ring. Roughly estimating the shielding effect of the carbethoxyl group based on distance and angle, we find it very difficult to state clearly which one, α or β, is more affected. We have examined the spectral behavior of compound **4**.[8a] If the H_α and H_β signals of **4** are temperature variable and the resulting two conformers are found to be equally populated, then this nmr temperature dependence is caused by restricted rotation of the carbethoxyl group (because of the presence of symmetry (σ) in the ring), but not likely by nitrogen inversion.[8b] Compound **4** showed two doublets, H_α at τ 3.30 (d, J = 10.5) and H_β at τ 5.10 (d, J = 10.5) (proton H_γ is irradiated), at room temperature, but two overlapping doublets, τ 3.25, 3.35 (dd, J = 10.5) and τ 5.05, 5.15 (dd, J = 10.5), at $-50°$, T_c $-25°$ (CS_2 + THF-d_8, 100 MHz), $\Delta F_c^{\ddagger} \simeq 13$ kcal, each doublet being equally intense. The ethyl signal begins to broaden around $-100°$, very likely due to slow inversion of the ring system of **4** below this temperature. The chemical shifts of the α and β protons of **4** are almost equally affected. The situation is entirely different in the case of pyrrole,[7] where the ring geometry is fixed and the chemical shift of H_α is expected to be affected much more than that of H_β, as observed. Anastassiou, *et al.*, discussed the temperature independence of the ethyl signal of **1** but the chemical environments of the two rotamers (not invertomers) are equivalent, providing pseudorotation is rapid.[9] Below $-125°$ the ethyl group of **1** exhibited broadening which may be partly due to freezing of this pseudorotation.

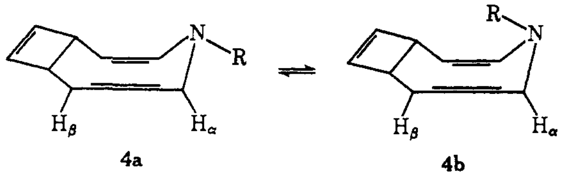
Thirdly, their "most compelling evidence in favor of suppressed nitrogen inversion derives from the effect of solvent polarity on the temperature of coalescence (T_c),"[3] comparing their data with those reported by Griffith and Roberts.[10] We must point out that the latter authors investigated only pyramidal nitrogen compounds, *N*-benzyl-*O*,*N*-dimethylhydroxylamine and its related compounds, and that it is not appropriate to compare these decisively different systems. Moreover, the solvent dependence of T_c for **4** was found to be parallel with that for **1**[3] (T_c for **4**, $-23°$ in $CDCl_3$, $-41°$ in CD_3CN; T_c for **1**, $-10°$ in $CDCl_3$, $-28°$ in CD_3CN), both **1** and **4** showing an 18° difference in T_c on changing the solvent from chloroform (ϵ 4.8) to acetonitrile (ϵ 38.8). *N*-Acylpyrroles behaved similarly: *N*-acetylpyrrole; T_c ($CDCl_3$) $-18°$;[11] (CD_3CN) $-33°$;[11] *N*-carbethoxypyrrole; T_c ($CDCl_3$) $-41°$; (CD_3CN) below $-45°$ (solvent frozen). Their argument that "rotation is restricted more effectively in polar (acetonitrile) than in nonpolar solvent (chloroform)" is not applicable to these cases. On the contrary, the reverse trend is observed, as shown above, and these phenomena of solvent dependence may possibly be general for the type of compounds in question.[12] Although in the absence of extensive studies, it is difficult to evaluate the data accurately, a simple and tentative explanation can be offered. Both **1**, **4**, and the *N*-acylpyrroles possess a substantial polar character in the transition state of hindered rotation due to the conjugation of the lone pair of nitrogen with ring double bonds. Thus T_c is lowered with increasing solvent polarity.

