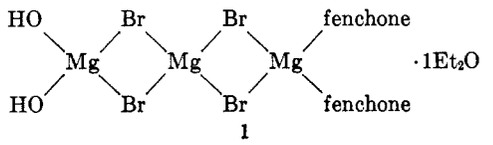
amount of basic magnesium in the complex, (b) determination of the bromide content by adding an excess of silver nitrate and collecting the silver bromide formed, and (c) determination of the total magnesium present in the precipitate as the 8-hydroxyquinolate.

The quantity of benzene, fenchone, and ether in the organic phase was determined by gas chromatography using a flame-ionization detector and standard mixtures. The standard mixtures were subjected to the aforementioned work-up procedure to correct for losses in extraction. A summary of the results from six different preparations of the precipitate are given in Table I along with the calculated values for a proposed structure (1).

TABLE I
COMPOSITION OF THE FENCHONE–GRIGNARD PRECIPITATE

Component	Obsd for precipitate, %	Calcd structure I, %	Difference, %
Bromide	40.2	39.70	0.5
Basic magnesium	2.82	3.02	0.2
Total magnesium	8.76	9.05	0.29
Fenchone	37.2	37.81	0.61
Ether	8.8	9.20	0.4
Carbon[a]	35.54	35.80	0.26
Hydrogen[a]	5.2	5.51	0.3
Benzene	0.0	0.0	...

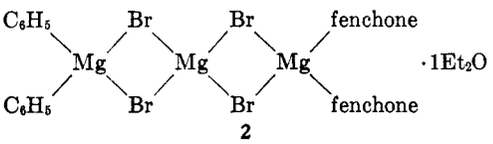
[a] Microanalyses for carbon and hydrogen were performed by Mr. J. Walter.



1

It is interesting to note that no benzene was observed. While the empirical formula for structure 1 is unique, structural formulas other than 1 can be written.

Since the hydroxyl groups could have resulted from the hydrolysis of phenylmagnesium bonds in a related structure 2 during the nitrogen-drying process, a sample of the precipitate was prepared in the usual fashion, rinsed free of Grignard reagent and excess ketone with Grignard dried ether, and then the precipitate was hydrolyzed without drying.



2

A gas chromatographic analysis indicated that the ether solution contained only traces of benzene from the approximately 10 g of precipitate. The magnesium hydroxide must therefore be formed before the drying process and the empirical formula as given by structure 1 does represent the precipitate formed in this process. It was found that when highly purified ketone and Grignard dried ether were used for the preparation of the complex the yield was drastically reduced.

Experimental Section

Reagents.—Tetrahydrofuran and ethyl ether, Baker anhydrous reagent grade, were used without purification except where noted. The Grignard reagent was prepared from Eastman Kodak's Grignard-grade magnesium turnings and bromobenzene. The fenchone from Eastman Kodak was distilled before use.

Preparation and Isolation of the Fenchone Precipitate.—To 23.0 g (0.15 mole) of fenchone dissolved in 50 ml of anhydrous ether was added with stirring 50 ml (2.9 *N*, 0.145 mole) of Grignard reagent prepared from bromobenzene. All preparations, transfers, and reactions were carried out under a nitrogen atmosphere. The precipitate was isolated by using nitrogen pressure to force the suspension through a sintered glass filter. The precipitate was rinsed with anhydrous ether (never exposing the precipitate to air) and dried to constant weight by passing a slow stream of dry nitrogen or argon through the precipitate contained on the sintered glass filter. Samples for hydrolysis, preparation of infrared pellets, and other tests were weighed out in a drybox which was constantly purged with nitrogen.

Determination of Basic Total Magnesium and Bromide.—A weighed sample of the precipitate was hydrolyzed with a known amount of dilute sulfuric acid. After extracting the aqueous phase with carbon tetrachloride an aliquot of the aqueous phase was back titrated with standard sodium hydroxide solution using phenolphthalein as the indicator to determine the amount of basic magnesium. The total amount of magnesium was determined on a second aliquot by precipitating the magnesium as the 8-hydroxyquinolate according to the method of Kolthoff and Sandall.[9]

A third aliquot of the aqueous phase was diluted with sufficient water to prevent precipitation of silver sulfate in the next step. A calculated excess of silver nitrate was used to precipitate the bromide ion as silver bromide. The results are summarized in Table I.

Determination of Fenchone, Benzene, and Ether.—The organic layer from the above extraction was gas chromatographed using an Aerograph Hi-Fi flame ionization detector and a 6 ft × 1/8 in. DEGS column at 50 and 160°. Synthetic mixtures which had been subjected to the same extraction procedure were used to calibrate the chromatograph. The results of multiple runs are given in Table I.

