

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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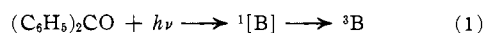
RECEIVED MAY 16, 1964

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

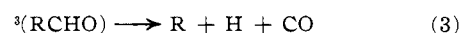
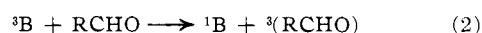
Sir:

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.

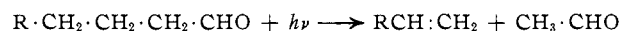
Recently Berman, Stanley, Sherman, and Cohen¹ reported that various aliphatic aldehydes may be decomposed by irradiation in the presence of benzophenone, presumably by the reactions



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).

but Michael and Noyes⁵ have reaffirmed the original suggestions. If the energy-transfer mechanism from benzophenone outlined in reactions 1 to 3 is correct, then the triplet state of the carbonyl compounds decomposes to free-radical products. These results show that it does not yield type 2 products. It can be inferred, therefore, that the type 2 decomposition takes place through a singlet intermediate as was originally suggested.

The free-radical products in the normal photodecomposition may well arise from a triplet state, but it is clear from the work of Parmenter and Noyes⁶ that the type 1 products (alkane and carbon monoxide) also arise from singlet excited states.

Acknowledgment.—The author wishes to thank the D.S.I.R. and the London Chemical Society for apparatus grants.

(5) J. L. Michael and W. A. Noyes, *J. Am. Chem. Soc.*, **85**, 1027 (1963).

(6) C. S. Parmenter and W. A. Noyes, *ibid.*, **85**, 416 (1963).

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An X-Ray Diffraction Study of Nonplanar Carbanion Structures

Sir:

Recently, spectroscopic investigations of the compound $\text{KC}(\text{CN})_3$ have been reported by Long, Carrington, and Cravenor,¹ and Miller and Baer.² An assignment can be made, on the basis of both infrared and Raman spectra, for either a planar trigonal or a pyramidal model for the anion. Both sets of investigators favor the planar structure. A preliminary X-ray diffraction study by Anderson and Klewe³ of $\text{KC}(\text{CN})_3$ also favors a planar anion within rather large experimental limits.

We have determined, by X-ray diffraction techniques, the crystal structure of the compounds ammonium tricyanomethide, $\text{NH}_4\text{C}(\text{CN})_3$, and pyridinium dicyanomethylide, $\text{C}_5\text{H}_5\text{N}^+\text{-C}^-(\text{CN})_2$. Complete three-dimensional refinements of both structures show the trigonal carbon atom environments to be significantly nonplanar.

Both compounds crystallize in the monoclinic system with the unit cell constants shown in Table I. Both structures were solved through Patterson projections down the short axis followed by a three-dimensional analysis based on packing and other considerations.

TABLE I

Space group	$\text{NH}_4\text{C}(\text{CN})_3$ $\text{C}_{2h}^2\text{-P2}_1/\text{c}$	$\text{C}_5\text{H}_5\text{N}_3$ $\text{C}_{2h}^2\text{-P2}_1/\text{m}$
<i>a</i>	9.055 ± 0.007 Å.	7.87 ± 0.02 Å.
<i>b</i>	3.87 ± 0.010 Å.	12.512 ± 0.004 Å.
<i>c</i>	17.325 ± 0.014 Å.	3.86 ± 0.01 Å.
β	104.6 ± 0.2°	114.8 ± 0.1°
<i>Z</i>	4	2

The structure of $\text{NH}_4\text{C}(\text{CN})_3$ was refined by two-dimensional Fourier and least-squares techniques fol-

(1) D. A. Long, R. A. G. Carrington, and R. B. Cravenor, *Nature*, **196**, 371 (1962).

(2) T. A. Miller and W. K. Baer, *Spectrochim. Acta*, **19**, 73 (1963).

(3) P. Anderson and B. Klewe, *Nature*, **200**, 464 (1963).

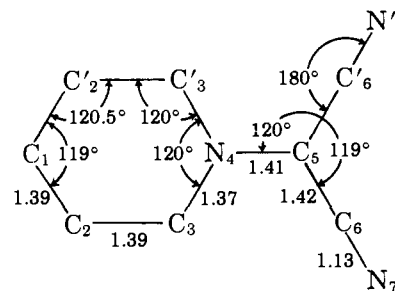


Fig. 1.—Bond distances and angles in pyridinium dicyanomethylide.

lowed by a complete full matrix isotropic weighted least-squares. The final *R* value for the 112 independent (*h0l*) data was 8%. The *R* value for the 429 independent three-dimensional data was 10%. The observed dimensions of the $\text{C}(\text{CN})_3^-$ ion are: C-C bond length, 1.40, 1.40, and $1.40 \pm .01$ Å.; C-N bond length, 1.15, 1.14, and 1.16 ± 0.1 Å.; C-C-C bond angle $119^\circ 40'$, $119^\circ 31'$, and $119^\circ 32' \pm 1^\circ$; C-C-N bond angle 180, 180, and $180 \pm 1^\circ$. If one passes a plane through the three nitrogen atoms of this ion, the central carbon atom is found to be 0.13 Å. above this plane and the cyanocarbon atoms are all 0.08 Å. above this plane. Each C-C-N unit makes an angle of 3° with respect to its projection in this plane. There are no abnormal interionic distances.

The structure of $\text{C}_5\text{H}_5\text{N}^+\text{-C}^-(\text{CN})_2$ was refined by the same procedure as that employed for $\text{NH}_4\text{C}(\text{CN})_3$. The final value of *R*, based on 325 independent (*hkl*) data was 12%. The observed dimensions of the molecule are shown in Fig. 1. The molecule lies across a crystallographic mirror plane through atoms 1 and 4. The pyridinium ring as well as the trigonal carbon atom are coplanar within ± 0.01 Å. The two cyano groups are inclined with respect to this plane such that the distance from the plane to atoms 6 and 7 are 0.08 Å. and 0.13 Å., respectively. All distances reported in this molecule have an associated estimated standard deviation of ± 0.01 Å.

It thus appears that in both these systems a significant deviation from planarity of the carbanion group exists, even though the possibility of resonance stabilization of a planar configuration is possible. Detailed accounts of these results will be presented elsewhere.

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RECEIVED JUNE 12, 1964

Cubane

Sir:

We have completed the synthesis and fundamental characterization of the hydrocarbon cubane.

The bromocyclopentadienone dimer I, prepared as described in an earlier communication,¹ is converted

(1) P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 962 (1964).