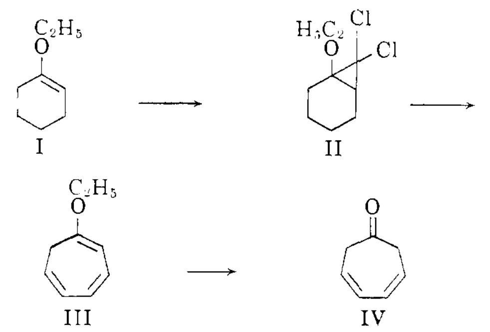

The structure of compound IV was initially assigned on the basis of its unusual ultraviolet spectrum [λ_{max}^{EtOH} 204 mμ (ϵ 6820), $\lambda_{shoulder}^{EtOH}$ 278 (ϵ 602), $\epsilon_{290\ m\mu}$, 567] and the excellent correspondence of its infrared spectrum with that previously published for 3,5-cycloheptadienone.[3] The structural assignment was confirmed by the n.m.r. spectrum of the compound,[7] which showed a strong doublet at 168 and 173 cps. (weight 3.8) with very weak absorption at 134, 141, and 202 cps. (weight 0.6). The hydrogens on the double bonds formed a complex multiplet from 315 to 363 cps. (weight 3.6). Further evidence for the structure of IV was obtained by its conversion to cycloheptanone 2,4-dinitrophenylhydrazone, m.p. and m.m.p. 143–145°, to 3,5-cycloheptadienyl p-nitrobenzoate, m.p. 81–81.5° (reported 81.5–82.5°),[3] and to its Diels–Alder adduct with N-phenylmaleimide, m.p. of adduct 204–205° (reported 199–202°)[3] by the methods previously described.[3]

Application of this method to the synthesis of other cycloalkadienones and to the synthesis of the isomeric tropolones is under study.

Acknowledgment.—This work was supported by a grant from the National Science Foundation (NSF-G14458).

[7] The n.m.r. spectrum was run at 56.4 megacycles/sec. in carbon tetrachloride using tetramethylsilane as an internal standard. We are indebted to Drs. John E. Wertz and William Schwabacher for determining this spectrum for us.

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NOVEL SELECTIVITY IN REDUCTION OF KETONES BY LITHIUM N-DIHYDROPYRIDYLALUMINUM HYDRIDE

Sir:

We have shown previously that lithium N-dihydropyridylaluminum hydride (I) is a selective reducing agent for certain aldehydes and ketones, but is without effect on carboxylic esters and acids.[1] Upon further investigation of the relative reactivities of various ketones, we have observed that diaryl ketones are much more reactive toward I[2] than are either dialkyl or arylalkyl ketones, both in intermolecular and intramolecular competition experiments. This novel selectivity is in direct contrast with the results of Brown on the rates of sodium borohydride reduction in isopropyl alcohol,[3] where the reactivity of pertinent ketones was acetone > acetophenone > benzophenone. Indeed, as far as we are aware, the reactivity sequence reported below is without precedent in previous studies of nucleophilic addition to carbonyl groups, where aryl substitution generally enhances ground state stability by resonance and further may retard nucleophilic attack because of steric effects.[3,4]

Initial competitive experiments were carried out by allowing equimolar amounts of benzophenone and a second ketone to react with excess I in pyridine for several hours. For example, after one hour the product mixture from benzophenone and 2-octanone showed only a trace of the former (weak infrared absorption at 6.1 μ), but an 83% recovery of the latter (by vapor phase chromatography). Similarly, when benzophenone and 1-tetralone were kept with I for three hours, then worked up, infrared showed essentially complete consumption of the diaryl ketone and the tetralone was recovered in 95% yield as the 2,4-dinitrophenylhydrazone. A second series of experiments was conducted on individual ketones, using aliquots of the same sample of I. The following ketones were completely reduced (by infrared) after three hours exposure to excess I[5]: benzophenone, 4,4'-dichlorobenzophenone, 4-chlorobenzophenone, 4,4-dimethylbenzophenone and fluorenone. On the other hand, after twelve hours, these ketones were incompletely reduced, using the same ratio of reactants as above (yields of product alcohol, as determined by v.p.c.): 2-octanone (69%), acetophenone (33%), 4-methoxyacetophenone (29%), 3-methoxyacetophenone (70%), and benzyl methyl ketone (58%).

