ester (1.00 g.) melted at 100–101°, and remelted at 99.5–100.5°, $[\alpha]_D$ +93.5° (2% in ethanol). No O–H stretching band was observed in the region of 3 μ in its infrared spectrum.

Anal. Calcd. for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.55; H, 9.38.

Acknowledgment.—The authors wish to express their appreciation to L. E. Brown, Analytical, Physical-Chemical and Physics Section, Southern Utilization Research and Development Division, for the elemental analyses reported in this manuscript.

OLUSTEE, FLORIDA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEXAS SOUTHERN UNIVERSITY]

Some Further Reactions of 2,6-Dimethyl-4-pyrone

BY L. L. WOODS

RECEIVED OCTOBER 12, 1957

Continuing the investigation of the fundamental chemical nature of the mononuclear 4-pyrones, we are reporting two new reactions of 2,6-dimethylpyrone and an expansion of a previously published[1] reaction on the same compound.

Boon[2] and co-workers have been able to condense aromatic aldehydes with the methyl groups of 2,6-dimethyl-4-pyrone to give bis-(arylmethylenes) and efforts in this Laboratory to adapt the method to produce mono-(arylmethylenes) failed.

The condensation of aldehydes with methylated polynuclear 4-pyrones reported by Schönberg[3] and his co-workers failed with 2,6-dimethyl-4-pyrone, the aldehyde always being recovered.

Good yields of mono-(arylmethylene) derivatives of 2,6-dimethyl-4-pyrone were finally obtained simply and in good yield using potassium hydroxide as the condensing agent (Table I).

Chlorination of the mono-(arylmethylene) derivatives with sulfuryl chloride caused addition of two atoms of chlorine except with Id from piperonal which gave a trichloride by concurrent addition and substitution.

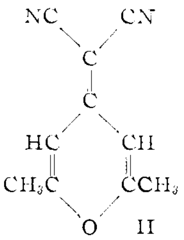
The recent publication of Mustafa[4] in which the condensation of two molecules of polynuclear 2-aryl-1,3-benzoxaz-4-thiones was reported, suggested the reaction of malononitrile with 2,6-dimethyl-4-pyrone which gave 4-(dicyanomethylene)-4H-pyran (II) in excellent yield.

Malononitrile was selected in preference to other compounds with active methylenes to remove the oxygen of the pyrone carbonyl since it does not react with acetic anhydride, or with any group of the dimethylpyrone other than the carbonyl oxygen. The nitrile thus produced is easily hydrolyzed to the dibasic acid, characterized by the diphenacyl derivative.

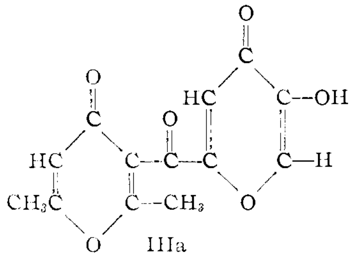
In a previous publication[1] the acylation of 2,6-dimethyl-4-pyrone with an aromatic acid in the presence of zinc chloride at the temperature of boiling xylene was described. This reaction has been extended to produce a few derived pyrones (IIIa-d). With succinic acid, cyclization rather than diketone formation occurred to yield a furan (IIIb). The diketone from levulinic acid also reacted further to give IIIc, a cyclic ketone containing a 7-membered ring.

The pyrone carbonyl of 2,6-dimethyl-4-pyrone and of compounds IIIb, IIIc and IIId is unaffected by potassium borohydride, but the expected reduction of the reactive carbonyl of the last three occurred. 2,6-Dimethyl-3-comenyl-4-pyrone (IIIa) failed to give a recognizable product.

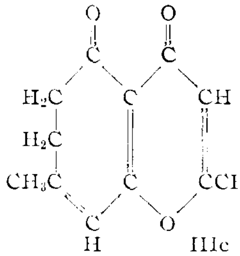
Infrared data are given for compounds II, IIIa and IIIc.



II



IIIa



IIIc

Experimental[5]

Preparation of Compounds Ia–d.—A solution of 2 g. of potassium hydroxide in 50 ml. of absolute methanol was treated with 0.05 mole (6.2 g.) 2,6-dimethyl-4-pyrone and 0.05 mole of the aldehyde and allowed to stand at room temperature for 24 hours. The solid or semi-solid, was broken up, poured into 250 ml. of water containing 10 ml. of concentrated hydrochloric acid and the precipitated material was collected, air-dried then recrystallized from absolute ethanol. Physical properties and analytical data for this series are given in Table I.

