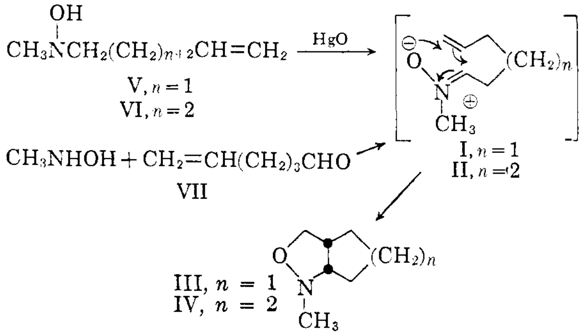


In addition, 5-hexenal (VII) was isolated and characterized as its 2,4-dinitrophenylhydrazone.

The oxidation of dialkylhydroxylamines proceeds through several intermediates to give nitrones.[2,3] Isolation of III and VII again demonstrates the preferential formation of the most highly substituted nitrone groups in such oxidations.[2]

In order to validate the occurrence of an intermediate nitrone (*e.g.*, as opposed to a radical anion),[3] we have investigated a second route to I and III. Nitrous acid deamination of a mixture of the 3-aminocyclohexanols[4] furnished 5-hexenal (VII) (38%), b.p. 118–121°. Equimolar quantities of VII and freshly prepared N-methylhydroxylamine gave after purification a 40% yield of the isoxazolidine III.

As additional structure proof, III was reduced with zinc and acetic acid to an oily aminoalcohol. The oxalate melted at 180–181° and did not depress the melting point of a sample of the oxalate of synthetic N-methyl-*cis*-2-hydroxymethylcyclopentylamine[1,5] (m.p. 181–181.5°).

When applied to the next higher homolog VI,[1] the mercuric oxide oxidation afforded *cis*-N-methyl-8-oxa-7-azabicyclo[4.3.0]nonane (IV) (18 %), b.p. 70–72° (15 mm.).[6] The infrared spectrum of IV was free of bands in the OH, NH, carbonyl or carbon–carbon double bond region. It formed a hydrogen oxalate, m.p. 95–95.8°.[5] Treatment with zinc and acetic acid produced an aminoalcohol, the infrared spectrum of which was identical with that of N-methyl-*cis*-2-hydroxymethylcyclohexylamine (m.p. 45–46°, hygroscopic)[5] prepared by lithium aluminum hydride reduction of the *N*-*cis*-2-carboxycyclohexylformamide,[5,6] m.p. 200–201°. Both the reduction product and the synthetic aminoalcohol formed hydrogen oxalates melting at 104–105° (m.m.p. 103–105°). From the crude oxidation mixture 6-heptenal as its 2,4-dinitrophenylhydrazone, m.p. 95.5–96°,[5] was isolated. Identity was established by reduction of its diethyl acetal and conversion to heptanal-2,4-dinitrophenylhydrazone.

In addition to applications to other systems,[7] we are investigating various oxidation procedures as preparative routes to the isoxazolidines themselves and the unsaturated aldehydes which can subsequently react with the appropriate monoalkylhydroxylamine.

Acknowledgment.—We are grateful to the Research Corporation for a generous grant in support of this work.

[3] D. H. Johnson, M. A. T. Rogers and G. Trappe, *J. Chem. Soc.*, 1093 (1956).

[4] R. R. Burford, F. R. Hewgill and P. R. Jefferies, *ibid.*, 2937 (1957).

[5] Satisfactory analytical results have been obtained for all of the new compounds described herein.

[6] Prepared by formylation of *cis*-2-aminocyclohexanecarboxylic acid. We wish to thank Professor A. C. Cope for informing us of a procedure for the preparation of this acid *via* the reduction of anthranilic acid.

[7] We have been informed by Professor R. Huisgen (private communication) that he and his co-workers have effected the additions of certain stable nitrones to strained olefins such as norbornylene.

