no evidence whatsoever for the existence of the longer wave length peak. However, our spectrum is in satisfactory agreement with that reported by v. Kiss and Gerendàs.[8] The only previous work on the other cobalt(II) complex ions seems to be that of Samuel,[9] who found the maximum absorption of the cobalt(II) ammine complex to lie at 519 mμ, which does not agree very well with our peak at 496 mμ.

It may be seen from Table I that excepting the oxalate complexes the wave lengths of maximum absorption of both the nickel and cobalt complex ions decrease as the stability of the complex ions increases. This behavior has been previously reported for the visible bands of the nickel complexes.[3]

The displacements of the absorption show that for both types of ions the separation of the energy levels responsible for the absorption increases as the stability of the complex ions increases. This is of interest in view of the previously mentioned difference in the magnetic behavior of cobalt and nickel ions, for if it be assumed, as seems reasonable, that the magnetic and optical properties involve the same energy levels, only the cobalt ion moments calculated from the Curie–Weiss equation are in accord with the view that the orbital moment and the energy level separation are connected by an inverse type of relationship. Such a view is justified theoretically[10] for nickel ion, and seems to be a good preliminary assumption for cobalt ion. Within the limits of these assumptions, it would appear that the magnetic moments of cobalt ion should be calculated from the Curie–Weiss equation.

(8) v. Kiss and Gerendàs, Z. physik. Chem., **180A**, 117 (1937).
(9) Samuel. Z. Physik, **70**, 43 (1931).
(10) Schlapp and Penney, Phys. Rev., **42**, 666 (1932).

It is possible further to compare the spectral and magnetic data of nickel ion by means of the Schlapp and Penney[10] theory. Schlapp and Penney relate the magnetic susceptibility with the splitting of the ground energy level by a crystalline electric field of cubic symmetry. Using the magnetic data of Russell, Cooper and Vosburgh[3] and of Field and Vosburgh,[2] we have calculated that the over-all splittings of the ground level of nickel ion in the aquo, oxalate, ammine, ethylenediamine and o-phenanthroline complexes are 18.7, 19.9, 23.1, 29.0 and 30.1 $\times$ 10^3 cm.$^{-1}$, respectively. Assuming that the shortest wave length optical band results from transitions between the highest and lowest of the decomposed levels (except for the oxalate band at 252 mμ), the corresponding spectral values are 25.3, 25.5, 27.4 and 29.0 $\times$ 10^3 cm.$^{-1}$, no value being obtainable from our data for the o-phenanthroline complex. The agreement is such as to indicate that the Schlapp and Penney theory gives the order of magnitude of the splitting of the ground level in nickel ion. However, attempts to interpret other aspects of the absorption by means of this theory do not meet with much success.

Summary

The absorption spectra of several complex ions of nickel(II) and cobalt(II) in aqueous solution have been measured. In both nickel and cobalt the wave lengths of maximum absorption shift to smaller values as the stability of the complex ions increases. The results were discussed briefly in connection with the magnetic properties of the complex ions.

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Alkylthio-(trifluoromethyl)-benzenes[1,2]

BY EARL T. MCBEE AND PETER J. GRAHAM

As a part of an extensive investigation of the properties of trifluoromethyl-substituted benzenes and their derivatives, alkylthio-(trifluoromethyl)-benzenes were synthesized. The preparation and properties of the thio compounds were correlated with alkoxy-(trifluoromethyl)-benzenes.[3]

Müller, Scherer and Schumacher[4] reported the preparation of (trifluoromethylthio)-3-(trifluoromethyl)-benzene from (trichloromethylthio)-3-(trifluoromethyl)-benzene by an adaptation of

(1) From the doctoral thesis of Peter J. Graham.
(2) Presented before Division of Organic Chemistry at the 111th meeting of the American Chemical Society, Atlantic City, N. J., April, 1947.
(3) E. T. McBee, R. O. Bolt, P. J. Graham and R. F. Tebbe, THIS JOURNAL, **69**, 947 (1947).
(4) F. Müller, O. Scherer and W. Schumacher, to Gen. Aniline Works Inc., U. S. Patent 2,108,606, February 15, 1938.

reactions performed by Zincke,[5] who prepared (trichloromethylthio)-4-methylbenzene.

