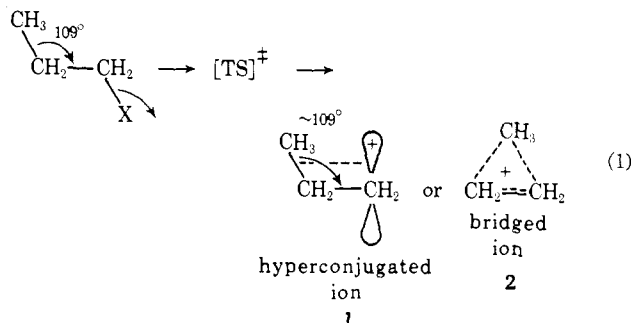


Importance of Hyperconjugation in Cyclopropylcarbanyl Derivative Solvolyses¹

Sir:

Professor Saul Winstein² suggested the possibility that hyperconjugation and bridging were descriptions of a single delocalization phenomenon involving little or much movement of the hyperconjugated or bridging group illustrated for propyl cation (eq 1). We adopted



this proposal into the idea of vertical stabilization^{3,4} of such cations, assigning as limiting vertical stabilization the cation having essentially the starting state geometry. The calculations of Radom, *et al.*,^{5a} indicate that 1-propyl cation has a structure closer to 1 than to 2.

Turning to more strained C-C bonds we found a very large σ - π conjugation effect in vertical ionization potentials of, *e.g.*, cyclopropylbenzene or homocubylbenzene,^{3b} and suggested, in agreement with theoretical calculations,⁷ that the cyclopropyl, homocubyl, etc., groups supply electron density by σ - π conjugation without significant bridging.

Olah and Liang⁸ have compared the ¹³C nmr chemical shifts in the rigid 3-nortricyclyl cation 3 with those of open analogs such as 1-cyclopropyl ethyl cation 4 and

(1) Supported by the National Science Foundation, Grant No. 36381X.

(2) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952).

(3) (a) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971); (b) T. G. Traylor, N. A. Clinton, and R. S. Brown, *ibid.*, **92**, 5228 (1970).

(4) Others⁵⁻⁹ have also adopted Winstein's proposal, although Olah and Liang⁸ mysteriously contrast their statement "no dichotomy exists between charge delocalization in carbocations with and without significant movement (bridging *vs.* hyperconjugation)"^{8,9} and our statement "... we show in this series of papers that participation and hyperconjugation do in fact merge."^{3a} We wish to distinguish an apparent semantic difficulty from the basic difference between our interpretation and that of Professor Olah. We differ with respect to the extent of nuclear movement. We favor near-starting-state neighboring σ -bond geometry for solvolysis transition states accelerated by neighboring strained σ bonds, whereas Olah, *et al.*,⁸ apparently favor nearly symmetrical bridging unless the system is constrained not to bridge.

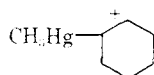
(5) (a) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 311 (1972); (b) L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **94**, 5935 (1972).

(6) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972).

(7) W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, **96**, 302 (1974), and references cited therein.

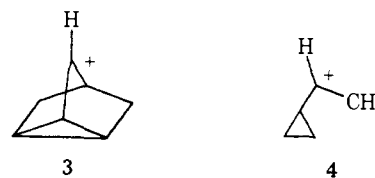
(8) (a) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **95**, 3792 (1973); (b) G. A. Olah and P. R. Clifford, *ibid.*, **95**, 6067 (1973).

(9) Although Olah and Liang^{8a} maintain that hyperconjugation and bridging constitute a continuum of effect, Olah and Clifford,^{8b} in a more recent paper, deny this continuum for the neighboring mercury group. They state that the " β -mercury-substituted carbenium ions," *e.g.*, the "hypothetical"



should have a cmr chemical shift "similar to that of the sp² carbon in isopropyl cation, *i.e.*, ~ -125 ppm." This clearly does not recognize

have concluded that there is much less delocalization of the cyclopropyl electrons in 3 than there is in 4. Be-



cause 3 is presumably too rigid to rearrange to a bridged structure, they suggest that this cation represents "a limiting example of charge delocalization with minimal nuclear movement," *i.e.*, vertical stabilization, and that vertical stabilization is relatively unimportant in the stabilization of 4.

