0.70 g. was shown by infrared analysis to be the starting alcohol IX.

The main fraction from the column was then dissolved in 13 ml. of 5% methanolic potassium hydroxide and boiled under reflux for 3 hours to effect hydrolysis. The solution was then diluted with water and extracted with ether. After the ether solution was washed with water, it was dried over sodium sulfate and concentrated. The residue was taken up in hexane and chromatographed over alumina. The first fraction from the column gave 460 mg. of a colorless oil whose infrared spectrum showed the absence of a hydroxyl and the presence of a vinyl group. Presumably this was a diene fraction resulting from dehydration. The second fraction, consisting of 460 mg. (32% based on unrecovered IX) of a colorless oil, had an infrared spectrum in accord with IV but appeared to be a mixture of isomers. This was dissolved in 8 ml. of pyridine and heated with 600 mg. of *p*-phenylazobenzoyl chloride for 10 min. The mixture was poured into water with stirring and the supernatant liquid decanted from the insoluble gum. After the residue had been washed again with aqueous carbonate and separated by decanting, it was taken up in hexane and passed onto an alumina column. Development of the column was done first with hexane–benzene mixtures and finally with pure benzene. A number of fractions were taken and from one of these there was obtained an oil which, on prolonged standing, gave large orange crystals, m.p. 68–70°. The infrared spectrum of a solution of these crystals in chloroform was superimposable with that obtained from the *p*-phenylazobenzoate of IV derived from α-erythroidine.

Anal. Calcd. for $C_{26}H_{28}N_2O_3$: C, 76.34; H, 6.41; N, 6.36. Found: C, 76.07; H, 6.44; N, 6.79.

Hofmann Degradation of Dihydro-α-erythroidine.—A solution of 2.0 g. of the methiodide of dihydro-α-erythroidine[3] in 30 ml. of water was passed over an ion exchange column (Dowex 2-X4). When the eluate was concentrated, it gave the betaine XVII as a crystalline solid. The betaine was then decomposed by heating it in a short-path still at 175–185° at 25 mm. to give 350 mg. of distillate as a colorless oil. From previous experience in the β-erythroidine series,[9] it was anticipated that the distillate would be a mixture of the "normal" and "abnormal" Hofmann products. Therefore, the oil was taken up in pentane and chromatographed over alumina. From the pentane eluate there was obtained 90 mg. (9%) of "abnormal" Hofmann product. Changing the eluent to ether gave a second fraction of 240 mg. (17%) of a colorless oil which is presumed to be the "normal" Hofmann product.

The picrate of the "abnormal" Hofmann product formed readily in ethanol and was obtained after recrystallization from ethanol in good yield as yellow crystals, m.p. 166–167° dec. A mixture of these crystals with those of the picrate (m.p. 164–167°) from the "abnormal" product (XIV) in the β-erythroidine case[9] showed no depression of melting point. Also, the infrared spectra of the two samples were identical.

Isomerization of Dihydro-α-erythroidine to Dihydro-β-erythroidine.—A solution of 2.85 g. of dihydro-α-erythroidine in 14.3 ml. of a 10% aqueous sodium hydroxide solution was boiled under reflux in a nitrogen atmosphere for three hours. The reaction mixture was cooled in an ice-bath and concentrated hydrochloric acid added until the *p*H was below 2.0. After the solution had stood for three hours, sodium bicarbonate was added carefully until the *p*H was just above 7. The solution was then extracted five times with chloroform and the combined extracts were dried and concentrated. The resulting yellow oil, when seeded with a crystal of authentic dihydro-β-erythroidine, immediately crystallized to give 2.60 g. (91%) of white crystals, m.p. 73–78°. The corresponding hydrobromide was prepared by dissolving 2.30 g. of these crystals in ethanolic hydrobromic acid. There deposited 2.40 g. (84%) of light tan crystals, m.p. 228–229°. One recrystallization from ethanol gave the hydrobromide of dihydro-β-erythroidine as white crystals, m.p. 231–232°, $\alpha^{30}D$ +109° (1% solution in water).[18]

Regeneration of the free base from the hydrobromide gave white crystals (93% yield), m.p. 80–82°, undepressed by admixture of an authentic sample of dihydro-β-erythroidine. Also, the infrared spectrum of the base was identical with that of dihydro-β-erythroidine and showed the complete absence of the characteristic absorption bands of dihydro-α-erythroidine.

