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

Anal. Calcd. for the *p*-nitrophenylhydrazone, $C_{12}H_{15}N_3O_2$: C, 61.78; H, 6.49. Found: C, 61.76; H, 6.48. Calcd. for the 2,4-dinitrophenylhydrazone, $C_{12}H_{14}N_4O_4$: 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
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RECEIVED NOVEMBER 24, 1944

Condensation of Chloromaleic Anhydride with Substituted Propenylbenzenes

BY MARTIN E. SYNERHOLM

The condensation of maleic anhydride with isosafrole 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 grams 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.

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

Derivative	Yield, g.	Solvent	M. p., °C.	Formula	Analyses,[2] % 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

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(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 acid[2] in a similar manner, but it is less desirable than trifluoro-

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(1) Wahl und 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.

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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 $Fe(CN)_6^{\equiv}$ 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.

The use of certain recently developed collodion and protamine collodion membranes[3,4] makes such investigations possible. These "megapermselective" membranes combine extreme ionic selectivity with great permeability for the nonrestricted ion species; the electronegative collodion 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 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).

TABLE I

DONNAN EQUILIBRIA ACROSS MEGAPERMSELECTIVE COLLODION MEMBRANES[a]

				Equilibrium state					
		Original state mMoles per liter		Experimental mMoles per liter		Calculated mMoles per liter		Ratio in/out	
No.	Solute	In	Out	In	Out	In	Out	Experimental	Calcd.
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[b]	..	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.

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[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).