acid in the presence of boron fluoride was to be expected from the work of Nieuwland and his collaborators[3] who found that simple olefins condensed with phenols and carboxylic acids to produce phenolic ethers and esters, respectively.

Experimental

The polymeric material was usually prepared by passage of gaseous boron fluoride[4] into the sample to the point of saturation. Heat was immediately evolved and the temperature was allowed to rise to 70–80°. The color darkened to a deep chocolate brown and the viscosity increased markedly. The material was then allowed to cool to room temperature overnight and was taken up in ether. The ethereal solution was washed exhaustively with water and dried over anhydrous magnesium sulfate. Removal of the ether was accomplished by heating on a hot-plate and finally in vacuum for several hours. The residual oil was clear brown in color, and possessed the odor of coconuts.

Saponification of the polymer was carried out in the usual manner with alcoholic potassium hydroxide. The alcohol was evaporated, the residue acidified and extracted with ether. The ether solution was then dried over magnesium sulfate, filtered and evaporated. The residual oil was finally warmed and placed in high vacuum.

The iodoform test on the saponified polymer was carried out in the usual manner using methanol (negative blank) as solvent. The unrecrystallized iodoform melted at 116–119.2°; authentic specimen, m. p. 116–118.5°; mixed m. p. 121°.

Anal. Calcd. for $C_{10}H_{19}CO_2H$: acid no., 184.2; I_2 no., 184.2. Found: acid no., 196.9; I_2 no., 173.4. Calcd. for polymer: I_2 no., 358; sap. eq., 196.9. Found: I_2 no., 429.7; sap. eq.,[5] 196.7; acid no., 467.8. Calcd. for saponified polymer: acid no., 207.3; I_2 no., 452.5; acetyl value (g./OH), 510. Found: acid no., 249[6]; I_2 no., 467.4; acetyl no., 505.

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[3] Nieuwland, *et al.*, THIS JOURNAL, **54**, 3694 (1932); **56**, 2054, 2689 (1934).

[4] Samples of polymer prepared with boron fluoride etherate appeared to be identical with those upon which this report is based.

[5] Indicator used was Clearol Blue (see Fehnel and Amstutz, *Ind. Eng. Chem., Anal. Ed.*, **16**, 53 (1944).

[6] The acid number of the saponified polymer varied considerably and directly with the time and extent of heating during isolation. Reësterification occurred.

THE WM. H. CHANDLER LABORATORY OF CHEMISTRY
LEHIGH UNIVERSITY
BETHLEHEM, PENNSYLVANIA RECEIVED FEBRUARY 9, 1944

p-(2,5-Dimethylpyrryl-1)-phenyl-magnesium Bromide and -Lithium

BY HENRY GILMAN AND GORDON J. O'DONNELL

In connection with studies on nitrogen heterocycles, directions have been developed for the preparation of *p*-(2,5-dimethylpyrryl-1)-phenylmagnesium bromide and the corresponding organo-lithium compound. The yields of the RM compounds are quite satisfactory, and directions are also given for the preparation of the precursory *p*-(2,5-dimethylpyrryl-1)-phenyl bromide in 90% yield.

Experimental

***p*-(2,5-Dimethylpyrryl-1)-phenyl Bromide.**—This compound was prepared in accordance with the general procedure of Hazelwood, Hughes, and Lions.[1] To a warm solution of 172 g. (1 mole) of *p*-bromoaniline in 114 g. (1 mole) of acetonylacetone was added one or two drops of concd. hydrochloric acid. On the addition of the hydrochloric acid, the solution assumed a dark red color, and a vigorous reaction set in immediately with droplets of water forming on the surface of the solution. After the initial reaction subsided, the mixture was refluxed for three hours under an air condenser. The reaction mixture was poured upon crushed ice, and the precipitate was filtered. The yield of product melting at 72–74° was 240 g. (96%). Recrystallization from ethanol gave 225 g. (90%) of compound melting at 74°.