Criticisms¹⁰ of the use of cmr chemical shifts for such purposes suggest the investigation of other common methods which relate more directly to stabilization of transition states for solvolyses. These involve the observation of the effect of ring closure upon: (1) solvolysis rates, (2) sensitivity to substituent, (3) ionization potentials.

We first compare the effect upon rates themselves in Table I. If, upon ring closure, the open chain com-

Table I. The Effect of Closing a Cyclopropane Ring on Rates of Secondary Alkyl Tosylate Solvolyses

Structures		log k_B/k_A	Ref
A	B		
		5.5 ^a	11, 12 ^b
		8.4	12 ^{c,d}
		8.8	e

^a For R = H. If R = alkyl this value probably increases to ~ 7.5 . ^b J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4303, 4311 (1968). ^c P. v. R. Schleyer, J. L. Fry, L-K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970). ^d Y. E. Rhodes and V. G. Difate, *ibid.*, **94**, 7582 (1972). ^e H. G. Richey and N. C. Buckley, *ibid.*, **85**, 3057 (1963).

pound 6 were gaining some stabilization not available to 10, then the effect of ring closure should be larger for 5 \rightarrow 6. It obviously is not. In fact, a comparison of 7 \rightarrow 8 with 9 \rightarrow 10 is definitive in this respect.

Let us compare the effect of ring closure upon sensitivity to substituent. Peters and Brown^{11,12} have

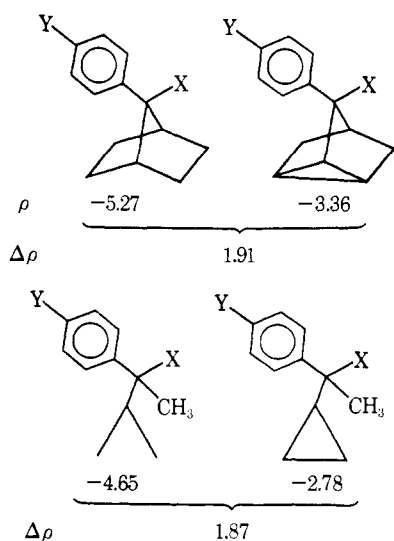
the delocalization of the MeHg-C σ bond in such geometry *even though we had conclusively demonstrated such delocalization to be almost as effective as that of an amino group.*^{3a}

(10) (a) H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, **95**, 2400 (1973). (b) The fact that cmr spectra of 7-norbornyl cation are not available for comparison also weakens the arguments concerning delocalization in 3-nortricyclyl cations.

(11) E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, **95**, 2397 (1973).

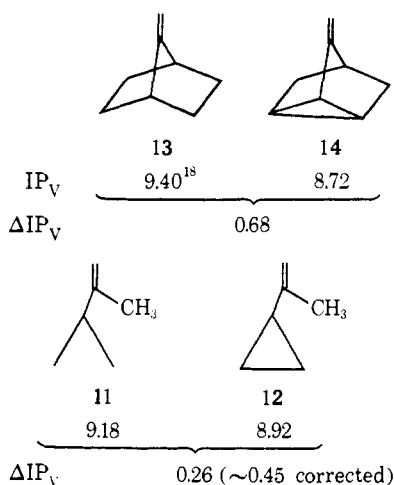
(12) H. C. Brown, *Accounts Chem. Res.*, **6**, 377 (1973).

tabulated the ρ values for the solvolyses of the compounds shown below.



Again, the effect of closing the ring upon the ρ slope is the same in the two systems.

We have also prepared olefins^{13,14} related to **3** and **4** and determined the effects of ring closure upon ionization potentials.¹⁵⁻¹⁷



The changes in ionization potential upon ring closure are 0.68 eV for the rigid systems **13** \rightarrow **14** and, after correction for two alkyl groups,¹⁹ about 0.45 eV for **11** \rightarrow **12**. These changes correspond pretty well with the changes in solvolysis rates.