Alkylthio-(trifluoromethyl)-benzenes were prepared by treating a bromo- or chloro-(trifluoromethyl)-benzene with a sodium alkyl sulfide in an alcoholic solvent. The conditions for the reaction depend upon the reactivity[3] of the bromo- or chloro-(trifluoromethyl)-benzene which is directly comparable to the corresponding bromo- or chloronitrobenzene. It is well known that the chlorine in 3-chloronitrobenzene is of about the same order of activity as chlorobenzene but that the activity of the chlorine increases with the number of nitro groups ortho and para to it. For example, 1-chloro-2,4,6-trinitrobenzene is the most active of the chloronitrobenzenes. Simi-

(5) T. Zincke and W. Frohneberg, Ber., **43**, 845 (1910).

TABLE I
ALKYLTHIO-(TRIFLUOROMETHYL)-BENZENES

Compound	M. p., °C.	B. p., °C., (743 mm.)	B. p. °C.	B. p. Mm.	$n^{25}D$	d^{25}_4	Fluorine, % Calcd.	Fluorine, % Found	Mol. wt. Calcd.	Mol. wt. Found
2-CF₃C₆H₄SCH₃	3.7–5.0	208–209	96	25	1.509	1.308	29.7	29.5	192	192
3-CF₃C₆H₄SCH₃	a	192–193	91	25	1.497	1.270	29.7	29.7	192	194
4-CF₃C₆H₄SCH₃	37	198.5–199	80	20	...	...	29.7	29.3	192	...
2,4-(CF₃)₂C₆H₃SCH₃	20.3–21.7	204–205	88.5	12	1.464	1.453	43.8	43.7	260	263
2,5-(CF₃)₂C₆H₃SCH₃	17.0–18.5	195–196	74	10	1.458	1.445	43.8	43.8	260	263
2,6-(CF₃)₂C₆H₃SCH₃	20.4–22.0	205–206	67	12	1.464	1.453	43.8	43.7	260	262
2,4,6-(CF₃)₃C₆H₂SCH(CH₃)₂	a	212–213	63	3	1.428	1.437	48.0	48.0	356	352
2,4,6-(CF₃)₃C₆H₂S-n-C₁₂H₂₅	41	...	..	..	...	...	35.5	34.8	...	...

a Sets to a glass at −50 to −65°.

larly, 1-chloro-2,4,6-tris-(trifluoromethyl)-benzene is the most active of the chloro-(trifluoromethyl)-substituted benzenes investigated.

Reaction between 1-chloro-2,4,6-tris-(trifluoromethyl)-benzene and a sodium alkyl sulfide occurs rapidly at room temperature, whereas reaction between sodium methyl sulfide and a 1-chloro-2,4-bis-(trifluoromethyl)-benzene occurs only slowly at the temperature of refluxing methanol. 2-Chloro-(trifluoromethyl)-benzene reacts slowly in a pressure autoclave at temperatures as high as 200°. Thus, the reactivity of halogen in an aromatic ring increases with the number of (trifluoromethyl) groups ortho and para to it. 2-Bromo-(trifluoromethyl)-benzene reacts much faster than 2 - chloro - (trifluoromethyl) - benzene under comparable conditions. This illustrates again that the bromine atom is much more susceptible than chlorine to such metathetical reactions.

The sodium alkyl sulfides used in these preparations were prepared by dissolving the alkanethiol in an alcoholic solution of sodium methoxide or sodium hydroxide. The chloro-(trifluoromethyl)-benzenes were prepared by procedures described previously.[3]

Experimental

Methylthio-3-(trifluoromethyl)-benzene.—Five-hundred grams of a methanol solution containing 125 g. of sodium methyl sulfide[6] was charged into a one-liter steel autoclave with 338 g. of 3-bromo-(trifluoromethyl)-benzene.[7] The autoclave, which was capable of withstanding pressures in excess of 40 atmospheres, was sealed and then heated electrically to 210° in 7 hours and cooled slowly to room temperature. The contents of the autoclave were washed out with water and steam distilled. The vapors from the steam distillation which were not condensed by a water-cooled condenser were passed through alkaline sodium plumbite before exhausting them to an efficient hood. The organic layer of the steam distillate was washed twice with water, and then dried. Rectification gave 15 g. of material boiling below 160° followed by 236 g. (82% yield and conversion) of methylthio-3-(trifluoromethyl)-benzene and 10 g. of pot-residue.

Methylthio-2-(trifluoromethyl)-benzene.—One-hundred-eighty grams of 2-chloro-(trifluoromethyl)-benzene, 200 ml. of methanol and 180 g. of sodium methyl sulfide were charged into an iron autoclave of one-liter capacity.

(6) A. H. Blatt, "Org. Syntheses," Coll. Vol. 2, J. Wiley and Sons, Inc., New York, N. Y., 1943, p. 345.

