

such as di-isopropylphenol, carbon-carbon and carbon-oxygen coupling compete.

An example employing nitrobenzene as solvent and pyridine as the ligand will serve to illustrate the reaction. Thus, a solution of 0.04 g. (0.0004 mole) of copper (I) chloride in 30 ml. of nitrobenzene containing 9 ml. of pyridine was shaken with oxygen (one atmosphere) in a closed reaction vessel attached to an oxygen buret. After the copper (I) had been oxidized to the divalent state, 0.977 g. (0.008 mole) of 2,6-dimethylphenol was added, and shaking was continued. After 26 minutes the stoichiometric (equation 1) amount of oxygen was absorbed, and the reaction was allowed to continue for 18 minutes longer to give a total oxygen absorption of 101.5%. The product was isolated by precipitation in 1% (vol.) concentrated aqueous hydrochloric acid in methanol, resuspended in 5% (vol.) concentrated aqueous hydrochloric acid in methanol, and finally reprecipitated in methanol from chloroform solution. After drying in vacuum, there was obtained 0.81 g. (84%) of almost colorless polymer of intrinsic viscosity 0.95 decil./g. (chloroform, 25°) and osmotic molecular weight 28,000. *Anal.* Calcd. for C_8H_8O : C, 79.9; H, 6.7; found: C, 79.7; H, 6.8. The infrared spectrum of this polymer showed no evidence of hydroxyl.

The identical high molecular weight linear polymer is obtained by oxidation of 2,6-dimethyl-4-halophenol, where the halogen is either chlorine or bromine. However, the halide ion released deactivates the catalyst; thus it is necessary to use equimolar amounts of catalyst.

Further details of the reaction, its scope and a discussion of its mechanism will be published in the near future.

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PERFLUOROVINYL METALLIC COMPOUNDS¹

Sir:

Recently described² new perfluoroalkyl tin compounds, $R_3SnC_nF_{2n+1}$ ($R = \text{phenyl, alkyl}$), on treatment with electrophilic reagents (H^+ or BCl_3 , etc.) release alkyl or phenyl groups in preference to perfluoroalkyl groups.³ In terms of relative electronegativity of radicals based on preferential fission of groups from organometallic compounds⁴ this result is surprising. However, although perfluoroalkyl groups are very electronegative, *e.g.*, trifluoriodomethane on hydrolysis yields trifluoromethane not trifluoromethanol, it is conceivable that when such a group is bonded to a tin atom also carrying alkyl or phenyl groups it is the tin-bonded carbon atom of the perfluoroalkyl group

(1) This research was supported by the United States Air Force under Contract No. AF 49(638)-518, monitored by the Air Force Office of Scientific Research of the Air Research and Development Command.

(2) H. D. Kaesz, J. R. Phillips and F. G. A. Stone, *Chem. Ind.*, 1409 (1959).

(3) With base, in nucleophilic attack, perfluoroalkyl groups are cleaved preferentially.

(4) See H. O. Pritchard and H. A. Skinner, *Chem. Reviews*, **55**, 745 (1955), and references cited therein.

which is the relatively electron deficient center and not the tin-bonded carbon atoms of alkyl or aryl groups. This could arise through the strong inductive effect of fluorine atoms acting on a carbon atom linked to tin. In these compounds it is reasonable to assume that the carbon atoms are sp^3 -hybridized. For this reason, and also because of their intrinsic interest, it was pertinent to prepare the hitherto unknown perfluorovinyl metallics where sp^2 -hybridized carbon atoms would be bonded simultaneously to fluorine and to metals. In such compounds the α -carbon atom of a perfluorovinyl group might well be relatively electron rich because of its filled $p\pi$ -orbital. A possible route to such compounds is by vinylation of metal halides with perfluorovinyl Grignard, a reagent known to us as $CF_2=CFMgI$,⁵ but inaccessible because of rarity of the iodide from which it is derived. However, we have found that the commercially available halide $CF_2=CFBr$ readily forms a Grignard in tetrahydrofuran.⁶

