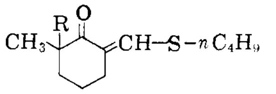
grouping appeared to be a derivative of an α-hydroxymethylene ketone.[1] Using as model ketones 2-methylcyclohexanone, 1-decalone and Δ^6-octalone-1,[2] we found that both the enol ethers[3] and enamines[4] were unsuitable. In both instances the blocking group exerted a profound deactivating effect on the ketone, and the yields on alkylation were poor. The well-known low conjugative effect of the sulfur atom led us to investigate the corresponding α-alkylthiomethylene derivatives, and we now wish to report that the *n*-butylthiomethylene grouping admirably satisfies our requirements and appears to be the most convenient such group yet developed.

Thus hydroxymethylation,[3] and then etherification of the crude product using *n*-butyl mercaptan and the benzene azeotropic procedure led to 2-*n*-butylthiomethylene-6-methyl-cyclohexanone (I, R = H), b.p. 103–105° (0.05 mm.) (95%) (C, 67.54; H, 9.61; S, 15.29); 2-*n*-butylthiomethylene-1-decalone, b.p. 129° (0.05 mm.) (84%) (C, 71.38; H, 9.56; S, 12.81) and 2-*n*-butylthiomethylene-Δ^6-octalone-1 (II, R = H), m.p. 64–64.5° (78%) (C, 71.75; H, 8.68; S,12.92). Although the above etherification procedure is quite convenient, an even milder process was developed whereby the α-hydroxymethylene derivative in pyridine solution at 0° is treated successively with *p*-toluenesulfonyl chloride and alkyl mercaptan. Under these basic conditions there resulted a 64% yield of the octalone derivative (II, R = H) and a 60% yield of the 2-benzylthiomethylene-1-decalone, m.p. 78–79° (C, 75.68; H, 7.96; S, 11.24) was obtained using benzyl mercaptan.



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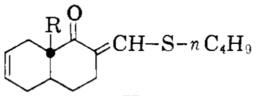

II

The 2-*n*-butylthiomethylene derivatives reacted readily with methyl iodide in *t*-butyl alcohol and potassium *t*-butoxide, and the resulting products were easily isolatable. Thus the 6,6-dimethylcyclohexanone derivative (I, R = CH_3), b.p. 89–91°(0.07 mm.) (C, 68.85; H, 9.82; S, 14.18) was obtained in 84% yield; the 9-methyl-1-decalone derivative, b.p. 138° (0.2 mm.) (C, 72.07; H, 9.83; S, 12.14) in 85% yield; and the *trans*-9-methyl-Δ^6-octalone-1 derivative (II, R = CH_3), b.p. 125–127° (0.06 mm.) (C, 72.41; H, 9.16; S, 12.37) in 80% yield.

Removal of the *n*-butylthiomethylene grouping was accomplished readily by refluxing the derivatives in aqueous diethyleneglycol with potassium hydroxide. In this manner we obtained a 77% yield of 2,2-dimethylcyclohexanone,[3] a 78% yield of 9-methyl-1-decalones[3] and a 83% yield of *trans*-9-methyl-Δ^6-octalone-1, b.p. 127–128° (21 mm.) (C, 80.26; H, 9.87); the 2-furfurylidene derivative, prepared in 73% yield, had m.p. 76–78° alone or on admixture with an authentic sample.[5]

Vapor phase chromatography of the 9-methyl-1-decalone indicated this to be a 60:40 mixture of *cis* and *trans* isomers, while similar analysis of the 9-methyl-Δ^6-octalone-1 showed the presence of only one isomer, *i.e.*, the *trans*-fused system (*vide supra*). In the latter case, therefore, the angular methylation is highly stereoselective.[6]

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[1] Neither the arylidene group [W. S. Johnson, This Journal, **65**, 1317 (1943)] nor the dithioketal group [R. B. Woodward and A. A. Patchett, *J. Chem. Soc.*, 1131 (1957)] could be considered as the former requires a tedious removal sequence and the latter was found to deactivate the ketone drastically (unpublished results from these laboratories).