(7) J. H. Simons and E. O. Ramler, THIS JOURNAL, 66, 389 (1944).

The autoclave was heated with continuous rocking to 200° in 6 hours and then cooled to room temperature. The contents of the autoclave were washed out with water and steam distilled. The organic layer was dried over anhydrous sodium sulfate and rectified. The rectification yielded 115 g. of 2-chloro-(trifluoromethyl)-benzene, 12 g. of 2-methoxy-(trifluoromethyl)-benzene and 13 g. (19% yield) of methylthio-2-(trifluoromethyl)-benzene.

Methylthio-4-(trifluoromethyl)-benzene was prepared in a similar manner from 4-chloro-(trifluoromethyl)-benzene.

1-Methylthio-2,4-bis-(trifluoromethyl)-benzene.—A solution containing 230 g. of methanol and 77 g. of sodium methyl sulfide was mixed with 83 g. of 1-chloro-2,4-bis-(trifluoromethyl)-benzene[3] in a one-liter round-bottom flask fitted with a reflux condenser. The reaction mixture was refluxed for six hours. A crystalline precipitate of sodium chloride was obtained after about 45 minutes of refluxing. The reaction mixture was cooled and diluted with enough water to dissolve the salt and to obtain an adequate separation of the organic products. The organic layer was separated and combined with chloroform extracts of the aqueous layer. The combined solutions were washed with water and dried. Rectification gave 12.6 g. of 1-chloro-2,4-bis-(trifluoromethyl)-benzene and 56.4 g. (77% yield) of 1-methylthio-2,4-bis-(trifluoromethyl)-benzene.

1-Methylthio-2,6-bis-(trifluoromethyl)-benzene was prepared in a similar manner from the corresponding chloro-bis-(trifluoromethyl)-benzene.

1-Isopropylthio-2,4,6-tris-(trifluoromethyl)-benzene.—1-Chloro-2,4,6-tris-(trifluoromethyl)-benzene was prepared by the successive chlorination and fluorination of mesitylene according to the procedure described for the preparation of the various chloro-bis-(trifluoromethyl)-benzenes.[3] A 250-ml. three-necked flask was fitted with an air-driven stirrer, a thermometer and a dropping funnel. Eight grams of sodium hydroxide, 100 ml. of isopropyl alcohol and 24 g. of 2-propanethiol were placed in the flask and heated to 50°. The clear solution was cooled to 10° and 32 g. of 1-chloro-2,4,6-tris-(trifluoromethyl)-benzene was added dropwise with rapid stirring over a period of fifteen minutes. A rapid reaction occurred as the mixture was warmed slowly to room temperature. The mixture, after refluxing for one hour to ensure completion of the reaction, was diluted with 300 ml. of water. The organic layer was separated and combined with chloroform extracts of the aqueous alcohol layer. The combined solutions were washed twice with water and dried. Rectification under reduced pressure gave 30 g. (84% yield and conversion) of 1-isopropylthio-2,4,6-tris-(trifluoromethyl)-benzene.

n-Dodecylthio-2,4,6-tris-(trifluoromethyl)-benzene was prepared in a similar manner.

Tebbe for certain chemical intermediates, and of A. M. Ribley for analytical data.

Summary

Alkylthio-(trifluoromethyl)-benzenes containing one, two and three trifluoromethyl groups have been prepared by the action of a sodium or potassium alkyl sulfide on a trifluoromethyl-substituted bromo- or chlorobenzene in an alcoholic solvent.

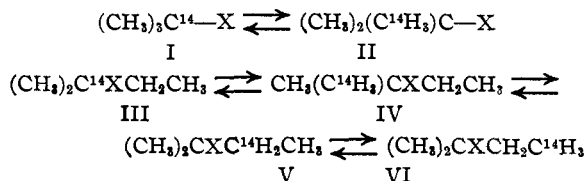# Rearrangements of Carbon Atoms in t-Butyl and t-Amyl Derivatives[1,2]

BY JOHN D. ROBERTS, ROBERT E. MCMAHON AND JACK S. HINE

Rearrangements of the Wagner–Meerwein type of alkyl derivatives with polar catalysts are commonly considered to proceed through carbonium ion intermediates.[3] Where such rearrangements may lead to several products, it is often possible to predict which product will be formed most readily by postulating that the most favorable sequence of carbonium ion intermediates should involve ions of maximum stability formed by successive 1,2-shifts of hydride or alkide ions.[4] The order of carbonium ion stability (tertiary ≫ secondary > primary) is usually inferred from the solvolytic reactivities of alkyl halides in ionizing (but weakly nucleophilic) solvents such as formic acid.[5]

