

point of the *p*-nitrophenylhydrazone was depressed by the addition of pure *p*-nitrophenylhydrazine, m. p. 157°.

Anal. Calcd. for the *p*-nitrophenylhydrazone, C₁₂H₁₁N₃O₂: C, 61.78; H, 6.49. Found: C, 61.76; H, 6.48. Calcd. for the 2,4-dinitrophenylhydrazone, C₁₂H₁₁N₄O₄: C, 51.79; H, 5.07. Found: C, 51.82; H, 4.81.

Attempts to prepare the *p*-methoxy- and *p*-bromophenylhydrazones by similar methods were not successful.

The authors are indebted to Miss Joy Swan for some of the analyses.

DEPARTMENT OF CHEMISTRY
CARNEGIE INSTITUTE OF TECHNOLOGY
PITTSBURGH 13, PENNSYLVANIA

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Condensation of Chloromaleic Anhydride with Substituted Propenylbenzenes

BY MARTIN E. SYNERHOLM

The condensation of maleic anhydride with iso-

DERIVATIVES OF 3-METHYL-3,4-DIHYDRONAPHTHALENE-1,2-DICARBOXYLIC ACID ANHYDRIDE

Derivative	Yield, g.	Solvent	M. p., °C.	Formula	Analyses, %			
					Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
6,7-Methylenedioxy	10	Benzene	176-177	C ₁₄ H ₁₀ O ₅	65.1	65.0	3.91	3.95
6-Methoxy-7-hydroxy	9	Xylene	225-226	C ₁₄ H ₁₂ O ₅	64.7	65.0	4.65	4.69
6-Ethoxy-7-hydroxy	6	Toluene	192-196	C ₁₅ H ₁₄ O ₅	65.7	65.6	5.14	5.07

safrole to form 6,7-methylene-dioxy-3-methyl-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic acid anhydride has been reported by Hudson

and Robinson.¹ They similarly condensed isosafrole with ethyl acetylenedicarboxylate, obtaining the corresponding 3,4-dihydronaphthalene derivative as the acid anhydride, m. p. 178°.

The latter compound has now been shown to form when chloromaleic anhydride is heated in xylene with isosafrole. Analogous compounds formed when chloromaleic anhydride was condensed with isoeugenol and 2-ethoxy-4-propenylphenol.

Experimental.—The procedures were similar for the three cases. Thirteen grains of chloromaleic anhydride, 15 g. of the propenyl compound, and 50 ml. of xylene were refluxed for six hours. The color turned to a bright red and hydrogen chloride was eliminated during the reaction. On cooling, the products crystallized from the xylene. The yields and properties are tabulated.

(1) Hudson and Robinson, *J. Chem. Soc.*, 715 (1941).

(2) Analyses by Elisabeth Heber-Smith.

BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH, INC.
YONKERS 3, NEW YORK RECEIVED NOVEMBER 7, 1944

COMMUNICATIONS TO THE EDITOR

TRIFLUOROACETIC ACID AS A CONDENSING AGENT

Sir:

I wish to report the use of trifluoroacetic acid as an agent for the condensation of acetic anhydride with anisole to produce *p*-methoxyacetophenone. The reaction proceeds well (63%, or 91% if allowance is made for recovered anisole) at moderate temperatures (60-70°). Trifluoroacetic acid has several advantages over other reagents commonly employed for such condensations: there is no demethylation of anisole or the product; there is little if any heat of reaction so that all reagents may be mixed at one time; no stirring is required; no corrosive gases are used or formed; the trifluoroacetic acid may be recovered.

Procedure.—On mixing 15 g. of anisole, 14.8 g. of anhydrous trifluoroacetic acid, and 27 g. of acetic anhydride, heat (of mixing) was evolved and a pink color was produced. On warming to 60-70° the color deepened into cherry red. After six hours at 60-70° the mixture was poured into

water. The acids were removed by shaking with water and the organic layer was extracted with alkali, but no phenol or *p*-hydroxyacetophenone was found. On vacuum distillation there were isolated 4.7 g. (31%) of anisole and 13.1 g. (63%) of *p*-methoxyacetophenone, b. p. 134-137 at 15-16 mm. This material crystallized and melted over the range 30-36°. The crude semicarbazone formed in 76% yield melted at 193-195°. On recrystallization it melted at 195.6-197.0° cor. These facts indicate that almost pure para derivative was produced.¹ The mixed melting point with purified semicarbazone from commercial *p*-methoxyacetophenone (Eastman Kodak Co.) was not depressed. In a similar experiment, except that the reaction was carried out at 110-125°, a much smaller yield of ketone was obtained as tars were formed.