Chloro Derivatives of Ia–d.—One gram of the crude compound was treated with 5 ml. of sulfuryl chloride at room temperature. The vigorous reaction was complete within 10 minutes and the complex was then broken up by adding 50 ml. of water. The yellow or orange solid was collected, dried in air, and recrystallized from absolute ethanol (boiling heptane with the chloro derivative of Id). Table II contains physical properties and analytical data for this series.

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(1) L. L. Woods, *J. Org. Chem.*, **22**, 341 (1957).

(2) A. A. Boon, K. J. McKinzie and J. Trotter, *Proc. Chem. Soc.*, **30**, 205 (1914).

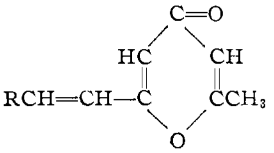
(3) (a) A. Schönberg, M. M. Sidky and G. Aziz, THIS JOURNAL, **76**, 5115 (1954); (b) A. Schönberg, A. E. K. Fateen and E. M. A. Sammour, *ibid.*, **78**, 4689 (1956).

(4) Ahmed Mustafa and A. E. A. A. Hassin, *ibid.*, **79**, 3846 (1957).

(5) All analyses and molecular weight determinations were made by Dr. Carl Tiedcke. Melting points were taken on a Fisher-Johns melting point assembly.

TABLE I

MONO-(ARYLMETHYLENE) DERIVATIVES OF 2,6-DIMETHYL-4-PYRONE



	$\mathrm{R\overset{\overset{O}{\|}}{C}{-}H}$	Yield, %	M.p., °C.	Empirical formula	Analyses, % Calculated C	H	N	Found C	H	N
Ia	Furfural	57	204–205	$C_{12}H_{10}O_3$	71.27	4.98		70.98	4.84	
Ib	*m*-Nitrobenzaldehyde	100	Softens above 158, melts 166–169	$C_{14}H_{11}NO_4$	65.36	4.31	5.44	65.07	4.08	5.74
Ic	*o*-Chlorobenzaldehyde	84	Softens above 185, melts 190–192	$C_{14}H_{11}ClO_2$	68.16	4.49		67.94	4.70	
Id	Piperonal	73	226–230 dec.	$C_{15}H_{12}O_4$	70.30	4.72		70.12	4.94	

TABLE II

CHLORO DERIVATIVES OF Ia-d SERIES

Compd.	Color	M.p., °C.	Empirical formula	Chlorine, % Calcd.	Found
Ia	Brown	Darkens and softens above 86, dec. above 103	$C_{12}H_{10}Cl_2O_3$	25.96	26.45
Ib	Yellow	Darkens rapidly above 156, dec. above 179	$C_{14}H_{11}Cl_2NO_4$	21.60	21.28
Ic	Orange	Softens above 155, melts with dec. 184–189	$C_{14}H_{11}Cl_3O_2$	33.49	33.70
Id	Orange	Softens above 100, melted at 108–110 and resolidified to a solid	$C_{15}H_{11}Cl_3O$	29.41	29.68

TABLE III

ACYLATION OF 2,6-DIMETHYL-4-PYRONE WITH ACIDS

	Product	Acid	Yield, %	M.p., °C.	Empirical formula	Carbon, % Calcd Found	Hydrogen, % Calcd. Found
IIIa	2,6-Dimethyl-3-comenyl-4-pyrone	Comenic	71	Dec. above 276	$C_{13}H_{10}O_6$	59.56 59.19	3.84 3.54
IIIb	2,5-Bis-(2,6-dimethyl-4-oxo-4H-pyran-3yl)-furan	Succinic	58	198–199.5	$C_{18}H_{16}O_5$[a]	69.22 68.94	5.16 5.34
IIIc	8-Oxa-5,9-dimethylbicyclo[5.4.0]-undeca-1(7),5,9-triene-2,11-dione	Levulinic	100	187–190	$C_{12}H_{12}O_3$[b]	70.67 70.23	5.92 5.52
IIId	3,3′-Phthaloyl-bis-(2,6-dimethyl-4-pyrone)	Phthalic	99	Softens above 178, melts 193–195	$C_{22}H_{18}O_6$	69.83 69.49	4.79 4.56

[a] Mol. wt. calcd., 312.3; found (Rast camphor): 307, 311, 298, 295. [b] 2,4-Dinitrophenylhydrazone, prepared as given for 2,6-dimethyl-3-acetyl-4-pyrone.[1] *Anal.* Calcd. for $C_{18}H_{17}N_5O_5$: N, 18.26. Found: N, 18.63.