Isomerization of α-Erythroidine to β-Erythroidine.—A solution of 1.20 g. of α-erythroidine hydrochloride in 12 ml. of a 10% aqueous sodium hydroxide solution was boiled under reflux for 3 hours. When the reaction mixture was worked up as described in the previous experiment, there was obtained 700 mg. (67%) of white crystals, m.p. 94–98°, undepressed by admixture of authentic β-erythroidine (m.p. 97–99°). Also, the infrared spectrum of the base was identical with that of β-erythroidine and showed the absence of absorption bands peculiar to α-erythroidine.

The corresponding hydrochloride was prepared in 83% yield as white crystals, m.p. 230.5–231.5° dec., undepressed by admixture of an authentic sample of β-erythroidine hydrochloride. Again, the infrared spectra of the two hydrochlorides were identical.

ROCHESTER, N. Y.

(18) K. Folkers and F. Koniuszy (U. S. Patent 2,370,651, March 6, 1945) give for dihydro-β-erythroidine hydrobromide, m.p. 231–231.5°, $\alpha^{25}D$ +107.5° (in water).

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY BRANCH, CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE TEST STATION]

An Improved Synthesis of 5-Substituted Tetrazoles

BY WILLIAM G. FINNEGAN, RONALD A. HENRY AND ROBERT LOFQUIST[1]

RECEIVED MARCH 5, 1958

An improved synthesis of 5-substituted tetrazoles has been devised. Alkyl- or arylnitriles and inorganic azides react readily in solvents such as dimethylformamide and diethyl sulfoxide. Relatively low reaction temperatures and short reaction times are effective, and the need for pressure equipment is eliminated. The effects caused by varying the solvent, the electronegativity of the substituent on the nitrile and the nature of the azide salt have been studied and a tentative mechanism for the reaction is advanced.

The previously described syntheses of 5-alkyl- and aryltetrazoles, although generally capable of giving good yields, are not all adaptable to larger scale use. In several instances they suffer the disadvantage of requiring the independent preparation of non-aqueous solutions of hydrazoic acid. Multi-step reaction sequences[2,3] proceeding *via* imino ethers, hydrazides and azides, result in only modest yields. Reactions using solutions of hydrazoic acid in benzene, toluene or xylene, or sodium azide and acetic acid in butanol either in glass[4] or pressure equipment[5] at high temperatures require extended reaction times of four to seven days. The recently described synthesis of 5-substituted tetrazoles by the reaction of aluminum

(1) University of Michigan, Ann Arbor, Mich.

(2) W. Oberhummer, *Monatsh.*, **63**, 285 (1933).

(3) A. Pinner, *Ber.*, **27**, 984 (1894).

(4) R. M. Herbst and K. R. Wilson, *J. Org. Chem.*, **22**, 1142 (1957).

(5) J. S. Mihina and R. M. Herbst, *ibid.*, **15**, 1082 (1950).

azide with aliphatic nitriles in tetrahydrofuran[6] overcomes many of these difficulties, but an examination of the experimental evidence indicates that only one-third of the available azide groups is utilized.

In an attempt to simplify and improve the synthesis of 5-substituted tetrazoles the reaction of certain azide salts such as ammonium, substituted ammonium, sodium and lithium azides, with nitriles in organic solvents, such as dimethylformamide, was investigated carefully. With the ammonium and substituted ammonium azides, the reaction has been found to be general and can be made to give excellent yields of 5-substituted tetrazoles after very reasonable times. For example, with aliphatic and electropositively substituted arylnitriles, conversions of 90% or better can be achieved in 18 to 24 hours at temperatures of 125°. With electronegatively substituted nitriles even lower reaction temperatures and shorter reaction times can be used.

Dimethyl sulfoxide and dimethylformamide are equally good solvents for some azide salts, and are superior to the monomethyl and ethyl ethers of ethylene and diethylene glycol.[7] For this and other reasons, the former two solvents are also much better media in which to perform this reaction. Dimethylformamide is preferable to dimethyl sulfoxide since the higher boiling point of the latter makes its removal much more difficult. The various azides studied were prepared *in situ* by double decomposition reactions of sodium azide and the appropriate chloride salts. Since the solvents used are high boiling, the reactions were run at atmospheric pressure in glass equipment. No experimental difficulties were encountered other than the occasional but temporary sublimation of ammonium azide to the cooler portions of the reaction flask and the condenser.