It appeared especially desirable to demonstrate the above selectivity intramolecularly in suitable diketones. For this purpose, we have prepared 4-(*p*-benzoyl)-phenyl-2-butanone (II), m.p. 36–37°, by benzoylation of 4-phenyl-2-butanone in carbon disulfide with aluminum chloride (*Anal.* Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.68; H, 6.46: λ_{max}^{EtOH} 259 (log ϵ 4.3)). The orientation of the entering benzoyl group was established by oxidation of II to *p*-benzoylbenzoic acid. The infrared spectrum of II showed well separated carbonyl bands at 5.9 μ ($R_2C{=}O$) and 6.1 μ ($Ar_2C{=}O$), which proved useful for following the course of reduction by complex I. When II (5 mmoles) reacted with excess I (30 mmoles) in pyridine for three hours, and was worked up as

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[1] P. T. Lansbury and J. O. Peterson, *J. Am. Chem. Soc.*, **83**, 3537 (1961).

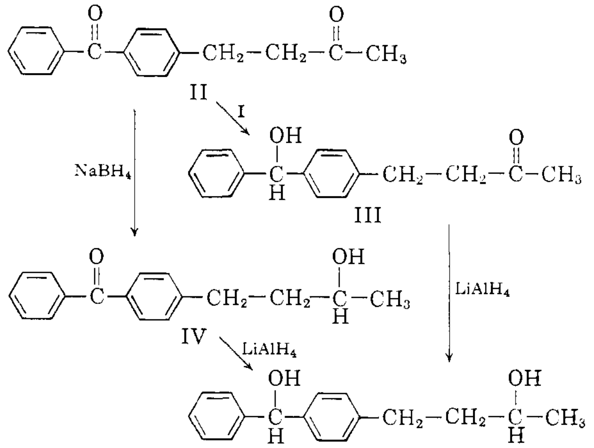
[2] Concerning the structure of I, evidence that dihydropyridyl moieties coordinated to aluminum are the source of hydride ion has been previously noted (ref. 1). By studying hydride and/or deuteride transfer to benzophenone from complexes prepared from pyridine-4-D and $LiAlH_4$ or $LiAlD_4$, it has been further established that both 1,2- and 1,4-dihydropyridyl groups are present in approximately the statistical amounts. A further complication, however, is the possibility that the complex may contain from one up to four dihydropyridyl groups per aluminum (*cf.* J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 2835 (1961)) and this is supported by elemental analyses of crystalline samples of I, which do not fit any of the expected values for a single structure.

[3] H. C. Brown, O. H. Wheeler and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957).

[4] H. C. Brown and K. Ichikawa, *J. Am. Chem. Soc.*, **84**, 373 (1962).

[5] Subsequently, it was found that benzophenone and fluorenone are completely reduced in five minutes when treated with 25 mole % excess I, as above. The other diaryl ketones would most likely react at a comparable rate.

usual, the crude product showed strong absorption at 5.9 μ and only a very weak band at 6.1 μ, indicative of ketol III as the major carbonyl component. Separation of the product mixture by gradient elution chromatography afforded 8% recovered II, 56% of III and 36% of the diol (V) resulting from complete reduction. The structure of III follows from its infrared spectrum (>C=O at 5.9 μ) and the absence of strong ultraviolet absorption in the 240–300 mμ region, as well as its further reduction to the diol. Compound V, preparable from II, III, or IV by reduction with lithium aluminum hydride, was obtained as an oil, which could not be separated into individual racemates. It was, however, analytically pure (*Anal.* Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.66; H, 7.73; infrared: O—H stretching at 2.7–3.0 μ) and gave rise to a crystalline bis-3,5-dinitrobenzoate, m.p. 70–74° (50% ethanol), (*Anal.* Calcd. for $C_{31}H_{24}N_4O_{12}$: C, 57.77; H, 3.75: Found: C, 58.18; H, 3.91). On the other hand, treatment of II with an equimolar quantity of sodium borohydride in ethanol and processing as above gave 46% of ketol IV ($\lambda_{\max}^{\mathrm{EtOH}}$ 259, log ϵ 4.3) and 54% diol V, but no II or III. Clearly, further study of reaction conditions should lead to enhanced yields of III and IV, with less concomitant diol formation.