Reaction of Malononitrile with 2,6-Dimethyl-4-pyrone (II).—Three and three-tenths grams of malononitrile (0.05 mole), 6.1 g. of 2,6-dimethyl-4-pyrone and 25 ml. of acetic anhydride were heated under reflux for 45 minutes. The unreacted acetic acid was aspirated off and the residue was washed with 50 ml. of boiling water and collected to give 7.2 g. of soft brown material. Recrystallization from boiling heptane produced a brown powder which sublimed above 180° and melted 190–192°.

Anal. Calcd. for $C_{10}H_8N_2O$: C, 69.58; H, 4.91; N, 16.41. Found: C, 69.75; H, 4.68; N, 16.27.

Hydrolysis of II.—Three and five-tenths grams of II was heated under reflux for 24 hours in a mixture of 20 ml. of ethanol and 20 ml. of concentrated hydrochloric acid and poured into water. A greenish-yellow solid (2 g.) was recovered which when recrystallized from absolute ethanol gave IIa, a brown powder, m.p. 259.5–261°.

Anal. Calcd. for $C_{10}H_{10}O_5$: C, 57.14; H, 4.79. Found: C, 57.32; H, 4.34.

The Diphenacyl Derivative of IIa.—The filtrate from the above recrystallization was treated with 1 g. of sodium bicarbonate, 5 ml. of water, 20 ml. of ethanol and 1 g. of phenacyl bromide. The mixture was heated under reflux for 90 minutes and poured into a large volume of water. The brown precipitate was dried and recrystallized once from absolute ethanol and then from boiling heptane, m.p. 186–188°.

Anal. Calcd. for $C_{26}H_{22}O_7$: C, 69.94; H, 4.96. Found: C, 69.69; H, 4.71.

Acylation of 2,6-Dimethyl-4-pyrone Series IIIa–d.—A mixture of 12.4 g. (0.1 mole) of 2,6-dimethyl-4-pyrone, 30 g. of fused zinc chloride, 100 ml. of xylene and 0.1 mole of comenic acid or 0.05 mole, respectively, of succinic acid, levulinic acid or phthalic acid was heated under reflux for 24 hours. The xylene was decanted from the cooled mixture and the dark residue was heated with 100 ml. of water containing 20 ml. of concentrated hydrochloric acid. The acylated pyrone was collected from the cooled mixture and dried in air.

Purification was effected by recrystallization several times from absolute ethanol or dioxane; IIIa was crystallized several times from dioxane containing three or four drops of concentrated hydrochloric acid. Table III lists physical properties and analytical data on this series.

Reduction of IIIa–d Series with Potassium Borohydride.—The general method consisted of heating 2 g. of the crude substance in 50 ml. of absolute methanol until no more of the compound appeared to dissolve, filtering off any residue and then adding 3 g. of potassium borohydride to the cooled filtrate. After the initial reaction had subsided the flask was stoppered loosely and allowed to stand overnight. The mixture was then made acid with 10 ml. of hydrochloric acid, diluted with 150 ml. of water and extracted with two 100-ml. portions of benzene. The benzene was dried over anhydrous sodium sulfate and allowed to evaporate. The product was repurified by sublimation. A sample of 2,6-dimethyl-4-pyrone was run through this procedure as a control. No reduction was observed. Table IV lists physical properties and analytical data on this series of substances.

TABLE IV

REDUCTION WITH POTASSIUM BOROHYDRIDE

	M.p., product, °C.	Yield, %	Empirical formula	Analyses, % Calculated C	H	Found C	H
IIIb	130–132	15	$C_{18}H_{18}O_5$	68.77	5.77	68.59	5.49
IIIc	127–129	35	$C_{12}H_{14}O_3$	69.88	6.84	69.59	6.72
IIId	135	11	$C_{22}H_{22}O_6$	69.09	5.79	68.88	5.54

Infrared Data.—Infrared spectra were determined on three of the above compounds on a Perkin-Elmer model 21 infrared spectrophotometer using a potassium bromide wafer. Only the strong absorption bands are listed: compound II, 2210, 1665, 1586, 1512, 1344, 1181, 921 and 847 cm.$^{-1}$; compound IIIa, 3368, 3095, 1734(broad), 1636, 1610(broad), 1550(broad), 1213(broad-shoulder 1228), 1155, 945 and 915 cm.$^{-1}$; compound IIIb, 1655, 1575, 1534, 1338 and 1201 cm.$^{-1}$.

Acknowledgment.—The author wishes to express his gratitude to the Robert A. Welch Foundation for financial support.

