As we cannot observe reactions of BH_3 with rate constants less than 10^6 l./(mol sec), it is evident that BH_3 reacts quite readily with stable boron hydrides. Not only do these observations define a characteristic reaction of BH_3, but they also imply that the higher homologs of BH_3, *i.e.*, B_4H_8[10] and B_9H_{13},[11] should act in like manner. Whether they do so or not remains to be shown by experiment. The full details of these experiments will be published in due course.

[10] R. E. Hollins and F. E. Stafford, *Inorg. Chem.*, 9, 877 (1970).

[11] J. Plesek, S. Hermanek, B. Stibr, and F. Hanousek, *Collect. Czech. Chem. Commun.*, 32, 1095 (1968).

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Homogeneous Catalysis of Friedel–Crafts-Type Reactions by Arene–Group VIB Tricarbonyls

Sir:

We wish to report some preliminary results of a new method of homogeneous catalysis of Friedel–Crafts-type reactions by the half-sandwich compounds $ArM(CO)_3$ (Ar = arene; M = Cr, Mo, W). We have observed that these catalysts promote reactions such as alkylation, acylation, sulfonylation, dehydrohalogenation, and polymerization, generally very conveniently and in high yields. The discussion in this paper will be confined to the Mo system, since it has been studied most extensively; however, the same reactions are promoted more or less conveniently by the Cr and W systems, research on which is currently in progress.

Table I. Examples of Reactions Catalyzed by $ArMo(CO)_3$

Substrate	Organic chloride	Added catalyst	[Catalyst], *M*	Reaction conditions	Comments
Toluene	*tert*-Butyl chloride	$Mo(CO)_6$	6.5×10^{-3}	Reflux, 5 hr	84.6% alkylation
Toluene	*tert*-Butyl chloride	$(tol)Mo(CO)_3$	6.5×10^{-3}	Reflux, 1 hr	81.8% alkylation
Toluene	*tert*-Butyl chloride	$AlCl_3$	Heterogeneous	Reflux, 0.75 hr	88% alkylation
Toluene	$C_6H_{11}Cl$	$Mo(CO)_6$	2.5×10^{-3}	Reflux, 24 hr	84.5% alkylation
Toluene	$C_6H_5CH_2Cl$	$Mo(CO)_6$	2.5×10^{-3}	Reflux, 12 hr	100% alkylation (90% methyl diphenylmethane; 10% polymer)
Anisole	*tert*-Butyl chloride	$Mo(CO)_6$	2.5×10^{-3}	135°, 24 hr	79% alkylation (100% para)
Phenol	*tert*-Butyl chloride	$Mo(CO)_6$	2.5×10^{-3}	Refluxing heptane, 18 hr	93% *p*-*tert*-butyl phenol, 3% 2,4-di-*tert*-butyl phenol
Anisole	CH_3COCl	$Mo(CO)_6$	5×10^{-3}	100°, 36 hr	68% acetylation (90% para, 4% ortho)
Toluene	Tosyl chloride	$Mo(CO)_6$	5×10^{-3}	Reflux, 36 hr	43% sulfonylation
Anisole	Tosyl chloride	$Mo(CO)_6$	5×10^{-3}	135°, 24 hr	22% sulfonylation
	$C_6H_5CH_2Cl$	$Mo(CO)_6$	5×10^{-3}	100°, 1 hr	100% polybenzyl
Durene	*p*-$ClCH_2C_6H_4CH_2Cl$	$Mo(CO)_6$	5×10^{-3}	120°, 3 hr	90% condensation polymer
Diphenyl ether	*m*-$ClSO_2C_6H_4SO_2Cl$	$Mo(CO)_6$	5×10^{-3}	Decalin solvent, 140°, 16 hr	Low to moderate yields of condensation polymer
	tert-Butyl chloride	$Mo(CO)_6$	3×10^{-2}	Reflux, 20 hr	No reaction, 96% $Mo(CO)_6$ recovered
	tert-Butyl chloride	$(tol)Mo(CO)_3$	5×10^{-2}	Reflus, 4 hr	Large amounts of HCl evolved, two polymeric substances obtained

Table I reports some examples of the reactions investigated. Whereas the reactions appear to be general, the examples in the table are those in which products are formed in highest yields in direct reaction.