Hydrolysis of the Precipitate without Drying.—The preparation of the precipitate was carried out as given above with the exception that the precipitate was washed by decantation using a nitrogen pressure siphon and Grignard dried ether. The precipitate was not dried but directly hydrolyzed with dilute sulfuric acid and the aqueous layer was extracted with ether. The ether layer was found to contain only traces of benzene.

Reaction of the Precipitate with Excess Phenyl Grignard.—A 5-g sample of the nitrogen-dried precipitate was suspended in 50 ml of 2.9 *N* phenyl Grignard reagent and the mixture was heated to reflux temperature for a period of 48 hr. From this reaction was isolated 75 mg of an impure carbinol with an infrared spectrum identical with one obtained from the addition product formed from phenyllithium and fenchone.

(9) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952.

Synthesis of Pyridazine Derivatives. XII. Friedel–Crafts Reaction with 3,6-Dichloropyridazine

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In connection with our studies in the pyridazine field[1] we were interested in investigating the behavior of 3,6-dichloropyridazine as an alkylating agent in the Friedel–Crafts reaction.

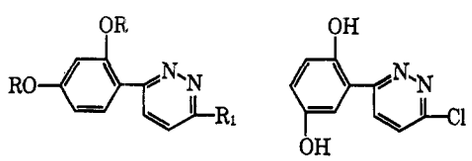
The inertness of halogenated heterocycles as alkylating agents in the Friedel–Crafts reaction is well known

(1) Part XI: A. Pollak, B. Stanovnik, and M. Tišler, *Monatsh. Chem.*, in press.

and the only recorded examples of such alkylations are with 2-chloroquinoline and 4,7-dichloroquinoline[2] or with 2-substituted 4,6-dichloro-1,3,5-triazines and 2,4,6-trichloro-1,3,5-triazine.[3]

We wish to report alkylation of resorcinol and hydroquinone with 3,6-dichloropyridazine under the conditions of a Friedel–Crafts reaction. Formation of I (R = H, R_1 = Cl) and II was effected by treating the corresponding phenol with 3,6-dichloropyridazine in the presence of anhydrous $AlCl_3$ in nitrobenzene. The structure of I (R = H, R_1 = Cl) was proved on the basis of elemental analysis and infrared and nmr spectra. The *ortho* ring protons of resorcinol appear at τ 2.09 and 3.44 (relative to TMS) in the nmr spectrum as an AB quartet, the B portion of which is further split by coupling with *meta* H_3. No *para* coupling was observed. The two *ortho* heteroannular protons are located as a quartet at τ 1.58 and 2.09. Both hydroxyl groups could be acetylated to give I (R = CH_3CO, R_1 = Cl) and the chlorine atom could be substituted with hydrogen in a hydrogenolysis reaction with hydrazine in the presence of palladium on carbon.

Attempts to replace the chlorine with a methoxy group failed and also attempts to use 6-chloroimidazo-[1,2-*b*]pyridazine[4] as an alkylating agent proved to be unsuccessful. At lower temperatures a very stable complex with $AlCl_3$ was formed, but at higher temperatures a complete decomposition occured.



I

II

Experimental Section

Melting points were determined on a Kofler apparatus and are corrected. The infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. The nmr measurements were determined in dimethyl sulfoxide solution on a Varian A-60 instrument, using tetramethylsilane (TMS) as an internal standard. The aluminium chloride used was anhydrous reagent grade. The nitrobenzene used was reagent grade material and was washed with water, dried over anhydrous $MgSO_4$, and distilled. The phenols used were reagent grade material.

3-Chloro-6-(2′,4′-dihydroxyphenyl)pyridazine (I, R = H; R_1 = Cl).—To a solution of 22.4 g (0.15 mole) of 3,6-dichloropyridazine in 200 ml of anhydrous nitrobenzene, 25.0 g (0.225 mole) of resorcinol was added. Into the externally cooled and stirred mixture 20.0 g (0.15 mole) of anhydrous $AlCl_3$ was added portionwise at such a rate that the temperature remained below 20°. After the addition of $AlCl_3$ was complete, stirring was continued and the mixture was heated on an oil bath at 100° for 1.5 hr. After this period the evolution of hydrogen chloride was practically completed. The cooled reaction mixture was poured into a mixture of 500 ml of water, 500 g of ice, and 50 ml of concentrated HCl. The supernatant liquid was separated from the suspension in nitrobenzene by decantation and washed successively with several portions of water (1000-ml total) until free of acid. The suspension in nitrobenzene was transferred to a distilling flask and nitrobenzene distilled off with steam. The residue was treated with 100 ml of cold methanol, filtered, and air dried. Recrystallization from methanol–water (2:1) afforded colorless needles (21.5 g, 65% yield) with a melting point of 225–226°. The infrared spectrum (Nujol) indicated the presence of OH functions (absorption band at 3289 cm^{-1}). The nmr spectrum of the compound showed the following peaks: AB quartet centered at τ 1.58 and 2.09 for $H_{4,5}$, $J_{4,5}$ = 9 cps; AB quartet centered at 2.09 and 3.44 for $H_{5',6'}$, $J_{5',6'}$ = 10 cps. Part B is split, $J_{3',5'}$ = 2.5 cps, by *meta* $H_{3'}$ (*para* coupling, $J_{3',6'}$, was not observed) and doublet for $H_{3'}$, centered at 3.42, J = 2.5 cps.