There is no reason to believe that the nitrogen atom is a typical pyramid, and if it deviates slightly from trigonal coplanarity, the inversion barrier should be low and cannot be as high as the measured value, approximately 13 kcal/mole. In contrast, the rotational barrier for *N*,*N*-dimethylcarbamate is 16.5 kcal/mol.[13] Considering the well-known fact that the introduction of a double bond in conjugation with the lone pair of nitrogen lowers the barrier,[7,14] 13 kcal/mol is just as expected for the energy required for the hindered rotation of **1**. Finally, we wish to point out that C_2 symmetry for ring systems **1**, **2**, and **3** is justified when the pseudorotation of the C–X–C (X = O, NR, CH_2) bond mentioned above proceeds very rapidly, compared with the nmr time scale, or **1** possesses an energy minimum at the middle point of this pseudorotation.

Acknowledgment. We thank Professors F. A. L. Anet and J. M. Lehn for helpful discussions on this subject and the National Research Council of Canada and the Defence Research Board for financial support.

---

(8) (a) S. Masamune and N. T. Castellucci, *Angew. Chem., Int. Ed. Engl.*, 3, 582 (1964). (b) A referee suggested the addition of the following explanation to clarify this statement. If slow nitrogen inversion occurs between **4a** and **4b**, it could cause a temperature dependence of the nmr spectra of **4**. In this case, it is highly unlikely that **4a** and **4b**



4a **4b**

will be exactly equally populated, as Dreiding models indicate a large difference in stability between the two conformers.

(9) *N*-Carbethoxyazepineiron tricarbonyl, which is quoted in ref 3 as an example to exhibit the splitting of the ethyl group, is obviously not an appropriate model, because at cold temperatures $Fe(CO)_3$ is fixed on one side, destroying the symmetry of the whole ring system. The ethyl group of the two rotamers resulting from hindered rotation of the carbethoxyl group experiences different chemical environments.

(10) D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 4089 (1965).

(11) These temperatures are corrected and somewhat different from those reported (*cf.* ref 7).

(12) For the cases of simple disubstituted amides, see J. C. Woodbrey and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 13 (1962).

(13) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, 66, 540 (1962).

(14) D. G. Gehring and W. A. Mosher, *J. Org. Chem.*, 31, 3436 (1966); *cf.* the behavior of **4**.

* Address correspondence to this author.

K. Hojo, S. Masamune*
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

Received June 16, 1970

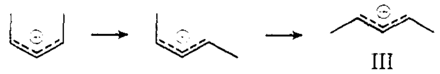
Energy Barriers for Rotation about Carbon–Carbon Bonds in Allyl Cations

Sir:

For I → II and II → III, isomerization rates gave E_a of 17.5 and 24.0 kcal/mol and log A of 11.8 and 14.0, respectively.[1] Three paths were considered: (a) rotation about $C \overset{..}{=} C$; (b) recombination to a neutral allyl derivative, rotation, and dissociation; and (c) disrotatory closure and opening. Path c was eliminated because it requires I → III whereas paths a and b require eq 1 as observed. A fourth path (d) must be added. This is loss of proton to the diene, rotation, and reprotonation. Path d requires the sequence in eq 1. No evidence was available for distinguishing paths a, b, and d.

---

(1) P. von R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, 91, 5174 (1969).



I II III (1)

E_a and log A were reported for rotation about C=C in the 1,1-dimethylallyl cation and the pentamethylallyl cation.[2] These values have been drastically revised,[3] and values of $\Delta G^{\neq}$ for rotation for seven additional allyl cations were added.[3] Evidence against path b was the observation that coalescence temperatures (T_c) were not changed by a twofold change in [Cl^-]. However, this is too small a variation in [Cl^-] for confidence and there was still little reason for choosing path a over c or d, or for eliminating errors due to shift of δ with temperature.

We have now studied the 1,1,3,3-tetramethylallyl cation IV in detail and have obtained reasonably good evidence that the nmr coalescence temperature at 55° is due to path a. The E_a of 15.7 ± 0.9 kcal/mol and log A of 11.3 ± 0.6 are thus the most reliable parameters yet obtained for rotation about C=C in an allyl cation.

The nmr spectrum of IV in HO_3SF consisted of the same three singlets (δ 2.95, 3.00, and 7.78) as found in sulfuric acid.[4] As the temperature is raised from 0 to 95°, the two methyl bands begin to broaden at 35°, coalesce at 55 ± 3°, and narrow to a singlet of natural line width (1.0 Hz) at 95°. The process is reversible and there is no viscosity broadening or other line-shape changes in the band of the internal standard, $(CH_3)_4N^+$.