I have also used trichloroacetic acid² in a similar manner, but it is less desirable than trifluoro-

(1) Wahl and Silberzweig, *Bull. soc. chim.*, [4] 11, 69 (1912), give 36°, 197°, of 138-139° as melting points of ketone and semicarbazone and boiling point of ketone at 15 mm.

(2) Unger, *Ann.*, 504, 269 (1933).

acetic acid. Further uses of trifluoroacetic acid as acid condensing agent are being explored.

THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

MELVIN S. NEWMAN

RECEIVED JANUARY 6, 1945

MEMBRANE EQUILIBRIA WHICH INVOLVE ONLY THE IONS OF STRONG INORGANIC ELECTROLYTES

Sir:

The experimental study of membrane equilibria has been confined in the past to systems containing colloidal or semicolloidal ions as "non-diffusible" ions, and systems in which the $\text{Fe}(\text{CN})_6^{=}$ ion acted as such in conjunction with a copper ferrocyanide membrane.^{1,2} For lack of suitable membranes—except for this unique case—Donnan equilibria involving only strong inorganic electrolytes could not be studied.

selective" membranes combine extreme ionic selectivity with great permeability for the non-restricted ion species; the electronegative colloidion membranes are impermeable to all inorganic anions but permeable to the alkali cations, the electropositive membranes being impermeable to all cations and permeable to the anions of the strong monobasic inorganic acids. The ionic screening action of the membranes in these cases is primarily an electrical, not a mechanical (sieve), effect.

The ratios of the activity coefficients of the K^+ , Na^+ and NH_4^+ salts in the pairs of solutions given in Table I are nearly identical. This permits the use without appreciable error of the simplified original formulas of Donnan^{1,2} which refer to analytical concentrations rather than to activities.

The experimental study of membrane equilibria which may involve any desired combination

TABLE I
DONNAN EQUILIBRIA ACROSS MEGAPERMESELECTIVE COLLODION MEMBRANES^a

No.	Solute	Original state		Equilibrium state				Ratio in/out	
		mMoles per liter In	mMoles per liter Out	Experimental		Calculated		Experimental	Calcd.
				mMoles per liter In	mMoles per liter Out	mMoles per liter In	mMoles per liter Out		
A	NH_4^+	30.0	..	22.4	7.50	22.5	7.50	2.99 ± 0.02	3.00
	K^+	..	10.0	7.5	2.5	7.50	2.50	3.00 ± 0.10	3.00
	Cl^-	30.0	10.0	29.8	10.1	30.0	10.0	2.95 ± 0.02	3.00
	Sucrose ⁶	..	33
	Vol.	30 ml.	30 ml.
B	NH_4^+	50.2	2.51	37.4	3.79	37.5	3.78	9.9 ± 0.2	9.9
	K^+	..	2.56	12.0 ^c	1.27 ^c	12.7	1.29	9.5^c	9.9
	C_2O_4^-	25.1	2.54	24.7	2.53	25.1	2.54	9.8 ± 0.2	9.9
	Sucrose ^b	..	39
	Vol.	25 ml.	250 ml.

^a The membranes are impermeable to anions, permeable to cations. ^b Sucrose is added in the proper concentration to establish osmotic equilibrium. ^c K^+ concentration is calculated by difference.

The use of certain recently developed colloidion and protamine colloidion membranes^{3,4} makes such investigations possible. These "megaperm-

(1) F. G. Donnan, *Chem. Rev.*, **1**, 73 (1924).

(2) T. R. Bolam, "The Donnan Equilibria," Bell and Sons, London, 1932.

(3) C. W. Carr and K. Sollner, *J. Gen. Physiol.*, **28**, 119 (1944); C. W. Carr, H. P. Gregor and K. Sollner, *J. Gen. Physiol.*, **28**, 179 (1944).

(4) H. P. Gregor, Ph.D. Thesis, Minneapolis, 1945 (in preparation).

of uni-univalent, and many combinations of uni-polyvalent electrolytes is of interest not only for the colloid chemist and the biologist, but also "may prove of value in the investigation of ionic activity coefficients" (Donnan).

DEPARTMENT OF PHYSIOLOGY
THE MEDICAL SCHOOL
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

KARL SOLLNER
HARRY P. GREGOR

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