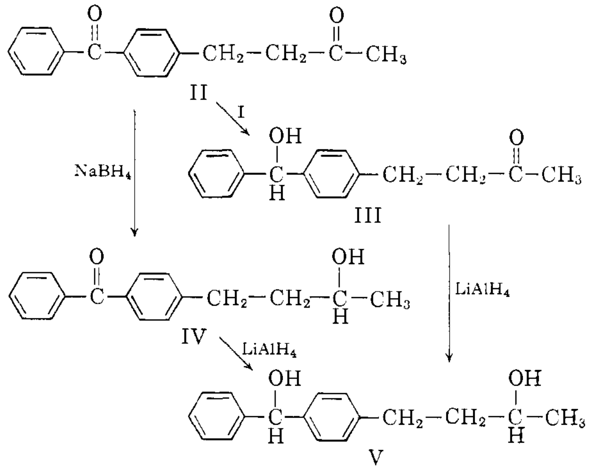
usual, the crude product showed strong absorption at 5.9 μ and only a very weak band at 6.1 μ, indicative of ketol III as the major carbonyl component. Separation of the product mixture by gradient elution chromatography afforded 8% recovered II, 56% of III and 36% of the diol (V) resulting from complete 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 (λ_{max}^{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; λ_{max}^{EtOH} ϵ 359 (22,400); for IV 2,4-DNPH, C, 64.01; H, 5.18; N, 12.80; λ_{max}^{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).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BUFFALO
BUFFALO 14, NEW YORK
PETER T. LANSBURY
JAMES O. PETERSON

RECEIVED APRIL 2, 1962

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).

experiment in which phenylmercuric bromide was treated with potassium chloride in a solvent mixture consisting of *tert*-butyl alcohol, chloroform and benzene for 4 hr. with high speed stirring, no halide exchange producing phenylmercuric chloride was observed. In addition, phenyl-(bromodichloromethyl)-mercury,[4] prepared by the above reaction in which bromodichloromethane was used in place of chloroform, was shown to be inert toward chloride ion under similar conditions.

These results speak strongly against a dihalocarbene insertion mechanism for the reaction of phenylmercuric chloride with haloforms and potassium *tert*-butoxide. Were such a mechanism to obtain, phenyl-(bromodichloromethyl)-mercury would be the product expected in the phenylmercuric bromide–chloroform–potassium *tert*-butoxide reaction in view of the demonstration that neither phenylmercuric bromide nor phenyl-(bromodichloromethyl)-mercury undergo exchange with chloride ion under the conditions used. Our results indicate that the formation of the phenyl-(trichloromethyl)-mercurial isolated proceeded by simple nucleophilic displacement of bromide ion by the trichloromethyl anion. Hine[5] demonstrated the intermediacy of this anion in the formation of dichlorocarbene by the basic hydrolysis of chloroform, and the lifetime of such carbanion intermediates (relative to their decomposition to dihalocarbenes) is sufficiently long to allow other reactions besides dihalocarbene formation to be observed. Also pertinent is the fact that nucleophilic displacement of chloride ion from mercury in organomercuric chlorides (*e.g.*, by iodide ion[6]) is known to occur readily. It therefore is not surprising to encounter a displacement reaction such as the one demonstrated by us.

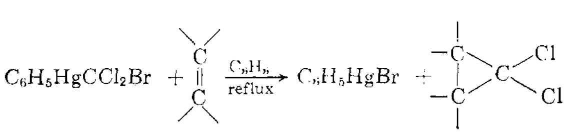
$$\mathrm{C_6H_5HgBr + CCl_3^- \longrightarrow C_6H_5HgCCl_3 + Br^-}$$

When bromine-containing haloforms were used in this reaction, the products were those expected, *e.g.*

$$\mathrm{C_6H_5HgCl \xrightarrow{CHCl_2Br,\ \mathit{t}\text{-}C_4H_9OK} C_6H_5HgCCl_2Br}$$

but the interpretation of these reactions is complicated by the fact that exchange between bromide ion (from the haloform-base reagent mixture, which is used in twofold excess) and phenylmercuric chloride does occur.