With halides of metals and metalloids this perfluorovinyl Grignard affords a variety of new perfluorovinyl compounds. Dimethyltin dichloride yields bis-(perfluorovinyl)-dimethyltin, $Me_2Sn(CF_2=CF)_2$ (b.p. 58° (38 mm.)), 65% yield (calcd. for $C_6H_6F_6Sn$: C, 23.2; H, 2.0. Found: C, 22.9; H, 1.9). With trifluoroacetic acid the perfluorovinyltin compound gives trifluoroethylene quantitatively (identified by infrared spectrum). Methyl groups are not cleaved.

Similarly alkylperfluorovinyltin compounds with boron halides afford perfluorovinylhaloboranes, *e.g.*, $CF_2=CFBCl_2$ (analyzed as its Me_3N adduct; calcd: C, 27.0; H, 4.0; N, 6.3. Found: C, 27.2; H, 4.3; N, 6.1; and by hydrolysis to yield $CF_2=CFH$ quantitatively), b.p., 38.5° (extrap.). This reaction is similar to that of $Bu_2Sn(CH=CH_2)_2$ with boron halides.⁷

Many properties of the perfluorovinyl compounds contrast strikingly those of their vinyl or perfluoroalkyl analogs: $Me_2Sn(CF_2=CF)_2$ is air sensitive, $Me_2Sn(CH=CH_2)_2$ is not; $CF_2=CFBCl_2$ slowly forms BF_3 , $CH_2=CHBCl_2$ is stable; and $(CF_2=CF)_3As$ (b.p. 57.5° (83 mm.)) is stable to base, but $(CF_3)_3As$ is hydrolyzed readily.

(5) J. D. Park, R. J. Seffl and J. R. Lacher, *THIS JOURNAL*, **78**, 59 (1956).

(6) During our work this Grignard was also formed by I. L. Knunyants, R. N. Sterlin, R. D. Yatsenko and L. N. Pinkina, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1345 (1958); *C.A.*, **53**, 6987g (1959), but only its hydrolysis with acid was studied.

(7) F. E. Brinckman and F. G. A. Stone, *Chem. Ind.*, 254 (1959); Abstracts of papers presented at 135th Meeting A.C.S. Boston, April, 1959, p. 26-M.

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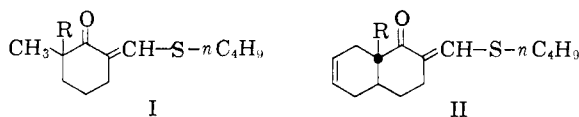
THE *n*-BUTYLTHIOMETHYLENE GROUPING: A SUPERIOR BLOCKING GROUP FOR THE ALKYLATION OF KETONES

Sir:

Recently, we had need of protecting the methylene adjacent to a ketone with a grouping that would not deactivate the carbonyl and could be removed easily after alkylation. The most promising such

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 ethers³ and enamines⁴ 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-methylcyclohexanone (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.



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 = CH₃), 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 = CH₃), 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-decalones³ 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

(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).

(7) Public Health Service Research Fellow of the National Heart Institute.

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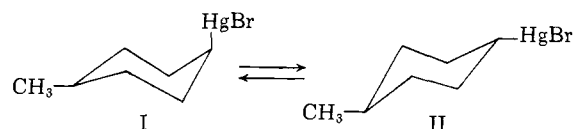
JAMES A. MARSHALL⁷

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ORGANOMERCURIALS. V. THE CONFORMATIONAL PREFERENCE OF THE BROMOMERCURI GROUP¹

Sir:

In establishing the configuration of *cis*- and *trans*-4-methylcyclohexylmercuric bromides, it was found that the benzoylmercuri 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* value³ ($A = -\Delta F = RT \ln$ (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.



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 $\pm 5\%$. 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-

(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).

(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).