TABLE I

CONVERSION OF BENZONITRILE TO 5-PHENYLTETRAZOLE

0.2 mole of benzonitrile, 100 ml. of dimethylformamide except where indicated and 0.22 mole of sodium azide, 7 hours at 123–127°; product isolated by method A of the Experimental procedure

Added salt or catalyst	Amount, mole, %	Yield, %
None		24.9
NH_4Cl	10	59.6, 54.1
$(n\text{-}C_4H_9)_2NH_2Cl$	5	51.6
$C_6H_5NH_3Cl$	5.8	57.2
$C_6H_5NH_3Cl$	10	73.8
$C_2H_5SO_3H$	4	51.3
$C_2H_5SO_3H$[a]	8	16.3
BF_3-diethyl ether	10	55.6
$(CH_3)_4NCl$	100	40.4
LiCl	100	48.6
H_2O	5 ml.	5.8

[a] 100 ml. of 2-methoxyethanol.

The general mechanism for the reaction appears to be a nucleophilic attack of azide ion on the carbon of the nitrile group, followed by ring closure of the imino azide to form the tetrazole ring. Apparently, a $+\delta$ charge on the nitrile carbon is necessary for the azide ion attack since conditions which enhance or favor such a charge increase the rate of reaction. The reaction has been found to be subject to general acid catalysis. Hydrazoic acid, amine hydroazides and Lewis acids, such as BF_3, more than double the yield of 5-phenyltetrazole from benzonitrile when added in amounts from 4 to 10 mole % of the sodium azide in a 7-hour reaction at 123–127°. Coördination of a Lewis acid or proton with the nitrile nitrogen would generate a $+\delta$ charge on the nitrile carbon and facilitate the approach of the azide ion

$$RC{\equiv}N + H^+ \longrightarrow R\overset{+}{C}{=}NH$$

$$RC{\equiv}N + BF_3 \longrightarrow R\overset{+}{C}{=}N{:}\bar{B}F_3$$

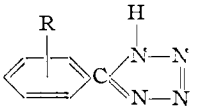
$$R\overset{+}{C}{=}NH + N_3^- \longrightarrow RC(N_3){=}NH$$

$$RC(N_3){=}NH \longrightarrow RC(=N{-}NH{-}N{=}N)$$

Electronegative substitution on the nitrile assists in the $+\delta$ charge formation and achieves a similar result. This is shown by the fact that perfluorocaprylonitrile and sodium azide react quantitatively in dimethylformamide solution in 24 hours at 100° to yield the expected 5-perfluoroheptyltetrazole.[8] Terephthalonitrile and 4-nitrobenzonitrile also react readily with sodium azide in dimethylformamide solution at 100°. The solubility of the azide salt also influences the rate of reaction: lithium and tetramethylammonium azides are very soluble in dimethylformamide and their rates of reaction with benzonitrile are greater than that of the moderately soluble sodium azide but less than the rates obtained with the equally soluble amine hydroazides.

Evidence to support the concept that the reaction proceeds *via* azide ion attack on the nitrile was found in the comparison of the reaction of ethyl cyanoacetate with hydrazoic acid in benzene and

TABLE II

5-SUBSTITUTED ARYLTETRAZOLES 

0.2 mole of the appropriately substituted benzonitrile, 0.22 mole of ammonium azide, 100 ml. of dimethylformamide, 3 hours at 100°

R	Yield,[a] %
4-NH_2–	10.4
4-CH_3O–	43.2
4-CH_3–	63.8
H–	75.6
4-NO_2–	96.9
3-NO_2–	99.5
4-CN–	90.5[b]

[a] The products were obtained following method A of the Experimental procedure except that the 5-(4-aminophenyl)-tetrazole was isolated by acidifying the aqueous solution to *p*H 5 with acetic acid. [b] A small quantity of 1,4-bis-(5-tetrazolyl)-benzene also was recovered.

(6) H. Behringer and K. Kohl, *Ber.*, **89**, 2648 (1956).

