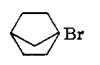
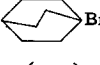



conformation for resonance stabilization of the free radical.

TABLE I
POLAROGRAPHIC HALF-WAVE POTENTIALS

Halide	$E_{1/2}^a$ (volts vs. Ag-AgBr)	Halide	$E_{1/2}^a$ (volts vs. Ag-AgBr)
 Br	-2.17	$C_6H_5CH_2Br$	-0.82
 Br	-1.79	$CH_3(CH_2)_{15}Br$	-1.79
		$CH_3(CH_2)_7Br$	-1.81
		$CH_3(CH_2)_3Br$	-1.81
 CH CB ⁺	-1.42	$CH_3(CH_2)_3Br$	-1.77
		CH_3CH_2Br	-1.70

^a Solutions 0.002 *F* in alkyl halide and 0.03 *F* in Et₄NBr.

The nature of the stabilization in the bromotriptycene reduction is not clear at this time. Conjugation with the aromatic systems is apparently excluded because of the unfavorable orientation of the rings, while a negative inductive effect⁴ could facilitate the reduction only if the potential-determining step involved a negatively charged transition state which led to such products as a carbanion, or a bromide ion plus a free radical.

The evidence now available for the reduction of non-bridgehead compounds does not distinguish between front-side attack on bromine and back-side attack on carbon. The difference of about 0.15 v. between the half-wave potentials of the acyclic compounds and that of 1-bromobicyclo[2.2.2]octane may be a consequence of mechanistic changeover. On the other hand, all reductions may occur *via* reductive attack on bromine, the more negative half-wave potentials for the bicyclo compounds being simply the result of steric strain in transition states leading to nonplanar free radicals. The difference of 0.1 v. between the half-wave potentials of 1-bromobicyclo[2.2.2]octane and 1-bromoadamantane reported by Lambert and co-workers⁵ agrees with this view, if it is assumed that an adamantyl free radical is slightly less strained than a bicyclooctyl free radical. The determination of half-wave potentials of less strained bicyclo compounds having one or more three-carbon bridges in addition to two-carbon bridges should be helpful in settling this point.

Acknowledgment.—The authors wish to thank Professor Paul D. Bartlett for a sample of 1-bromotriptycene, Professor C. A. Grob for a sample of bromobicyclooctane, and Professor Kenneth B. Wiberg for a sample of bromobicycloheptane.

(4) G. Wittig and W. Tochtermann, *Ann.*, **660**, 23 (1962).

(5) F. L. Lambert, A. H. Albert, and J. P. Hardy, *J. Am. Chem. Soc.*, **86**, 3155 (1964).

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RECEIVED MAY 7, 1964

Polarography of Organic Halogen Compounds. II. Sterically Hindered Alicyclic Bromides¹

Sir:

The polarographic reduction of three bridgehead bromides² might appear to vitiate any fundamental

(1) Part I: F. L. Lambert and K. Kobayashi, *J. Am. Chem. Soc.*, **82**, 5324 (1960).

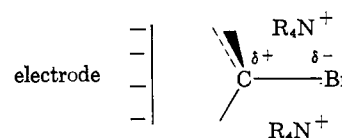
(2) J. W. Sease, P. Chang, and J. L. Groth, *ibid.*, **86**, 3154 (1964).

basis for the correlation of polarographic half-wave potentials of organic bromides with their classic displacement rates.^{1,3a} Further, Sease and co-workers² are led by their results to postulate the electroreduction of R-Br compounds as involving a displacement *on* bromine.

However, parallel work in our laboratories (Table I) indicates that the electrochemical reduction of bridgehead and hindered bromides supports our use of Elving's basic mechanism for the electrode process.³

Briefly stated: as the R-Br compound diffuses toward the immediate vicinity of the negative electrode, the bromine end of the C-Br dipole should be oriented away from the electrode surface.^{3b} The electrostatic field of the electrode acts to increase the polarization of the carbon-halogen bond as this C-Br portion of the molecule nears the electrode.

The reaction point just prior to the transition state is³



Depending on several factors⁴ the actual potential-determining step for an R-Br compound may involve direct ionization to form R⁺ and Br⁻ (SN1-like) or may involve adding an electron to a σ^* to form (R-Br)⁻ *i.e.*, an SN2-like step.

