to the pyrone ring is position 3 when kojic acid diacetate is acylated under the influence of trifluoroacetic acid.

In order to prove that II_B has the benzoyl group in position 3 it was postulated that such a compound would form a pyronopyrone[5] under the rearranging and cyclizing influence of fused potassium acetate and acetic anhydride, since no such compound should be formed from 2-acetoxymethyl-5-acetoxy-6-benzoyl-4-pyrone.

Unfortunately the cyclized product from II_B was a liquid. Efforts to purify the compound by distillation have been unsuccessful.

Compound II_F has been reported previously[6] elsewhere but the method gave a polymeric mixture. The above procedure gave superior results in every respect.

Compound II_C was chosen as representative of the II_{A-G} series so the malononitrile derivative and the 2,4 dinitrophenylhydrazone of the pyridone of II_C were prepared as proof of the ketonic nature of the substances formed during the reaction.

EXPERIMENTAL[7]

Preparation of compounds of I_{A-I} series. One-tenth mole of the aldehyde was mixed with 0.1 mole of the pyrone and 0.1 mole of powdered fused potassium acetate in a 500-ml. flask and the mixture was heated for 2 hr. at 120–130° in a

---

[1] The person to whom all communications concerning this article are to be directed.

[2] L. L. Woods, *J. Am. Chem. Soc.*, **80**, 1440 (1958).

[3] L. L. Woods, *J. Org. Chem.*, **22**, 341 (1957).

[4] L. L. Woods, *J. Am. Chem. Soc.*, **74**, 1105 (1952).

[5] L. L. Woods, *J. Org. Chem.*, submitted for publication.

[6] L. L. Woods, *Texas Jour. Sci.*, **11**, 28 (1959).

[7] All analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J. All melting points were determined on a Fisher-Johns apparatus.

TABLE I

Sample No.	Pyrone	Aldehyde	M.P.	Crude Yield, %	Formula	Calculated Carbon	Calculated Hydrogen	Calculated Nitrogen	Calculated Chlorine	Found Carbon	Found Hydrogen	Found Nitrogen	Found Chlorine
I_A	Chromanone[a]	Benzaldehyde	105–106	78	$C_{16}H_{12}O_2$	79.61	5.59			79.53	5.39		
I_B	Chromanone	*m*-Nitrobenzaldehyde	145–146	100	$C_{16}H_{11}NO_4$	68.32	3.94	4.98		68.01	4.14	4.72	
I_C	Kojic acid	Benzaldehyde	158	100	$C_{13}H_{12}O_5$	62.90	4.46			63.44	4.67		
I_D	α-Chloro-α-deoxy-kojic acid	Benzaldehyde	188.5	100	$C_{13}H_{11}ClO_4$	58.52	4.15		13.29	58.14	3.89		12.89
I_E	2,6-Dimethyl-4-pyrone	Salicylaldehyde	244–dec.	65	$C_{14}H_{14}O_4$	68.28	5.73			68.06	5.49		
I_F	Chromanone	Salicylaldehyde	156–157	90	$C_{16}H_{12}O_3$	76.17	4.43			76.08	4.25		
I_G	2,6-Dimethyl-4-pyrone	*m*-Nitrobenzaldehyde	95	74	$C_{14}H_{13}NO_5$	61.08	4.76	5.08		60.88	4.55	5.37	
I_H	Chromanone	*o*-Chlorobenzaldehyde	115–116	69	$C_{16}H_{11}ClO_2$	70.98	4.09		13.09	70.79	4.09		13.21
I_I	Chromanone	Phthalic anhydride	229	91	$C_{17}H_{12}O_5$	68.91	4.08			68.70	4.22		

[a] Benzodihydropyrone.

TABLE II

Sample No.	Pyrone	Acyl Derivative Used	Crude Yield, %	M.P.	Formula	Calculated Carbon	Calculated Hydrogen	Calculated Sulfur	Calculated Chlorine	Found Carbon	Found Hydrogen	Found Sulfur	Found Chlorine
II_A	Kojic acid diacetate	*p*-Tolyl chloride	100	115–116	$C_{18}H_{16}O_7$	62.78	4.68			62.84	4.55		
II_B	Kojic acid diacetate	Benzoyl chloride	83	143	$C_{17}H_{14}O_7$	61.81	4.27			61.59	4.20		
II_C	2,6-Dimethyl-4-pyrone	Benzoyl chloride	93	98	$C_{14}H_{12}O_3$	73.67	5.29			73.35	5.09		
II_D	Chromanone	Benzoyl chloride	91	97–98.5	$C_{16}H_{12}O_3$	76.17	4.79			76.34	4.58		
II_E	Kojic acid diacetate	Acetyl chloride	50	138	$C_{12}H_{12}O_7$	53.73	4.50			53.38	4.58		
II_F	2,6-Dimethyl-4*H*-pyran-4-thione	Benzoyl chloride	100	96–97	$C_{14}H_{12}SO_2$	68.82	4.94	13.12		68.42	4.70	13.46	
II_G	2-Chloromethyl-5-acetoxy-4-pyrone	Benzoyl chloride	43	103–104	$C_{15}H_{11}ClO_5$	58.74	3.61		11.56	58.38	3.64		11.91

Fisher Hi-Temp oil bath. The resulting melt was diluted with about 100 ml. of water to which 10 ml. of concentrated hydrochloric acid had been added, chilled and filtered. The purified compound was obtained by recrystallizing the crude product twice from absolute ethanol or heptane. Compound I_I was prepared by heating the melt at the above temperature for 21 hr.