The active form of the catalyst appears to be the arenetricarbonylmetal, rather than the hexacarbonyl, from experiments on *tert*-butyl chloride with $Mo(CO)_6$ and $ArMo(CO)_3$ (see Table I). Also shown in Table I, and supporting this view, is evidence that the catalyst decomposition products do not promote the reactions. If one of the reactants is aromatic, and the boiling point of the reaction mixture is sufficiently high (>80°), then the hexacarbonyl may be added and the catalyst generated in solution.

Although Bamford and coworkers have shown that $Mo(CO)_6$ reacts with organic halides *via* a free-radical mechanism,[1] we believe that reactions catalyzed by $ArMo(CO)_3$ proceed by way of carbonium ion generation. The polymerization of benzyl chloride, which yields polybenzyl in 100% yield in less than 1 hr, was used as a test of free-radical *vs.* carbonium ion mechanism. When the polymerization was carried out using high concentrations of free-radical traps such as galvinoxyl or 2,2-diphenyl-1-picrylhydrazyl, the reaction proceeded to completion unhindered. Alternately, when an attempt was made to promote polymerization by such free-radical initiators as azobis(isobutyronitrile), dibenzoyl peroxide, or cumene hydroperoxide, no reaction was observed. The actual mechanism of carbonium ion generation is not fully understood at this time; studies on this aspect are currently in progress.

In some of the reactions reported in Table I, the catalyst gradually decomposes and the reaction subsides. However, the reaction resumes upon further addition of small amounts of catalyst. In some cases, $ArMo(CO)_3$ can be isolated upon completion of the reaction; in these instances, addition of further amounts of the organic halide causes resumption of the reaction.

A comparison of the relative rates of reaction using preformed catalyst, $ArM(CO)_3$, and $Mo(CO)_6$ is shown in Table I. The observation that the reaction containing the preformed catalyst is much faster than that where $Mo(CO)_6$ is added and the catalyst generated in solution may be related to the fact that the rate of formation of $ArM(CO)_3$ is slow in the absence of ultraviolet light[2] or donor solvents such as diglyme.[3]

[1] C. H. Bamford, G. C. Eastmond, and F. J. T. Fildes, *Chem. Commun.*, 144, 146 (1970), and references contained therein.

In parallel reactions comparing catalysis of alkylation by $AlCl_3$ and $ArMo(CO)_3$, generally similar reaction times produced similar yields. However, the arenetricarbonylmetal compounds show distinct advantages over $AlCl_3$ in promoting Friedel–Crafts reactions, particularly in storing and handling of the catalysts, and also in reaction work-up where $AlCl_3$ functions as a homogeneous catalyst. In reactions involving $ArM(CO)_3$, the decomposed catalyst can simply be filtered from the solution, yielding the relatively uncontaminated reaction mixture.

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(2) W. Strohmeier, *Chem. Ber.*, **94**, 3337 (1961).

(3) R. P. M. Werner and T. H. Coffield, *Chem. Ind.* (*London*), 936 (1960).

Book Reviews

Art in Organic Synthesis. By Nitya Anand, Jasjit S. Bindra (Central Drug Research Institute, Lucknow), and Subramania Ranganathan (Indian Institute of Technology, Kampur). Holden-Day, Inc., San Francisco, Calif. 1970. xiv + 414 pp. $8.95.

The explosive development of synthetic organic chemistry in the last 30 years has left a great legacy in our understanding of selective reaction and stereochemical control. The authors of this book have sought to prepare a reference for rapid access to this information and have been spectacularly successful.

The strong point of this book and its most unique feature is the extensive use of flow charts. There are approximately 3000 structural formulas, many in full stereochemical projection, giving a tremendous pictorial impact to even a brief perusal of the pages. Somewhat more than 100 syntheses have been outlined with frequent reference to alternative and parallel approaches.

The text has been extensively cross-referenced by reaction name, reaction type, reagent, author, and subject. The alphabetical arrangement of the syntheses is particularly convenient to someone generally familiar with the work, but arrangement by compound type might be more sensible for readers less versed in the field. Perhaps the most interesting way to use this book is merely to open to a random page. The authors have dealt with a wide variety of organic compounds with considerable attention to steroids and alkaloids, polypeptides and polynucleosides, and strained and unusual compounds.

Technically the book has been well done. The formulas have been carefully and correctly reproduced. Editorial comments are short and pertinent. At its relatively modest price, the book will undoubtedly find its way onto the shelves of most chemists interested in synthesis, students, teachers, and researchers alike.