HOUSTON 4, TEXAS

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

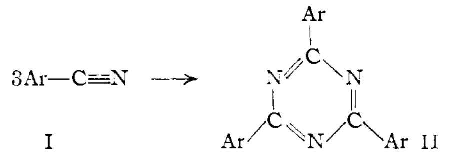
High Pressure-High Temperature Reactions. I. The Trimerization of Aromatic Nitriles

BY IRVING S. BENGELSDORF

RECEIVED OCTOBER 18, 1957

Under the extreme reaction conditions of high pressures (35,000–50,000 atm.) and high temperatures (350–500°), aromatic nitriles are trimerized readily, in the course of a few minutes, to the corresponding 2,4,6-tris-(aryl)-1,3,5-triazines. The conversion may proceed *via* a termolecular reaction or a dipolar intermediate produced by self-ionization under the extreme experimental conditions. Experimental evidence does not indicate a diradical intermediate. It has been shown that the high pressure is necessary, in conjunction with the high temperature, to achieve the trimerization. The quantitative trimerization of *o*-tolunitrile, in the presence of an acidic catalyst, suggests that this is an example of a reaction where extreme reaction conditions can overcome the steric hindrance of an "*ortho* effect."

Aromatic nitriles (I) have been observed to trimerize to the corresponding *s*-triazines (II) in the presence of chemical agents, such as acidic or basic catalysts.[1]



(A)

As in the polymerization of olefins, this trimerization reaction proceeds *via* a transition state of smaller volume than that of the uncombined reactants. This means that ΔV^*, the "volume of activation" in the van't Hoff isothermal equation (B), is negative; the rate of the reaction consequently will increase as the applied pressure is increased.

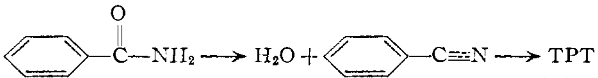
$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^*}{RT} \qquad \text{(B)}$$

Thus, Cairns, Larchar and McKusick[1] have shown that benzonitrile in methanolic solution at an initial pressure of 7500 atm. and a temperature of 125° over a period of 18 hours will give an 82% yield of the *s*-triazine. Under the same experimental conditions, but without methanol as a solvent, the yield of *s*-triazine was only 6%.

The present paper deals with the trimerization of aromatic nitriles under more extreme reaction conditions and without a solvent. Benzonitrile is found to give quantitative yields of 2,4,6-triphenyl-1,3,5-triazine (TPT) when it is subjected to pressures of 35,000–50,000 atm. and temperatures in the neighborhood of 400° for periods of 6–18 *minutes*.

The high pressure is necessary, in conjunction with high temperature, to effect the trimerization reaction, for if benzonitrile is heated in a sealed tube at 360° for 14 hours at a maximum autogenous pressure of 225 p.s.i., one obtains only a 2.5% yield of the triazine; the major part of the starting nitrile is recovered unchanged.

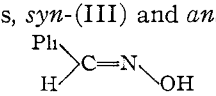
Since other high pressure-high temperature reactions have been observed to occur with a loss of water[2] the suggestion was considered that benzamide and other "hydrates" of benzonitrile could be dehydrated *in situ*, and that the nitrile would then trimerize (eq. C).



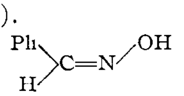
(C)

This reaction has been realized. Thus, at 50,000 atm. and a temperature of 465° for seven minutes, benzamide yielded 30% of TPT, 40% of unreacted amide and 30% of a charred residue; the odor of ammonia also was apparent and indicated partial decomposition of the starting material. The low yield of TPT possibly is connected with the fact that the starting material is a solid. It has been empirically observed in this work that low-melting materials, *i.e.*, liquids at room temperature (benzonitrile, m.p. −13°), give a better yield and a purer reaction product than do starting materials which are solids at room temperature (benzamide, m.p. 130°).

The results were quite different in a further attempt at dehydration, *in situ*, which involved the oxime of benzaldehyde, another "hydrate" of benzonitrile. Benzaldoxime, which is a structural isomer of benzamide, exists in two stereoisomeric forms, *syn*-(III) and *anti*-(IV).



III



IV

The latter, because of the *trans* elimination of the elements of water, is dehydrated readily to benzonitrile by chemical reagents; the *syn* isomer, however, is much more resistant to dehydration. This

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(1) T. L. Cairns, A. W. Larchar and B. C. McKusick, THIS JOURNAL, **74**, 5633 (1952), cite the major references to this reaction.

(2) I. S. Bengelsdorf, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1956, Abstracts p. 74-O.