(7) E. Lieber, T. S. Chao and C. N. Ramachandra Rao, *J. Org. Chem.*, **22**, 238 (1957).

(8) E. Lieber (private communication) observed no reaction between perfluoronitriles and hydrazoic acid in chloroform solution in the presence of sulfuric acid.

TABLE III

5-SUBSTITUTED TETRAZOLES, $RCHN_4$

R	M.p., °C.	Yield, %	Azide used	Reacn. temp., °C.	Reacn. time, hr.	Reacn. solvent	Method of workup	Recrystn. solvent	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	147–151 d.	69.2	$(CH_3)_3NHN_3$	105–110	22	DMF	B	Ethyl acetate	...	...	..	..	...	....
n-C_3H_7–	63–64	73.5	NH_4N_3	120–125	24	DMF	C	Isopropyl ether	...	...	..	..	...	....
$HOCH_2CH_2$–	83–84	93.3	NH_4N_3	120–125	24	DMF	B	Methyl ethyl ketone	31.57	31.59	5.30	5.23	49.10	49.17[a]
$CH_3OCH_2CH_2$–	66–67	100	NH_4N_3	120	18	DMF	B	Ethyl acetate	37.49	37.45	6.29	6.06	43.73	44.32
$C_2H_5O_2CCH_2$–	128–130	81	NH_4N_3	95	8	DMF	A	2-Propanol	38.46	38.30	5.16	4.48	35.89	35.83
$NaOSO_2CH_2CH_2$–	208–209 d.	[b]	NH_4N_3	120–125	7	DMF	B	95% ethanol	18.00	18.03	2.52	2.82	27.99	27.49[b]
$C_6H_5CH_2$–	123–125	84.1	NH_4N_3	120–125	7	DMF	A	Ethylene dichloride	...	...	..	..	...	[c]
$-CH_2-$	215–219 d.	100	NH_4N_3	95	16	DMF	B	Acetonitrile	23.68	23.65	2.64	2.86	73.66	73.42
$-(CH_2)_4-$[d]	204–205 d.	26	NH_4N_3	100	96	Et cell.[k]	A	95% ethanol	37.10	37.15	5.19	4.83	57.71	57.93
CH_3S–	150–151 d.	91.5	NH_4N_3	95	6	DMF	A	Water	...	...	..	..	...	....
$C_6H_5CH_2S$–	137.5–138.5	22	NH_4N_3	95	5	DMF	A	30% ethanol	49.98	49.58	4.19	4.15	29.15	28.88[c]
C_7F_{15}–	[f]	100	NH_4N_3	95	4	DMF	B		...	...	..	..	...	....
C_6H_5–	213–215 d.	100	NH_4N_3	125	7	DMF	A	Water	...	...	..	..	...	....
C_6H_5–	213–215 d.	90.6	$(CH_3)_3NHN_3$[g]	100	3	DMF	A	Water	...	...	..	..	...	....
C_6H_5–	213–215 d.	90	NH_4N_3	100	96	Et cell.[k]	A	Water	...	...	..	..	...	....
C_6H_5–	213–215 d.	51.3	NaN_3	Reflux	20.5	DMF	A	Water	...	...	..	..	...	....
C_6H_5–	213–215 d.	43.9	NaN_3	120–125	24	Dimethyl sulfoxide	A[h]	Water	...	...	..	..	...	....
C_6H_5–	213–215 d.	19.4	NaN_3	126	24	Me cell.[k]	A	Water	...	...	..	..	...	....
4-$H_2NC_6H_4$–	268–270 d.	...	...	...	..	.....		Water dimethyl-formamide	...	...	..	..	43.46	43.36, 43.51
4-NCC_6H_4–	>300 d.	...	...	...	..	.....		Water	56.13	56.58	2.94	2.47	40.93	41.35, 41.18[i]
1,4-(-C_6H_4-)	>300 d.	100	NH_4N_3	125	7	DMF	A	95% ethanol	44.85	44.40	2.82	2.71	52.32	53.07[j]