Despite the very considerable work which has been done on carbonium ion rearrangement reactions a number of important problems have not yet been solved. Among these is the question of carbonium ion structure in circumstances where at least two isomeric forms might be expected, each of comparable energy and obtainable from the others by simple 1,2-shifts. Such ions may be represented as a mixture of forms with energy barriers to interconversion depending on their structures and environment or else as single species of intermediate structure.[6] Little concrete experimental evidence bearing on this point is available except for the elegant study made by Winstein and Trifan[6b] of the solvolysis of exo-norbornyl p-bromobenzenesulfonate.[7] The magnitudes of the energy barriers to interconversion of isomeric carbonium ions have not been adequately evaluated and the present investigation is concerned with the ease of rearrangements of the following type in reactions which are commonly considered to involve either stepwise carbonium ion or direct concerted mechanisms. These rearrangements involving substances of identical carbon skeletons and nearly identical energies[8] were studied using C-14 as a tracer. It is expected that investigation of rearrangements between substances of identical energies

$$(CH_3)_3C^{14}—X \rightleftarrows (CH_3)_2(C^{14}H_3)C—X$$
$$\text{I} \qquad\qquad \text{II}$$

$$(CH_3)_2C^{14}XCH_2CH_3 \rightleftarrows CH_3(C^{14}H_3)CXCH_2CH_3 \rightleftarrows$$
$$\text{III} \qquad\qquad\qquad \text{IV}$$

$$(CH_3)_2CXC^{14}H_2CH_3 \rightleftarrows (CH_3)_2CXCH_2C^{14}H_3$$
$$\text{V} \qquad\qquad \text{VI}$$

should enable determination of the magnitude of interconversion energy barriers free of complications resulting from differences in energy between starting materials and products. This advantage is well exemplified by the behavior of the neopentyl cation which when generated in any irreversible reaction undergoes rapid and complete rearrangement to a t-amyl cation.[9] It is not known to what degree this ease of rearrangement is generally characteristic of carbonium ions since it is possible that the isomerization transition state is stabilized by contributions of resonance forms resembling the (more stable)

(1) Supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission.

(2) Preliminary communication, THIS JOURNAL, 71, 1896 (1949).

(3) (a) Whitmore, ibid., 54, 3274 (1932); Chem. Eng. News, 26, 668 (1947). (b) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 317–325.

(4) Mosher and Cox (Abstracts of September 1949 meeting of the American Chemical Society) have presented evidence for 1,3-shifts of methyl groups in the dehydration of 4,4-dimethyl-3-ethyl-2-pentanol.

(5) Bateman and Hughes, J. Chem. Soc., 945 (1940); Hughes, Trans. Faraday Soc., 37, 603 (1941).

(6) (a) Dewar, "The Electronic Theory of Organic Chemistry," The Oxford University Press, London, 1949, pp. 211–213; (b) cf. also references cited by Winstein and Trifan, THIS JOURNAL, 71, 2953 (1949).

(7) It should be noted that the existence of a carbonium ion of intermediate structure is not unequivocally demonstrated by the experiments of Winstein and Trifan since the racemization accompanying the solvolysis could be produced by processes other than

rearrangement of carbon skeleton. Work on the establishment of the structure of the norbornyl cation using C-14 as tracer has been in progress in this laboratory since 1947.

(8) It is recognized that the bond energies of C^{14}–C^{12} bonds are not identical with those of C^{12}–C^{14} bonds. The experimental findings with regard to the magnitude of "isotope effects" arising from such bond energy differences are confusing and, at present, no quantitative evaluation appears to be possible. We believe that isotope effects in our work should be small but there is no assurance that this is actually the case. See Beeck, Otvos, Stevenson and Wagner, J. Chem. Phys., 16, 255, 993 (1948); Meyerson and Daniels, Science, 108, 676 (1948); Bigeleisen, ibid., 110, 14 (1949); Yankwich and Calvin, J. Chem. Phys., 17, 109 (1949); Bigeleisen and Friedman, ibid., 17, 998 (1949); Stevens and Attree, Can. J. Research, 27B, 807 (1949); J. Chem. Phys., 18, 574 (1950) for isotope effects in other reactions.

(9) (a) Whitmore and Rothrock, THIS JOURNAL, 54, 3431 (1932). (b) Whitmore, Wittle and Popkin, ibid., 61, 1586 (1939). (c) Dostrovsky and Hughes, J. Chem. Soc., 166 (1946).