STUDIES ON THE CYCLOBUTADIENYL DIANION[*]

By Waldemar Adam[**]
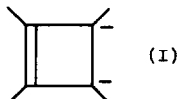
Department of Chemistry, University of Puerto Rico

Río Piedras, Puerto Rico

Simple molecular orbital theory has been quite successful in predicting the stability of charged, monocyclic pseudoaromatic systems. The cyclopropenyl cation (1), cyclopentadienyl anion (2) and the tropylium cation (3), are some well recognized examples. Recently this series has been extended by synthesizing the cyclooctatetraenyl dianion (4), and the cyclobutenium dication (5).

Application of the Hückel rule, $4n + 2$, predicts that the cyclobutadienyl dianion (I) should also possess aromatic stability since it has six p-electrons or $n = 1$. Experiments were directed toward the synthesis of this compound of theoretical


(I)

interest. Recent work by R. Criegee (6) produced well suited

starting materials for the synthesis of (I).

n-Butyl lithium (7) is frequently used to prepare organo-

lithium compounds which cannot be prepared readily by the direct

reaction of lithium with the halide. It was hoped that such me-

tal-halogen interchange between 3,4-dihalo-1,2,3,4-tetramethyl-

cyclobutene (II) and n-butyl lithium would occur readily result-

ing in the desired dianion (I). When the diiodide of (II) was

treated with n-butyl lithium at -70°C using dietyl ether as

(II) X=Cl, Br, I   (III)   (IV)
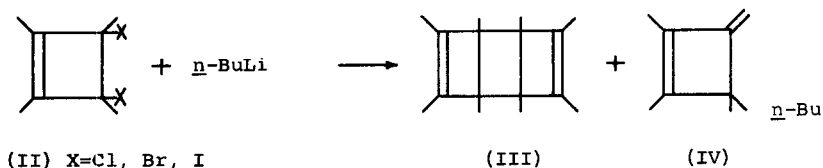
solvent and the resulting reaction mixture was decomposed with

methanol, there was isolated the syn-dimer of cyclobutadiene (8)

and (IV) in 41 and 20% yields, respectively. The structure of

the methylene cyclobutene* (IV) was assigned on the basis of

combustion data, I.R.-,U.V.-, and N.M.R.-spectra. The reaction

of the dichloride (II) with butyl lithium was very sluggish and

an appreciable reaction could only be observed above 30° afford-

ing a 25% yield of (IV). The dibromide was intermediate in its

_____

*G. Fischer, Technische Hochschule Karlsruhe, Germany, private
communication. (The reaction of the dichloride (II) with phenyl
lithium results in a similar product where the n-butyl group is
replaced by a phenyl group.)

reactivity. Gas chromatographic analysis of the reaction mix-
tures showed that not even traces of tetramethylcyclobutene (V)
were formed (9), and thus it is concluded that the reaction of
the dianion with methanol did not take place because the former
was not produced during the reactions.

Since the formation of t-alkyl lithium compounds is re-
ported (7) to be difficult in diethyl ether, the above reactions
were repeated using pentane as solvent. With the dichloride and
the dibromide the reaction was too sluggish to proceed at an ap-
preciable rate even at reflux temperatures. The diiodide did
react at room temperatures and gave a small yield of (IV).
Gas chromatographic analysis of the products again indicated the
absence of (V).

Thus metal-halogen interchange using n-butyl lithium failed
to produce (I) as a stable entity and interest was directed to-
ward the direct interaction of lithium with (II) in ammonia as
solvent. After treatment with water, a mixture of (III)   and
(V)   was obtained. The yields of (III) and (V) depended greatly

(II) X=Cl, Br, I   (III)   (V)

on the temperature, reactants, concentrations, order of addition,
and time of addition. Highest yields of (V), 78%, were realized

when a dilute solution of the dichloride (II) was added rapidly
to a dilute solution of lithium in ammonia at -33°C. When the
reaction mixture, after low temperature removal of ammonia, was
treated with deuterium oxide instead of water, (V) contained no
deuterium atoms as shown conclusively by the IR-and NMR- spectra.
This again indicates that the dianion (I) was not an intermediate
in this reaction and the experimental results can be interpreted
in terms of a stepwise transfer of the protons from ammonia to
the intermediary monoanion of (II). Trialkyl amines were used
as solvents in order to avoid the proton transfer of ammonia.
Unfortunately the alkali metals do not appreciably dissolve in
trimethyl or triethyl amine.