[2] P. D. Bartlett and G. F. Woods, This Journal, **62**, 2933 (1940).

[3] W. S. Johnson and H. Posvic, *ibid.*, **69**, 1361 (1947).

[4] A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1944).

[5] The authors wish to thank Professor W. S. Johnson for providing us with this sample.

[6] W. S. Johnson and D. S. Allen, Jr., This Journal, **79**, 1261 (1957).

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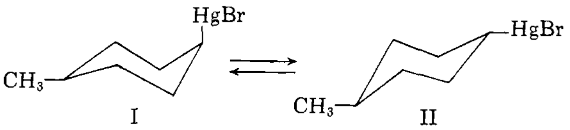
ORGANOMERCURIALS. V. THE CONFORMATIONAL PREFERENCE OF THE BROMOMERCURI GROUP[1]

Sir:

In establishing the configuration of *cis*- and *trans*-4-methylcyclohexylmercuric bromides, it was found that the benzoxymercuri group, as compared to the methyl group, has a relatively small preference for an equatorial over an axial conformation.[2] This observation has led to an examination of the *A* value[3] ($A = -\Delta F = RT$ ln (equatorial conformation/axial conformation) of the bromomercuri group. Unexpectedly within the limits of error, the bromomercuri group has no preference for an equatorial over an axial conformation (*A* value = 0). This result was obtained by measuring directly the position of equilibrium between *cis*-(I) and *trans*-(II)-4-methylcyclohexylmercuric bromides.



I II

The *cis*- and *trans*-4-methylcyclohexylmercuric bromides were isomerized in pyridine at 95° using benzoyl peroxide as the catalyst. The position of equilibrium was approached from both sides. The product composition was determined both by infrared analysis and by isolation of isomers; in the latter case a 92% recovery of products was obtained. The product distribution was 53% *cis*- and 47% *trans*-. This product distribution may indicate that the bromomercuri group prefers an axial orientation; however, slight decomposition occurs under the equilibrium conditions and the *trans*-isomer may decompose preferentially. This limits the accuracy of the data to about ±5%. These data are summarized in Table I.

In additional experiments, 4-methylcyclohexanone was reduced electrolytically at a mercury electrode at 55°. The resulting di-4-methylcyclohexylmercury which was formed under equili-

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] F. R. Jensen and L. H. Gale, This Journal, **81**, 1261 (1959).

[3] S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

TABLE I

EQUILIBRATION OF *cis*- AND *trans*-4-METHYLCYCLOHEXYLMERCURIC BROMIDES

Expt.	Solvent	Temp., °C.	Starting isomer	Method of analysis	% *cis*-	% *trans*-
1	Pyridine	95	*trans*-	Isolation of products	54	46
2	Pyridine	95	*trans*-	Infrared	52	48
3	Pyridine	95	*cis*-	Infrared	54	46

brating conditions, was cleaved stereospecifically with retention of configuration by mercuric bromide. The resulting mixture of *cis*- and *trans*-4-methylcyclohexylmercuric bromides contained an excess of the *cis*-isomer. Also the equilibration of the *cis*- and *trans*-4-methylcyclohexylmercuric bromides was carried out in dioxane at 98° using benzoyl peroxide as the catalyst. In these cases, greater decomposition occurred than in the equilibration in pyridine, product recovery being 65–70%. Again, the *cis*-isomer was present in greater concentration.

Although the present data do not permit an exact determination of the A value for the bromomercuri group, they indicate that the *A* value is approximately 0. This lack of a preference for an equatorial over an axial conformation probably is due, at least in part, to the long carbon–mercury bond and the high polarizability of the mercury atom, which minimize the a,a-1,3, bromomercuri group, hydrogen atom interactions. Eliel and Haber proposed that the relatively small equatorial preference of the bromo group (A = 0.73 kcal./mole) is due to a,a-1,3 London forces.[4] This type of attractive force, and more specific interactions, may be important with the bromomercuri group. The absence of a conformational preference for the bromomercuri group indicates that steric interactions are not necessarily directly related to the radii of the groups involved. The results presented here suggest that certain groups with large radii, such as the bromothallo group, may prefer the axial conformation.