Preparation of the phenacyl derivative of I_I. One g. of I_I and 0.5 g. of sodium bicarbonate were mixed in 5 ml. of water. When the reaction had subsided 40 ml. of absolute ethanol and 1 g. of phenacyl bromide were added. The mixture was refluxed for 1 hr. and then poured into about 200 ml. of water containing 10 ml. of concentrated hydrochloric acid. The precipitate was filtered off, dried in air, and recrystallized twice from absolute ethanol, m.p. 229–231°.

Anal. Calcd. for $C_{25}H_{18}O_6$: C, 72.45; H, 4.37. Found: C, 72.64; H, 4.15.

Preparation of compounds of II_{A-G} series. One-tenth mole of the pyrone was dissolved in 25 ml. of redistilled trifluoroacetic acid; to this mixture was added, all at once, 0.1 mole of the acyl halide. After thoroughly mixing the reactants the mixture was refluxed for 1 hr., during which time large volumes of hydrogen chloride were evolved.

The reaction product, usually of a brown or purple color, was poured into about 150 ml. of water. The crystallized compound was filtered off, dried in air, and recrystallized several times from absolute ethanol or from boiling heptane.

Bis-malononitrile derivative of II_C. One g. of II_C was mixed with 10 ml. of acetic anhydride along with about 800 mg. of malononitrile, and the resulting solution was refluxed for 1 hr. The brown solution when poured into water precipitated a dark compound which when recrystallized twice from heptane melted at 193–194°.

Anal. Calcd. for $C_{20}H_{12}N_4O$; N, 17.27. Found: N, 17.02.

2,4-Dinitrophenylhydrazone of pyridone of II_C. Six g. of II_C was dissolved in 50 ml. of absolute ethanol and then 10 ml. of concentrated ammonium hydroxide solution was added. The solution was chilled overnight in the refrigerator. A yellow precipitate of the pyridone was obtained, 2 g. of which were reacted with 2 g. of 2,4-dinitrophenylhydrazine in 100 ml. of boiling absolute ethanol. The solution was filtered after 5 min. Cooling the solution permitted an orange precipitate to collect. The compound was recrystallized once from ethanol, m.p. 201–202°.

Anal. Calcd. for $C_{20}H_{17}N_5O_5$: N, 17.20. Found: 17.34.

Acknowledgment. The authors wish to acknowledge with thanks the financial support of this research project by the Robert A. Welch Foundation.

TEXAS SOUTHERN UNIVERSITY
HOUSTON 4, TEX.

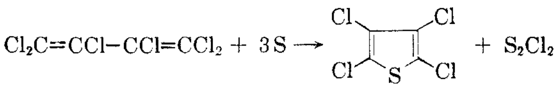
New Synthesis of Tetrachlorothiophene

EMIL J. GEERING

Received January 15, 1959

Tetrachlorothiophene has heretofore been prepared by the chlorination of thiophene, by methods involving the dehydrochlorination or dechlorination of one or more chlorine-addition intermediates.[1]

In the synthesis described herein,[2] tetrachlorothiophene is prepared by the interaction of hexachlorobutadiene and elemental sulfur. Formation of the thiophene ring is effected by replacement of two of the terminal chlorine atoms of hexachlorobutadiene by sulfur. The chlorine appears as sulfur monochloride. Both products are produced in essentially quantitative yields as defined by the following stoichiometry.



EXPERIMENTAL

A solution of 11,740 g. (45 moles—200% excess) of hexachlorobutadiene and 1443 g. (45 moles) of sulfur was heated at reflux (205–240°) under a 100 cm. distillation column packed with $^1/_8$ inch glass helices. As sulfur monochloride formed it was removed at the top of the column. During 13 hr. 1946 g. (14.4 moles) of sulfur monochloride was distilled off. The system was then put under 7.8 mm. of vacuum and after the excess hexachlorobutadiene containing some tetrachlorothiophene was removed, 2704 g. (12.2 moles, 81% yield) of tetrachlorothiophene was taken off at 91–94°. The latter portion of this fraction gave the following analysis.

Anal. Calcd. for C_4Cl_4S: Cl, 63.91; S, 14.45. Found: Cl, 63.7; S, 14.4.

The total yield of tetrachlorothiophene as calculated from infrared analysis of all distillation fractions was 99%. The product melted at 29.5–29.7° after crystallization from methanol.

In a second experiment the excess of hexachlorobutadiene was reduced to 10%. The sulfur was added in portions to the hexachlorobutadiene during the reaction in order to avoid the presence of undissolved sulfur. In this case the product was redistilled to remove traces of sulfur chloride. A 94.1% yield of tetrachlorothiophene was obtained, of which 76% was isolated as 99.5–99.7% pure product.

HOOKER CHEMICAL CORPORATION
RESEARCH AND DEVELOPMENT DEPARTMENT

---

[1] H. D. Hartough, *Thiophene and its Derivatives*, (The Chemistry of Heterocyclic Compounds series, A. Weissberger, ed.) Interscience Publishers, Inc., New York, 1952, pp. 180, 185.

[2] Further experimental data are included in a pending U. S. patent.

Studies in *p*-Cymene, IV. Some *N,N'*-Diarylthioureas

JOSEPH N. LECONTE[1a] AND WILLIAM N. CANNON[1b]

Received January 20, 1959

This study is a continuation of the work of LeConte and Chance[2] for the purpose of preparing new *N,N'*-diarylthioureas to be used in the antici-

---

[1] (a) Present address: East Carolina College, Greenville, N. C. (b) An abstract of a thesis submitted by William N. Cannon to the Graduate School, University of Georgia, in partial fulfullment of the requirements for the degree of Master of Science. Present address: Eli Lilly & Co., Indianapolis, Ind.

[2] J. N. LeConte and L. P. Chance; *J. Am. Chem. Soc.*, **71**, 2240 (1949).