It is clear that these three probes, while not giving ac-

(13) Nortricyclan-3-one was prepared according to the method of Meinwald and Crandall,¹⁴ converted to 3-methylenenortricyclane in 76% yield using the Wittig method, and the olefin was purified by gas-liquid chromatography: nmr (CCl_4) δ 4.7, s (1 H), 4.6 s (1 H), 2.2 broad (1 H), 1.5 m (6 H), 0.96 m (1 H); ir 3180, 3030, 2850, 1695 cm^{-1} (CCl_4). Other olefins, synthesized by standard procedures or purchased, were identified with known structures by nmr after purification by gas-liquid chromatography.

(14) J. Meinwald and J. Crandall, *Org. Syn.*, **45**, 74 (1966).

(15) Photoelectron spectra were determined on an instrument constructed according to Turner,¹⁶ as we have previously described.¹⁷

(16) D. W. Turner, *Advan. Phys. Org. Chem.*, **4**, 31 (1966); D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970.

(17) R. S. Brown, D. F. Eaton, A. Hosomi, T. G. Traylor, and J. M. Wright, *J. Organometal. Chem.*, in press.

(18) R. W. Hoffmann, R. Schüttler, W. Schäfer, and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **11**, 512 (1972).

(19) One alkyl group on the cyclopropane ring lowers the IP of phenylcyclopropane or 2-propenylcyclopropane about 0.1 eV.^{3b}

curate quantitative agreement, indicate that the rigid cyclopropyl carbonyl system is afforded at least as much stabilization as is the free-rotating system, in contrast to the conclusions based upon cmr spectra.^{20,21}

Finally, the calculations of Hehre and Hiberty⁷ indicate that the parent cyclopropyl carbonyl cation is "bisected" and that the slight movement in going from the starting cyclopropane to the cation is in the *opposite direction* to that leading to a bridged ion. This structure, according to our definitions³ and according to several theoretical and three experimental studies, is stabilized by hyperconjugation (vertical stabilization) in the usual sense and does not require the postulate of bridging in the usual sense.²

(20) Although Olah and Westerman²¹ state, "We cannot recollect, in contrast to Brown, any suggestion that ^{13}C nmr shifts could be used to predict solvolytic rates and stabilities of carbocations or any reason why they should," Olah and Liang⁸ had previously stated, "Both cmr and pmr parameters showed that the secondary cation 1-H and the tertiary cations 1- CH_3 and 1- C_2H_5 are stabilized by charge delocalization the degree of which, as anticipated, is greater in the former." The discussions in ref 8, typified by the sentence above, are almost entirely directed at stabilization of cations. We agree with Brown and with ref 21 that ^{13}C chemical shifts do not relate in any direct way to cation stabilities.

(21) G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 7530 (1973).

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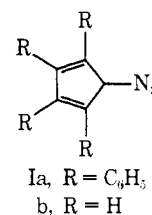
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Reactions of Diazocyclopentadienes. Preparation and Structure of Halogen Substituted Pentahaptocyclopentadienylrhodium Complexes

Sir:

Reaction of a diazoalkane with a transition metal compound may result in (a) complex formation with retention of the diazo group,¹ (b) insertion into metal halogen, hydride, or alkyl bond,² or (c) carbene formation.³ We report that the diazocyclopentadienes (Ia,b) insert into halogen-bridged dirhodium species to



give new halo-substituted cyclopentadienyl complexes IIa-e. Reaction 1 proceeds conveniently in benzene in nitrogen atmosphere at room temperature. The reactions are complete within 24 hr and can be followed by watching the disappearance of the band at 2060 cm^{-1} due to the nitrogen group. The products are air stable and range in color from yellow (IIa,b,e) to red (IIc,d). The ease with which these reactions produce halo-sub-

(1) S. Otsuka, A. Nakamura, T. Kayama, and Y. Tatsuno, *J. Chem. Soc., Chem. Commun.*, 1105 (1972).

(2) (a) M. F. Lappert and J. S. Poland, *Advan. Organometal. Chem.*, **9**, 397 (1970); (b) J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 1872 (1969).

(3) (a) P. Hong, N. Nishi, K. Sonogashira, and H. Hagihara, *J. Chem. Soc., Chem. Commun.*, 993 (1972); (b) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); D. J. Cardin, B. Cetinkaya, E. Cetinkaya, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 514 (1973).