[4] E. L. Eliel and R. G. Haber, THIS JOURNAL, **81**, 1249 (1959).

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THE FORMATION OF DINITROGEN TETRAFLUORIDE IN THE REACTION OF FLUORINE AND AMMONIA

Sir:

The preparation of dinitrogen tetrafluoride (N_2F_4) by the pyrolysis of nitrogen trifluoride over copper was reported recently.[1] We now wish to report the formation of this compound by the vapor phase reaction of fluorine and ammonia in a packed copper reactor.

Ruff and Hanke[2] investigated the vapor phase reaction of fluorine and ammonia in an unpacked copper reactor using both an excess of fluorine and of ammonia. The products in both cases were nitrogen trifluoride and ammonium fluoride (Equation 1), although the presence of other nitrogen fluorides was postulated.

$$4NH_3 + 3F_2 \longrightarrow NF_3 + 3NH_4F \qquad (1)$$

Yields of NF_3 were about 6%, based on the fluorine consumed. Evidently the ammonia was largely converted to nitrogen and hydrogen fluoride

$$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF \qquad (2)$$

We have reinvestigated this reaction in a packed T-shaped copper reactor, using both an excess of fluorine and of ammonia. Nitrogen was employed to dilute the reactants, and reaction proceeded smoothly with moderate evolution of heat. With excess fluorine, results paralleled Ruff's, although NF_3 yields were higher but, with excess ammonia, N_2F_4 also was obtained. The conditions employed are summarized in Table I.

TABLE I

REACTION CONDITIONS

	Excess F_2	Excess NH_3
Ammonia–fluorine ratio	1.1:1 (Stoichiometric = 1.33:1)	1.5:1 to 2.0:1
Nitrogen–fluorine ratio	5:1 to 20:1	5.0:1
Reactor packing	Copper shot or gauze	Copper gauze
Fluorine flow rate	1.3 to 2.5 liters/hr.	1.5 to 2.3 liters/hr.

The yields of NF_3 in the excess fluorine reaction were from 39 to 66% based on Equation 1. The combined product from a series of runs analyzed by mass spectral analysis had the composition: NF_3, 88.25%; CF_4, 9.40%; N_2O, 2.35%. The infrared spectrum agreed with a reference spectrum of NF_3.[3] (Carbon tetrafluoride probably was an impurity in the original fluorine.) Ammonium fluoride also was isolated and identified by chemical and infrared analysis.

In the excess ammonia reaction, unreacted ammonia was removed by water scrubbing or adsorbed on $CaCl_2$ or Linde molecular sieves. The gaseous products then were passed through a −78° trap and collected at −196°. Dinitrogen tetrafluoride was purified by removing more volatile impurities from a trap held at −142° (methylcyclopentane). The infrared spectrum of this purified fraction exhibited the same bands as reported by Colburn and Kennedy[1] and was virtually identical with that of a pure sample of N_2F_4 prepared in our laboratory by NF_3 pyrolysis. The band at 8.0 μ and the doublet at 8.92–8.97 μ are ascribed to C_2F_6 present in the original fluorine. Based on the fluorine converted to NF_3 and N_2F_4, the yields of N_2F_4 were as high as 11%, while NF_3 yields ranged from 6 to 24%.

The isolation of N_2F_4 and the higher yields of NF_3 obtained in our work are believed due, at least partly, to the use of a packed reactor. The copper packing reduces the intensity of the reaction and prevents the conversion of ammonia to nitrogen and hydrogen fluoride.

We wish to acknowledge the assistance of Mr. C. W. Schoenfelder in some phases of this work, and to thank Mr. L. Adlum for the infrared analyses,

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[1] C. B. Colburn and A. Kennedy, THIS JOURNAL, **80**, 5004 (1958).

[2] O. Ruff and E. Hanke, *Z. anorg. u. allgem. Chem.*, **197**, 394 (1931).

[3] E. L. Pace and L. Pierce, *J. Chem. Phys.*, **23**, 1248 (1955).