Reaction of *p*-(2,5-Dimethylpyrryl-1)-phenyl Bromide with Magnesium and with Lithium.—The Grignard reagent was prepared by conventional procedures, and the yield by acid titration[2] was 76%. From a second preparation, starting with 0.08 mole of the RBr compound, the yield of crude *p*-(2,5-dimethylpyrryl-1)-benzoic acid was 78%, and purification from ethanol gave a 72% yield of pure acid melting at 195–196°. The reaction with magnesium proceeds slowly, and ordinary catalysts like iodine or some activated magnesium, or some methylmagnesium iodide are helpful. There is no significant color change in the solution when reaction takes place, but color test I is of diagnostic value when methylmagnesium iodide is not used as a catalyst.

The organolithium compound was prepared by adding a solution of 12.5 g. (0.05 mole) of *p*-(2,5-dimethylpyrryl-1)-phenyl bromide in 60 cc. of ether to a stirred suspension of 1 g. (0.14 g. atom) of finely divided lithium in 30 cc. of ether. Twenty cc. of the solution was added at once, after which addition the mixture was warmed until the reaction started. The remaining solution was then added at a rate to maintain gentle refluxing. Carbonation by dry-ice gave 8.6 g. (80%) of *p*-(2,5-dimethylpyrryl-1)-benzoic acid which melted at 196–197° after crystallization from dilute ethanol. Identification was completed by a mixed m. p. determination with a sample prepared[1] by the condensation of *p*-aminobenzoic acid with acetonylacetone.

The observation that the bromide reacts more promptly with lithium than with magnesium finds a parallel in the preparation of RMgX and RLi compounds, in high yields, from *p*-dimethylarsinophenyl bromide and *p*-di-*n*-propylarsinophenyl bromide.[3]

Acknowledgments.—The authors are grateful to C. G. Stuckwisch and L. Fullhart, Jr., for assistance.

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[1] Hazelwood, Hughes, and Lions, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 92 (1937); [*C. A.*, **32**, 1695 (1938).]

[2] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

[3] Studies by L. Tolman and S. Avakian.

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IOWA STATE COLLEGE
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Double Invert Soaps: Symmetrical Di-morpholinium Salts

BY JOSEPH B. NIEDERL AND EDWARD J. KENNEY[1]

Since it appears that up to the present few symmetrical double invert soaps have been described in the literature, report is herewith given of such types of compounds. Thus methylene- and ben-

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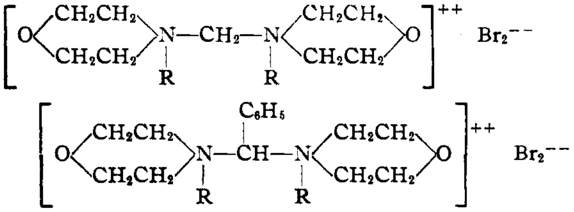
[1] Abstracted from the thesis of Edward J. Kenney presented to the Graduate School of St. Peter's College, Jersey City, N. J., in partial fulfillment for the degree of Master of Science, May, 1944.

zal-di-morpholine, prepared according to M. Zief and J. P. Mason,[2] were condensed with a variety of alkyl bromides, such as n-butyl, n-heptyl, n-octyl, tetradecyl and hexadecyl bromides, to yield the corresponding symmetrical di-morpholinium di-bromides possessing the following structures



R: n-C_4H_9-, n-C_7H_{15}-, n-C_8H_{17}-, n-$C_{14}H_{29}$-, n-$C_{16}H_{33}$-

Procedure

To 0.01 mole of methylene- or benzal-di-morpholine was added 0.02 mole of the respective alkyl bromide and 11 ml. of 95% ethyl alcohol. The mixture was then gently refluxed for four hours. The reaction material when solid, or otherwise after removal of the alcohol by evaporation under reduced pressure, was crystallized from ethyl acetate; yields, 50–70%.