Preliminary indications that the above selectivity is of appreciable scope have been gained by the conversions of 2-acetyl-9-fluorenone[6] to 2-acetyl-9-fluorenol and *p*-benzoylphenylacetone to *p*-(α-hydroxybenzyl)-phenylacetone in high yield by complex I. However, an attempted selective reduction of the 6-ketone function in 6-ketoestrone methyl ether was not successful, this being understandable in view of the efficient aryl conjugation of that group (*vide infra*).

Compounds III and IV, obtained by column chromatography as described, were converted to the 2,4-dinitrophenylhydrazones, m.p. 88–91° and 155–157°, respectively (*Anal.* Calcd. for $C_{23}H_{22}O_5N_4$: C, 63.59; H, 5.10; N, 12.90. Found: for III, 2,4-DNPH, C, 64.21; H, 5.22; N, 13.06; $\lambda_{\max}^{\mathrm{EtOH}}$ ϵ 359 (22,400); for IV 2,4-DNPH, C, 64.01; H, 5.18; N, 12.80; $\lambda_{\max}^{\mathrm{EtOH}}$ ϵ 381 (28,600). The absorption maxima of the dinitrophenylhydrazones are in good accord with those of model compounds, such as the corresponding derivatives of 2-butanone and 4-methylbenzophenone.

While it is somewhat premature to put forward specific mechanistic proposals in explanation of the above data, several points are quite clear. The highest reactivity toward I is observed in those ketones where an aryl group is forced out of conjugation with the carbonyl group,[7] thus allowing the −I effect to supersede the otherwise dominating resonance effect.[4] The abnormally high reactivity of phenyl *t*-butyl ketone toward sodium borohydride was rationalized in this manner.[4] Dialkyl ketones, *e.g.*, 2-octanone, are quite sluggish, because of the +I substituents surrounding the carbonyl group, but are somewhat more reactive than aryl ketones where resonance interaction is not inhibited, *e.g.*, acetophenone and 4-methoxyacetophenone.

The phenomena reported here are of both theoretical and synthetic interest. We anticipate that a careful study of substituent effects on reactivity will help to elucidate the novel reactivity of complex I, particularly the differences compared with sodium borohydride toward substrates such as II. This project is underway in our laboratory, as well as continued studies on the structure and selectivity of the reagent.

Acknowledgment.—We gratefully acknowledge the generous support of this research by the National Science Foundation (Grant No. G15739).

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[6] Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 5449 (1958).

[7] R. N. Jones, *ibid.*, **69**, 2141 (1945).

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CONCERNING THE MECHANISM OF FORMATION OF PHENYL-(TRIHALOMETHYL)-MERCURIALS

Sir:

Reutov and Lovtsova[1] recently described a useful synthesis of aryl-(trihalomethyl)-mercury compounds by the reaction of an arylmercuric halide with chloroform or bromoform and potassium *tert*-butoxide in benzene solution. The mechanism of this reaction was stated to involve insertion of a dihalocarbene into the mercury-halogen linkage, since the reaction conditions used paralleled those in the production of dihalocarbenes in the Doering–Hoffmann 1,1-dihalocyclopropane synthesis.[2] The interpretation of this synthesis of aryl-(trihalomethyl)-mercurials in terms of a novel carbene reaction appears to have gained some acceptance,[3] and this prompts us to report results which contradict this assumed mechanism. The experiments noted here are pertinent.

Reaction of phenylmercuric bromide with chloroform and potassium *tert*-butoxide in benzene at 0° with high speed stirring, following the reported procedure,[1] gave *only* phenyl-(trichloromethyl)-mercury, m.p. 116.5–118° (*n*-hexane), in 51% yield. Unreacted phenylmercuric bromide was recovered in 33% yield. Furthermore, in a separate

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[1] O. A. Reutov and A. N. Lovtsova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1716 (1960); *Doklady Akad. Nauk S.S.S.R.*, **139**, 622 (1961).

[2] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[3] See for instance "A Brief Survey of Carbene Chemistry," R. C. de Selms, *Org. Chem. Bull.* (*Eastman Kodak Co.*), **34**, No. 1 (1962).