The use of phenyl-(trichloromethyl)-mercury and phenyl-(tribromomethyl)-mercury in the synthesis of 1,1-dihalocyclopropanes has been reported by us.[7] It is of special interest from the synthetic standpoint that the presence of a bromine substituent in the trihalomethyl group greatly facilitates the reaction of these mercurials with olefins. Thus phenyl-(bromodichloromethyl)-mercury is far superior to phenyl-(trichloromethyl)-mercury in its reaction with olefins to produce exclusively 1,1-dichlorocyclopropanes, since reaction times of only a few hours are sufficient to give comparable (85–90%) yields in the case of the former mercurial. Phenyl-(dibromochloromethyl)-mercury[8] serves excellently as starting material for the synthesis of 1-bromo-1-chlorocyclopropanes by the same procedure. The mechanism of the phenyl-(trihalomethyl)-mercury-olefin reaction is under investigation. Details concerning these and related experiments will be reported at a later date.



Acknowledgment.—The authors are grateful to the U. S. Army Research Office (Durham) for generous support of this work.

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[4] M. p. 110–111°, with vigorous decomposition immediately upon melting. *Anal.* Calcd. for $\mathrm{C_7H_5Cl_2BrHg}$: Hg, 45.53; Cl, 16.09; Br, 18.14. Found: Hg, 45.82; Cl, 15.96; Br, 17.90.

[5] J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).

[6] D. Seyferth and R. H. Towe, *Inorg. Chem.*, **1**, 185 (1962).

[7] D. Seyferth, J. M. Burlitch and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

[8] M.p. 110–111° (dec.). *Anal.* Calcd. for $\mathrm{C_7H_5ClBr_2Hg}$: Hg, 41.36; Cl, 7.30; Br, 32.95. Found: Hg, 41.36; Cl, 7.07; Br, 32.71.

DEPARTMENT OF CHEMISTRY DIETMAR SEYFERTH
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS JAMES M. BURLITCH

RECEIVED MARCH 24, 1962

LARGE SECONDARY INTERMOLECULAR KINETIC ISOTOPE EFFECTS IN NON-EQUILIBRIUM SYSTEMS. ENERGIZATION BY CHEMICAL ACTIVATION

Sir:

The existence of very large, *normal*, secondary intermolecular kinetic isotope effects was pointed out recently by Rabinovitch and Current, and the quantum statistical basis of the phenomenon described.[1] These effects *may* arise quite widely in unimolecular systems in which the energized species are produced in some non-equilibrium distribution $f(\epsilon)$, *i.e.*, one in which the populations of the various energy levels of interest are not governed by the ambient temperature and statistical thermodynamic equilibrium considerations. The experimental techniques may in suitable cases include excitation by electron impact, light absorption, radiation, *etc.* In fact, thermal collisional activation may also be employed and, under conditions where non-equilibrium populations prevail (the lower pressure region of thermal unimolecular reactions), has been shown to give rise to very large *inverse* intermolecular secondary isotope effects.[2]

The above mentioned authors performed experiments involving excitation of vibrational and active rotational degrees of freedom by chemical activation,[3] in which the rates of C–H rupture of energized ethyl-d_1 and ethyl-d_3 radicals were compared at 25°, *i.e.*, $\mathrm{C_2H_4D^* \rightarrow C_2H_3D + H}$ and $\mathrm{C_2H_2D_3^* \rightarrow C_2HD_3 + H}$. The relative rates for this secondary isotope effect at lower pressures were $k_{\mathrm{d_1}}/k_{\mathrm{d_3}} \sim 2.2$, or a factor of ~1.5 per extra D atom. Although very large as compared with the customary effect per D atom in equilibrium unimolecular systems,[1] the total effect is below the frequently observed magnitude of C–H, C–D primary isotope effects in equilibrium[4] and non-equilibrium[5]

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[1] B. S. Rabinovitch and J. H. Current, *Can. J. Chem.*, **40**, 557 (1962).

[2] B. S. Rabinovitch, D. W. Setser and F. W. Schneider, *ibid.*, **39**, 2609 (1961).

[3] B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 730 (1959), *et seq.*

[4] L. Melander, "Isotope Effects in Reaction Rates," Ronald Press Co., New York, N. Y., 1960.