[a] Calcd. for $C_3H_6ON_4$: equiv. wt., 114.12. Found: equiv. wt., 114.37. [b] Because of difficulties encountered in isolation and purification the yield was not determined. Calcd. for $C_3H_6O_3NaS$: S, 16.02; equiv. wt., 200.16. Found: S, 16.09; equiv. wt., 261.9. This compound was initially isolated as the monohydrate. Calcd. for $C_3H_7O_4NaS$: H_2O, 8.25; equiv. wt., 218.18. Found: H_2O, 8.23; equiv. wt., 217.6, 219.8. [c] Calcd. for $C_8H_8N_4$: equiv. wt., 160.18. Found: equiv. wt., 161.17. [d] For comparison, 1,2-bis-(5-tetrazolyl)-ethane, m.p. 245–247°, and 1,8-bis-(5-tetrazolyl)-octane, m.p. 149–150°, were made by the procedure of Mihina and Herbst (ref. 5) in 47.2 and 66.4% yields, respectively. Calcd. for $C_4H_6N_8$: C, 28.91; H, 3.64. Found: C, 28.87; H, 3.74. Calcd. for $C_{10}H_{18}N_8$; C, 47.98; H, 7.25; N, 44.77; equiv. wt., 125.16. Found: C, 48.34; H, 6.93; N, 45.02; equiv. wt., 125.35. [e] Calcd. for $C_8H_8N_4S$: equiv. wt., 192.23. Found: equiv. wt., 191.73. [f] The tetrazole could not be induced to crystallize; the potassium salt was recrystallized from dioxane for analysis. Calcd. for $C_8N_4F_{15}K$: C, 20.18; N, 11.77; F, 59.85; K, 8.21. Found: C, 20.56; N, 11.84; F, 58.45; K, 8.93. [g] Comparable experiments using morpholinium azide and piperidinium azide gave 83.9 and 81.6% yields, respectively. [h] The sodium salt of 5-phenyltetrazole was precipitated by the addition of methylene chloride. The free 5-phenyltetrazole was obtained by solution of the salt in water and acidification with concentrated hydrochloric acid. [i] Calcd. for $C_8H_5N_5$: equiv. wt., 171.17. Found: equiv. wt., 169.1. [j] Calcd. for $C_8H_6N_8$: equiv. wt., 107.11. Found: equiv. wt., 109.3. [k] Et cell. = ethyl cellosolve; Me cell. = methyl cellosolve.

1-propanol solutions, and with ammonium azide in ethanol solution. A 6-day reaction at 100° is required to obtain a 22.9% yield of ethyl 5-tetrazolylacetate using hydrazoic acid in benzene solution; a 5-day reaction at 75° gave no yield. A 3-day reaction at 95° using hydrazoic acid in 1-propanol also gave no yield. By way of comparison, a 51.5% yield was obtained in 3 days at 100° using ammonium azide in ethanol. The 81% yield obtained in 8 hours at 95° (Table III), using ammonium azide in dimethylformamide solution, emphasizes the desirability of this solvent for the reaction.

The catalytic and solubility data are summarized in Table I.

It is evident from Table I that boron trifluoride-etherate is about as effective a catalyst as ammonium chloride and that chloride salts of progressively weaker amines are increasingly more effective catalysts. Water at the concentration indicated apparently has a detrimental effect, although no significant differences were noted between the use of ordinary commercial dimethylformamide and a rigorously dried, distilled grade.

Similar catalytic and solubility effects are observed in the reactions of aliphatic nitriles with azide salts. Butyronitrile and sodium azide, for example, do not react appreciably in dimethylformamide solution in 24 hours at 120–125°. Substitution of lithium azide for sodium azide resulted in a 4.9% yield of 5-*n*-propyltetrazole. The addition of 10 mole % of boron trifluoride-etherate to the reaction with sodium azide raised the yield of product to 30.5%. Under the same conditions, the use of equimolar amounts of ammonium chloride and sodium azide results in a 73.5% yield of 5-*n*-propyltetrazole (Table III).

The increase in rate of reaction of substituted benzonitriles and ammonium azide with increasing electronegativity of the substituent follows Hammett's σ-values for groups[9] as is shown in Table II.

Table III lists a variety of 5-substituted tetrazoles made by the procedure and indicates the general versatility of the reaction and the appropriate reaction conditions.