John T. Groves, *University of Michigan*

The Irreducible Representations of Space Groups. J. Zak, Editor, A. Casher, M. Gluck, and Y. Gur. W. A. Benjamin. Inc., New York, N. Y. 1969. x + 271 pp.

This book is essentially a list of tables with directions of usage. They have been derived by a method (solvability) different from that used originally by Kovalev (ray representations, also called weighted or loaded representations) in his pioneering work giving the first complete compilation of space group representations. Obviously the results should be equivalent, and those by Zak, *et al.*, do not presuppose a working knowledge of ray representations. They are also tabulated in a more convenient way (from this reviewer's stand point) and printed in a more pleasing format.

The tables have hopefully been checked by the authors against Kovalev's. This reviewer has only made a few spot checks and found them accurate (except the "international" symbol of C_{3h}, page 30). As usual, the reader is advised to pay attention to the particular notation convention used, which is fairly agreeable to this reviewer.

As the expert would only consult these tables for special points on the boundaries of the Brillouin zone, and even then only for nonsymmorphic space groups, the tempting question is: How many chemists will ever need to consult these tables? However, past experience may indicate that this reviewer may want to eat these words in a few years. Thirty years ago Bouckaert, Smoluchowski, and Wigner felt that physicists would hardly ever need them, which obviously is not the case now. When Zak, *et al.*, state (p 19) that "for representations...of basic importance in solids, it is sufficient to know the character tables in order to take into account the time reversal symmetry," they may also turn out to be overoptimistic. Like many other "representation" tables, these here (in contrast to Kovalev's) are actually only character tables.

Raoul Kopelman, *University of Michigan*

The Chemistry of the Isoquinoline Alkaloids. By Tetsuji Kametani (Tohoku University, Japan). American Elsevier Publishing Co., New York, N. Y. 1969. viii + 266 pp. $21.00.

This, the authoritative monograph in this area, has been written by one of the leading workers in the field. It is indispensable for libraries and a valuable book of reference for alkaloid chemists. The literature is covered exhaustively through about 1966. There are subject and alkaloid name indexes. The value of this book would be enhanced with time if supplemental volumes could be prepared.

Fortschritte der Chemie organischer Naturstoffe. Volume XXVII. Edited by L. Zechmeister (California Institute of Technology). Springer-Verlag, Vienna and New York. 1969. viii + 412 pp. $33.00.

This volume in the series contains reviews of cellulose ultrastructure and biogenesis (A. Frey-Wyssling), ethylene in nature (M. Spencer), spectroscopic studies of carotenoids (B. C. L. Weedon), stereochemistry in the vitamin D series (G. M. Sanders, J. Pot, and E. Havinga), flavonoids (K. Weinges, W. Bähr, W. Ebert, K. Goritz, and H.-D. Marx), constituents of *Amanita muscaria* (C. H. Eugster), marine toxins (P. J. Scheuer), and lysozyme (M. A. Raftery and F. W. Dahlquist). The literature is covered up to about 1968, although some 1969 references have been cited. There are good author and subject indexes.

P. W. Le Quesne, *University of Michigan*

Chemical Applications of Far Infrared Spectroscopy. By Arthur Finch, P. N. Gates, K. Radcliffe (Royal Holloway College), F. E. Dickson (Gulf Research and Development Co.), and F. F. Bentley (Wright-Patterson Air Force Base). Academic Press, London and New York. 1970. vii + 277 pp. $14.50.

The introductory chapter sets the stage for the sequential sections of the book. The authors, rightly so, realize that drums don't sound, bugles don't blow, and firecrackers don't ignite when you cross the 200-cm^{-1} point into the far-infrared; therefore, they have backed up this limit a bit to include the many torsional modes, bendings, and lattice vibrations which are found in the region below 400 cm^{-1}. Wisely included in the first chapter is a plot of the Boltzmann distribution of molecules in the various energy levels present in this low-frequency region to acquaint the reader with the possibilities of molecules existing with reasonable population in higher energy levels as well as the ground state. Amplifying this degree of disorder in the energy levels is a plot of entropy, given in Figure 5, as a function of frequency. From this figure, one can easily appreciate the contribution of low-frequency vibrations to molecular thermodynamic properties.