The behavior of the bridgehead bromides provides an illuminating test of this basic picture of the reduction mechanism. Steric interference by the bulky rings of the bridgehead compounds hinders close approach of the back side of the C-Br to the electrode. This should effectively prevent direct addition of an electron to a σ^* to form (R-Br)⁻ in an SN2-like process. Such steric interference to close approach should also decrease the polarizing influence of the electrode's field on the relatively distant C-Br group. Thus, because formation of neither an anion radical nor a carbonium ion can occur readily, reduction should not—and does not—take place at moderate potentials.

However, as the electrode potential is made more negative, a correspondingly greater polarization of the C-Br bond toward C^{δ+}-Br^{δ-} occurs. If the polarization proceeds far enough, *i.e.*, if the electrode potential is negative enough, ionization might be expected to occur, and to occur at potentials in an order determined by the relative ease of formation of the carbonium ions from the bridgehead compounds.⁵ The reduction potentials do follow this order, indicating that an ionic process of dissociation to carbonium ions³ (an SN1-like electrode process) may be the potential-determining step.⁶

(3) (a) P. J. Elving and B. Pullman [*Advan. Chem. Phys.*, **3**, 1 (1961)] reiterate Elving's valid cautions about using terms which are derived from homogeneous reaction kinetics (SN1, SN2) to apply to the heterogeneous electrode process. However, it would be profitable to use SN1-like or SN2-like if these terms describe potential-determining steps which are experimentally indicated as different by consistent correlation of $E_{1/2}$ values with homogeneous reaction rates. (b) *Ibid.*, **3**, 14 (1961).

(4) *E.g.*, steric influences in the R of RBr, polar effects in R, resonance stabilization of groups in R, bond strength of R-X, and the nature of the supporting electrolyte.

(5) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).

Additional support for such an ionic transition state involving carbonium ions is given by the difference in polarographic behavior between *endo*- and *exo*-norbornyl bromides. Both contain C-Br bonds whose carbon back sides are highly hindered; close approach of C-Br to the electrode is improbable. If ionization were to occur to form carbonium ions, it should take place in *exo*-norbornyl bromide more readily than in *endo*- because of anchimeric aid in the *exo*- bromide. Indeed, *exo*- norbornyl bromide reduces at a potential considerably less negative than the *endo*- compound.

Similarly, the back side of the carbon attached to the equatorial bromine in *trans*-4-*t*-butylcyclohexyl bromide is almost as hindered as a bridgehead bromide. In the absence of assisting electrical effects, it is expected from the mechanism here presented that the reduction should not occur until a very negative potential (-2.45 v.)—probably by an SN1-like ionization because SN2-like addition of an electron is impossible. In contrast, the *cis* compound with its axial bromine is far less hindered than any of the other bromides of this study but comparable to a hindered acyclic secondary bromide. It can be attacked from the rear of the carbon in the C-Br bond to form (R-Br)⁻. Indeed, *cis*-4-*t*-butylcyclohexyl bromide is found to reduce at a potential characteristic of hindered acyclic bromides.¹

A decision as to the correctness of the mechanism of Sease² or of that described with the support of this experimental work awaits further critical tests.⁷

TABLE I

HALF-WAVE POTENTIALS OF BRIDGEHEAD AND OTHER CYCLOALKYL BROMIDES^a

Bromide	E _{1/2} ^b
4-Bromocamphane	Not reducible to -2.7 ^c
1-Bromobicyclo[2.2.2]octane ^d	-2.48
1-Bromoadamantane ^e	-2.38
<i>endo</i> -Norbornyl bromide ^f	-2.43
<i>exo</i> -Norbornyl bromide ^g	-2.34
<i>trans</i> -4-Bromo- <i>t</i> -butylcyclohexane ^h	-2.45
<i>cis</i> -4-Bromo- <i>t</i> -butylcyclohexane ^h	-2.32

^a Experimental conditions as in ref. 1. ^b In volts vs. the S.C.E. ^c This result, although probable, is tentative because the purity of the 4-bromocamphane was not conclusively established. We thank Dr. S. Weinstein for a sample of the precursor, 4-camphylmercuric bromide. ^d We thank James W. Riechel for the preparation of this compound and Ted W. Reid for preliminary work on it. (A. A. Sayigh, Ph.D. Thesis, Columbia University, 1952.) ^e Reference 4. ^f J. D. Roberts, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3329 (1950). ^g J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950). ^h E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **24**, 143 (1959). We thank C. A. Flegal for preliminary work on this compound.