Anal. Calcd for $C_{10}H_7ClN_2O_2$: C, 53.94; H, 3.17; N, 12.58. Found: C, 53.71; H, 3.43; N, 12.81.

3-Chloro-6-(2′,4′-diacetoxyphenyl)pyridazine (I, R = CH_3CO; R_1 = Cl).—One gram of the above compound was dissolved in 6.0 ml of anhydrous pyridine, 9.0 ml of acetic anhydride was added, and the reaction mixture was set aside at room temperature for 24 hr. The separated crystals were filtered and the filtrate was evaporated *in vacuo* leaving more of the product. Recrystallization from methanol gave colorless needles (95% yield) melting at 175–176°. The infrared spectrum (Nujol) indicated the loss of the OH groups.

Anal. Calcd for $C_{14}H_{11}ClN_2O_4$: C, 54.80; H, 3.61; N, 9.13. Found: C, 55.01; H, 3.81; N, 9.22.

3-(2′,4′-Dihydroxyphenyl)pyridazine (I, R = H; R_1 = H).—To a suspension of 2.2 g of I (R = H, R_1 = Cl; 0.01 mole) in 50 ml of methanol, 7.5 ml of 80% hydrazine hydrate was added, the mixture was heated to boiling, and 0.3 g of palladium on carbon (10% Pd) was added. The mixture was heated under reflux for 30 min and filtered hot and the filtrate was evaporated *in vacuo*. After the addition of 40 ml of water the solution was neutralized with acetic acid to pH 7 and the formed precipitate was filtered, washed with water, and air dried. The product was crystallized from methanol–DMF (3:1) to give 1.75 g (94%) of colorless crystals, mp 274–275°.

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.28; N, 14.89. Found: C, 63.55; H, 4.24; N, 14.86.

3-Chloro-6-(2′,5′-dihydroxyphenyl)pyridazine (II).—This compound was prepared in essentially the same way as I (R = H, R_1 = Cl) starting with 7.5 g (0.05 mole) of 3,6-dichloropyridazine, 8.25 g (0.075 mole) of hydroquinone, 100 ml of nitrobenzene, and 6.7 g (0.05 mole) of anhydrous $AlCl_3$. The crude product, obtained in 64% yield, was purified from methanol–water (2:1) to give colorless needles which had mp 195–196°.

Anal. Calcd for $C_{10}H_7ClN_2O$: C, 53.94; H, 3.17; N, 12.58. Found: C, 53.92; H, 3.52; N, 12.65.

Acknowledgment.—We take pleasure in thanking Professor K. Balenović for providing facilities in connection with the recording of nmr spectra. This work was partially supported by the Yugoslav Federal Research Fund.

(2) G. Olah, "Friedel-Crafts and Related Reactions," Vol. 2, Part I, Interscience Publishers, Inc., New York, N. Y., 1964, p 433.

(3) (a) French Patent 1,381,452 (1964); (b) Netherlands Application 6,400,983 (1964); *cf. Chem. Abstr.*, **62**, 7782 (1965).

(4) B. Stanovnik and M. Tišler, *Tetrahedron*, in press.

Alcoholysis of 1-Chlorocarbonyl-2-chloro-4,5,6,7-tetrahydro-1H-azepine in Basic and Acidic Media

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1-Chlorocarbonyl-2-chloro-4,5,6,7-tetrahydro-1H-azepine (I), which is readily prepared in high yield from caprolactam and excess phosgene,[1] has been shown to undergo reaction with hypohalous acids[2] and nitric acid[3] to give α-substituted caprolactams. Hydrolysis in 10% hydrochloric acid yielded ϵ-aminocaproic acid

(1) British Patent 901,169 (to Stamicarbon N.V.) (July 18, 1962).

(2) J. H. Ottenheym and J. W. Garritsen, U. S. Patent 3,000,881 (Sept 19, 1961).

(3) B. J. Hoek, J. P. H. von den Hoff, and J. W. M. Steeman, U. S. Patent 3,093,635 (June 11, 1963).