The reactions of ammonium azide with methyl and benzyl thiocyanates are of interest in that the addition of azide to the nitrile group occurs preferentially with methyl thiocyanate, whereas the benzyl group is primarily displaced in benzyl thiocyanate. Hydrogen cyanide (as trimethylammonium cyanide) reacts readily with trimethylammonium azide to give tetrazole in moderate yield. No attempt was made to optimize the yield in this study, but the reaction offers an excellent method of obtaining tetrazole in a simple and inexpensive manner.

Attempts to synthesize 5-hydroxy- and 5-mercaptotetrazole by the reaction of trimethylammonium azide with trimethylammonium cyanate and thiocyanate, respectively, failed. Since a trace of 5-aminotetrazole (0.8%) and some sulfur were isolated from the latter reaction, these results suggest that 5-amino-1,2,3,4-thiatriazole was formed and subsequently decomposed. Lieber and Pillai[10] report that the latter compound decomposes readily to cyanamide or dicyandiamide and sulfur.

(9) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 121.

Experimental[11]

The commercially available nitriles[12] were used without purification. Perfluorocaprylonitrile was synthesized from perfluorocaprylic acid[13] by the method of Gilman and Jones[14] in 52% yield, b.p. 100–102° at 705 mm.

One general procedure for the synthesis of 5-substituted tetrazoles was employed; the method of product isolation was varied, however.

A mixture of the nitrile (0.2 mole), sodium azide (14.3 g., 0.22 mole), lithium chloride, the appropriate ammonium chloride or catalyst in the desired molar ratio and 100 ml. of solvent was stirred and heated for a period of time and temperature dependent on the reactivity of the nitrile. Suitable conditions for several types of nitriles can be deduced from the information given in Tables I, II and III. Ammonia and the lower alkylamines were evolved during reactions employing the corresponding ammonium azides. The solvent was then removed at reduced pressure on a steam-bath. At this point one of three procedures was followed: A. If the 5-substituted tetrazole was insoluble in water, the reaction residue was dissolved in 100 ml. of distilled water, and acidified with concentrated hydrochloric acid to *p*H 2 (caution: HN_3 evolved). After cooling to 5° in an ice-bath, the product was removed by filtration, washed with several portions of ice-water and dried. This procedure is suitable for most 5-substituted aryltetrazoles. B. If the 5-substituted tetrazole was soluble or partially soluble in water, the residue was dissolved in 100 ml. of water, made basic to a phenolphthalein end-point with 50% sodium hydroxide solution and evaporated to dryness at reduced pressure on a steam-bath to remove amines. The residue was redissolved in 100 ml. of water, acidified to *p*H 2 with concentrated hydrochloric acid and again evaporated to dryness at reduced pressure on a steam-bath to remove hydrazoic acid. The 5-substituted tetrazole was then extracted from the residue of sodium chloride with ethanol, methanol, etc. This procedure is appropriate for most 5-alkyltetrazoles. C. Alternatively, the final acidified aqueous solution in method B after partial evaporation to remove hydrazoic acid was cooled to room temperature, adjusted to *p*H 5 with base and treated with an aqueous solution of 0.1 mole of copper acetate. The precipitated copper tetrazole derivative was removed by filtration, washed with several portions of water, re-suspended in 100–200 ml. of water and heated with stirring to 50°. Hydrogen sulfide was bubbled into the suspension until the precipitation of copper sulfide was complete. After the copper sulfide had been removed by filtration, the 5-substituted tetrazole was recovered by evaporating the filtrate to dryness at reduced pressure. This procedure was useful for isolating small quantities of 5-alkyltetrazoles in preliminary investigations and for obtaining low melting 5-alkyltetrazoles in a good state of purity.

The physical constants of several previously unreported 5-substituted tetrazoles are lised in Table III.

Acknowledgment.—The authors are indebted to Dr. R. Boschan and Prof. W. Urry for their assistance and helpful discussions.

CHINA LAKE, CALIF.

(10) E. Lieber and C. N. Pillai, *J. Org. Chem.*, **22**, 1054 (1957).

(11) All melting points are uncorrected. Analyses by Galbraith Laboratories, Knoxville, Tenn., and Everett M. Bens of this Laboratory.

(12) Eastman Kodak Co., Rochester, N. Y.

(13) Complimentary sample, Minnesota Mining and Manufacturing Co., St. Paul, Minn.

(14) H. Gilman and R. C. Jones, THIS JOURNAL, **65**, 1458 (1943).