(6) If the radical anion stability of the bicyclo compounds [Cf. K. W. Bowers, G. J. Nolfi, Jr., and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 3707 (1963)] is found to follow the same order as the rate of formation of carbonium ions, this would make plausible an electrode process involving an SN2-like electron attack into the "cage" of methylene groups behind the C-Br to form a radical anion.

(7) This work was supported by National Science Foundation Grants G-11282 and, in part, GP-1438. Aid for summer research under the National Science Foundation Undergraduate Research Participation Program for J. W. Riechel (G-12126) and A. H. Albert (GE-987) is also gratefully acknowledged.

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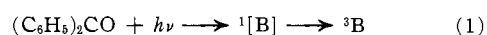
RECEIVED MAY 16, 1964

Excited States in the Photolysis of Carbonyl Compounds. The Photosensitized Decomposition by Benzophenone

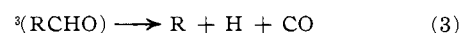
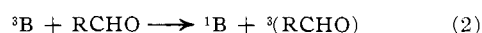
Sir:

This communication reports some experiments on the photosensitized decomposition of carbonyl compounds with benzophenone; from the results it is inferred that the excited state precursor of the "type 2" decomposition products in the direct photolysis of carbonyl compounds is a singlet excited state.

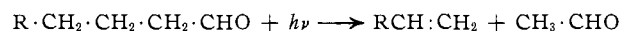
Recently Berman, Stanley, Sherman, and Cohen¹ reported that various aliphatic aldehydes may be decomposed by irradiation in the presence of benzophenone, presumably by the reactions



where ³B is a triplet excited state of benzophenone and



That an energy transfer process was involved rather than a direct reaction was suggested by the change in the quantum yield of photoreduction of benzophenone by alcohol, on the addition of aldehyde. The processes suggested differ from the direct photodecomposition in that the additional "type 2" reaction is apparently



absent as no olefinic products were reported.

To verify this last point, a number of comparative photolyses were carried out with 2-ethylhexanal, *n*-hexanal, butanal, heptan-2-one, and pentan-2-one. Two liquid samples of each compound were irradiated with a mercury arc after deoxygenation with a stream of nitrogen. The first sample was irradiated alone in a quartz test tube; the second was irradiated together with benzophenone (0.5 M) in a Pyrex test tube. Samples were taken during irradiation from the vapor phase by means of a syringe through a serum cap, and from the liquid phase after completion of the experiment. They were analyzed with a Perkin-Elmer Model 452 vapor phase chromatograph. For each compound a variety of products was obtained which could be interpreted in the light of previous observations,² but in each case the peak on the chromatogram which could be associated with the type 2 olefinic reaction product was absent from the products of the photosensitized decomposition with benzophenone. Thus, for example, with 2-ethylhexanal, hexanal, and heptan-2-one a peak due to butene was detected among the products from direct photolysis. This was absent from the samples irradiated with benzophenone.

Earlier workers³ have suggested that the type 2 decomposition proceeds *via* a singlet excited state. Ausloos and his co-workers⁴ have questioned this view

(1) J. D. Berman, J. H. Stanley, W. V. Sherman, and S. G. Cohen, *J. Am. Chem. Soc.*, **85**, 4010 (1963).

(2) For reviews, see J. N. Pitts, *J. Chem. Educ.*, **34**, 112 (1957); P. Borrell, *Nature*, **188**, 1002 (1960).

(3) V. Brunet and W. A. Noyes, *Bull. soc. chim. France*, 121 (1958); P. Borrell and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A262**, 19 (1961).

(4) R. P. Borkowski and P. Ausloos, *J. Am. Chem. Soc.*, **84**, 4044 (1962).