Metal-hydrogen interchange (10) was then considered as a
possible route to (I). The work was specially encouraged by the
recent communication on the preparation of the pentalenyl dianion
from the reaction of dihydropentalene with n-butyl lithium (11).
An analogous reaction of (V) with n-butyl lithium should result
in the desired dianion (I). When gas chromatographically pure
trans-isomer of (V) was allowed to react with n-butyl lithium
in pentane at reflux temperatures, and the resulting mixture was
decomposed with deuterium oxide, the product contained no deuterium
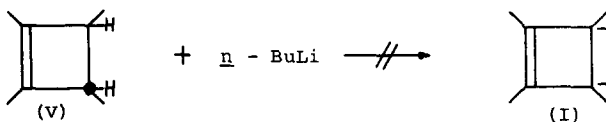
atoms as shown conclusively by means of IR-and N.M.R.-spectra.
In fact, the stereochemically pure _trans_-isomer was recovered
from the reaction mixture in approximately 90% yield. Since the
reaction of (II) with lithium in ammonia always resulted a 1:1
mixture of the _cis_- and _trans_-isomers of (V), by analogy one
would expect that the monoanion of (V) should also lead to a mix-
ture of _cis_- and _trans_-isomers upon treatment with deuterium
oxide. Since the product was shown to be exclusively _trans_-iso-
mer, and furthermore it did not contain any deuterium, it is
concluded that not even one hydrogen was abstracted from (V).

On the basis of all these results, it appears that the
allylic and tertiary hydrogens in (V) are not acidic and thus
the dianion (I) has no special stability. The failure to pro-
duce evidence for the formation of the tetramethylcyclobutadie-
nyl dianion (I) can be attributed to the destabilizing effect
of the electron-donating methyl substituents, and it is likely
that a tetraphenyl substituted dianion could be produced more
readily because of the stabilizing effect of the electron-with-
drawing and resonance-capable phenyl groups. We are currently
investigating this aspect of the problem.

Although simple molecular orbital theory predicts that
the dianion (I) should be stable because a closed shell struc-
ture of six electrons is attained (12), one serious drawback of
the simple molecular orbital theory is the fact that electron
repulsion terms are neglected (13).   For the dianion (I) we

have six electrons spread over four carbon atoms and such electron repulsions will be considerable. Including electron repulsion terms in determining the delocalization energy might very well predict a negligible resonance energy for the dianion (14).

REFERENCES

(1)   R. Breslow and C. Yuan, *J. Amer. Chem. Soc.* 80, 599 (1958).

(2)   Thiele, *Liebigs Ann.* 319, 226 (1901).

(3)   W. von Doering and L. H. Knox, *J. Amer. Chem. Soc.* 76, 3203 (1954).

(4)   T. J. Katz, *ibid.* 82, 3784 (1960).

(5)   H. H. Freedman and A. M. Frantz, Jr., *ibid.* 84, 4165 (1962).

(6)   R. Criegee, *Angew. Chem.* 74, 703 (1962).

(7)   R. G. Jones and H. Gilman, *Org. Reactions* VI, 339 (1951).

(8)   R. Criegee and G. Louis, *Chem. Ber.* 90, 417 (1957).

(9)   R. Criegee and K. Noll, *Liebigs Ann.* 627, 1 (1959).

(10)   H. Gilman, *Org. Reactions* VIII, 258 (1954).

(11)   T. J. Katz and M. Rosenberger, *J. Amer. Chem. Soc.* 84, 865 (1962).

(12)   R. Waack, *J. Chem. Educ.* 39, 469 (1962).

(13)   J. A. Pople, *J. Phys. Chem.* 61, 6 (1957).

(14)   A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, Chapt. 16, p. 449. John Wiley and Sons, Inc., New York, N. Y. (1961).