TABLE I

Compounds	Formulas	M. p., °C. (uncor.)	Analyses, % N Calcd.	Analyses, % N Found
4,4'-Methylenedimorpholinium di-bromides				
4,4'-Di-n-butyl	$C_{17}H_{36}N_2O_2Br_2$	144 (dec.)	6.08	6.22
4,4'-Di-n-heptyl	$C_{23}H_{48}N_2O_2Br_2$	141 (dec.)	5.14	5.17
4,4'-Di-n-octyl	$C_{25}H_{52}N_2O_2Br_2$	143 (dec.)	4.89	4.95
4,4'-Di-tetradecyl	$C_{37}H_{76}N_2O_2Br_2$	165 (dec.)	3.78	3.90
4,4'-Di-hexadecyl	$C_{41}H_{84}N_2O_2Br_2$	180 (dec.)	3.52	3.31
4,4'-Benzaldimorpholinium di-bromides				
4,4'-Di-n-butyl	$C_{23}H_{40}N_2O_2Br_2$	174	5.22	5.34
4,4'-Di-n-heptyl	$C_{29}H_{52}N_2O_2Br_2$	153	4.51	4.63
4,4'-Di-n-octyl	$C_{31}H_{56}N_2O_2Br_2$	156	4.32	4.39
4,4'-Di-tetradecyl	$C_{43}H_{80}N_2O_2Br_2$	175	3.43	3.72
4,4'-Di-hexadecyl	$C_{47}H_{88}N_2O_2Br_2$	178	3.21	3.10

THE CHEMICAL LABORATORIES OF
NEW YORK UNIVERSITY, WASHINGTON SQUARE COLLEGE,
NEW YORK CITY, N. Y., AND OF
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The System Sulfur Dioxide–Acetic Acid

BY W. H. SCHEUB AND C. R. MCCROSKY

To find out whether a definite compound of sulfur dioxide and acetic acid exists, the melting points of a series of mixtures of these two substances have been measured.

The acetic acid was dehydrated by successive treatments of glacial acetic acid with triacetyl borate and 20% oleum. In each treatment the mixture was first refluxed and then fractionally distilled. The mixtures were prepared by dissolving previously dried sulfur dioxide in the anhydrous acetic acid and were then frozen in a bath of solid carbon dioxide and acetone, or of liquid air. The melting points were determined by means of a chromel–alumel thermocouple and were accurate to well within ±0.1°. Melting points rather than freezing points were measured since the mixtures were found to supercool to a marked degree.

TABLE I

MELTING POINT DATA OF THE SYSTEM SULFUR DIOXIDE–ACETIC ACID

Mole % SO_2	M. p., °C.	Mole % SO_2	M. p., °C.
0.0	16.6	33.5	−40.4
7.7	11.5	46.4	−38.0
9.6	8.3	59.6	−38.7
13.1	−44.1	63.3	−39.2
18.0	−44.2	78.3	−75.6
24.7	−41.9	100.0	−72.7

The observations are collected in Table I and are represented graphically in Fig. 1.

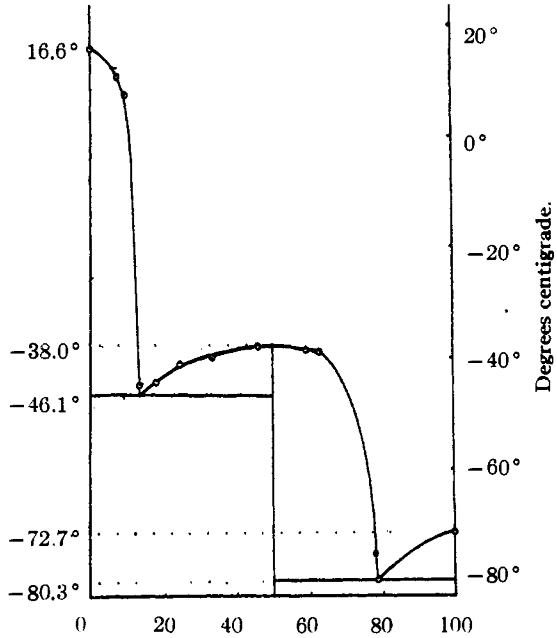

Fig. 1.

It can be seen that the melting point curve shows a maximum at 50 mole % sulfur dioxide and a temperature of −38°. The indicated compound, $HSO_2C_2H_3O_2$, solidifies in the form of thin, colorless flakes which show a tendency to sublime. The lower eutectic was established by a definite melting point at −80.3°; the upper eutectic at −46.1° was derived by extrapolation. These eutectic mixtures contained, respectively, 78.4 and 13.2 mole % of sulfur dioxide.

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SYRACUSE UNIVERSITY
SYRACUSE, NEW YORK

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(2) M. Zief and J. P. Mason, *J. Org. Chem.*, 8, 1 (1943).