DEPARTMENT OF CHEMISTRY
WAYNE STATE UNIVERSITY
DETROIT 2, MICHIGAN
NORMAN A. LEBEL
JONG JAI WHANG

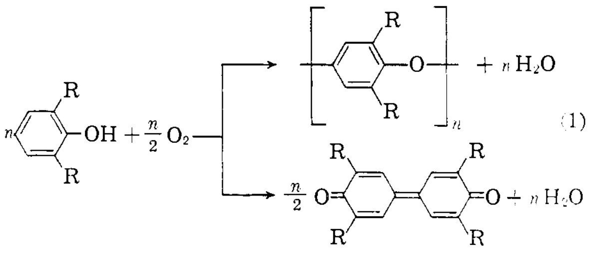
RECEIVED OCTOBER 6, 1959

POLYMERIZATION BY OXIDATIVE COUPLING

Sir:

We wish to report the discovery of a new oxidative coupling reaction leading to the preparation of high molecular weight 2,6-di-substituted-1,4-phenylene ethers. In the past only low molecular weight 2,6-di-substituted-1,4-phenylene ethers have been prepared. Thus, Dewar and James[1] in an extension of earlier work reported by Süs and coworkers,[2] attempted the synthesis of poly-2,6-di-substituted-1,4-phenylene ethers by the thermal decomposition of substituted benzene-1,4-diazooxides but only with limited success. More recently, Staffin and Price[3] have extended earlier work reported by Hunter and co-workers,[4] and have prepared low molecular weight poly-2,6-dimethyl-1,4-phenylene ether by oxidative displacement of the bromine in 4-bromo-2,6-dimethylphenol.

Our reaction employs a 2,6-di-substituted phenol and is carried out at room temperature by merely passing oxygen through a solution of the phenol in an organic solvent containing an amine and a copper(I) salt as a catalyst. The stoichiometry is as shown in equation 1.



(1)

When the substituent groups are small, as in 2,6-dimethylphenol, carbon-oxygen coupling occurs and linear polyphenylene ethers with intrinsic viscosities up to 3.4 decil./g. have been obtained. With bulky groups, as in 2,6-di-*tert*-butylphenol, carbon–carbon coupling occurs and the diphenoquinone is the sole product. In intermediate cases

[1] M. J. S. Dewar and A. N. James, *J. Chem. Soc.*, 917 (1958).

[2] O. Süs, K. Möller and H. Heiss, *Ann.*, **598**, 123 (1956).

[3] G. Staffin and C. C. Price, Fifth Joint Army-Navy-Air Force Conference on Elastomer Research and Development, October 15–17, 1958, Dayton, Ohio. See *Rubber World*, **139**, 408 (1958), for an abstract of this paper.

[4] W. H. Hunter and M. J. Morse, THIS JOURNAL, **55**, 3701 (1933), and earlier papers.

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.

GENERAL ELECTRIC A. S. HAY
RESEARCH LABORATORY H. S. BLANCHARD
P.O. BOX 1088 G. F. ENDRES
SCHENECTADY, NEW YORK J. W. EUSTANCE

RECEIVED SEPTEMBER 30, 1959

PERFLUOROVINYL METALLIC COMPOUNDS[1]

Sir:

Recently described[2] new perfluoroalkyl tin compounds, $R_3SnC_nF_{2n+1}$ (R = 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 compounds[4] this result is surprising. However, although perfluoroalkyl groups are very electronegative, *e.g.*, trifluoroiodomethane 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 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, $Me_2Sn(CF{=}CF_2)_2$ (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: $Me_2Sn(CF{=}CF_2)_2$ 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.

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[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.

[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.

MALLINCKRODT CHEMICAL LABORATORY H. D. KAESZ
HARVARD UNIVERSITY S. L. STAFFORD
CAMBRIDGE 38, MASSACHUSETTS F. G. A. STONE

RECEIVED SEPTEMBER 30, 1959

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