IV

V

VI

The methyl bands of IV had line widths (at 0–35°) of 4.0 Hz instead of the natural line width of 1.0 Hz. This broadening is believed to be due to reciprocal splitting in the gem dimethyl of about 1.0 Hz combined with a smaller splitting by a more remote methyl so that the system is at least $A_3B_3B'_3$ in complexity.

Four *approximate* methods were used to estimate E_a. The most complete was to treat the system as AB coupled and to use a computerized nonlinear regression analysis for extracting rates from nmr line shapes.[5] Rates, chemical shifts, and couplings were allowed to optimize for best fit. This led to E_a of 15.7 ± 0.9 kcal/mol and log A of 11.3 ± 0.6. Similar results were obtained assuming that the two methyl bands were uncoupled singlets. The simplest method was to use eq 2 and assume log A of 12.[6] This gave E_a of 17 kcal/mol. Using the analogous equation for an AB coupled system, $k = \pi\sqrt{\Delta\delta^2 + 6J^2}/\sqrt{2}$,[7] also gave E_a of 17 kcal/mol.

$$k = \pi\Delta\delta/\sqrt{2} = A\exp(-E_a/RT_c) \qquad (2)$$

It is evident that E_a is in the 15–18 kcal/mole region and is relatively insensitive to the assumptions made in approximating the small but complex coupling.[8]

Any possibility that the methyl bands were a doublet due to splitting by the vinyl H were dispelled by (a) the absence of splitting and natural line width of the vinyl H singlet, (b) the increase in $\Delta\delta$ from 0.05 to 0.085 in going from a 60- to a 100-MHz instrument, and (c) unchanged methyl bands on irradiation (decoupling) of the vinyl H.

It remains to eliminate the possibilities that the coalescence was due to mechanisms b, c, and d, described above, or to merging δ values.

Path b would be sensitive to the concentration of nucleophilic species. However, the coalescence temperature of 55 ± 3° remained constant on addition of either 0.85 mol of Cl^- (as $(CH_3)_4N^+Cl^-$) or 0–100% H_2SO_4. Path c was eliminated for eq 1, and it is improbable for IV, particularly because of the high energy of the requisite intermediate cyclopropyl cations.[9] Moreover, path c would not have led to the hybrid band of natural line width observed at 95°. Path d was eliminated by examining the rates of H–D exchange in 100% D_2SO_4. Methyl interchange was 10^3 faster than H–D exchange instead of equal as required by path d. This leaves path a. In support of path a, log A of 11.3 is in the range expected for a unimolecular process.

Evidence against a coincidental merging of δ values rests primarily on the fact that the mean band position remained constant at 2.975 throughout the coalescence from 25 to 95°. Supporting evidence was the change in band shapes. The broadening before coalescence is in contrast to a coincidental merging of δ values which occurred at −20°. In the latter, the 2.95 and 3.00 bands remained sharper as the coalescence proceeded.

The nmr spectrum of V[10,11] in HO_3SF was unchanged from 25 to 95°. Above 95°, rapid cyclization[10] prevented further observation. Taking log A to be 12 and the coalescence temperature to be >115°, the $\Delta\delta$ of 0.05[10,11] leads to E_a > 19 kcal/mol using eq 2.

The greater E_a for V relative to IV was anticipated. Cation V is expected to be planar. The cis 1,3-dimethyl groups would be only 2.40 Å apart in IV,[12] whereas the 2.0-Å van der Waals radii for CH_3[13] require a separation of 4.0 Å. Rotation about C=C must be partly accomplished in the ground state of IV. A similar situation exists in cation I and the similarity of E_a for I and IV supports each other.

A value of E_a > 13 kcal/mol was found for rotation about C=C in a stereoisomer of VI. Addition of a mixture of 2,8-dimethyl-1,3,5,7-nonatetraenes[11] to H_2SO_4–SO_2 at −30° gave the nmr spectrum of VI (methyl bands at 2.62 and 2.67)[11] along with that of an isomeric cation (methyl bands of equal intensity at 2.42 and 2.72). Irreversible isomerization to VI took place with k equal to 2×10^{-3} sec^{-1} at 20°. Assuming log A equals 12, E_a > 13 kcal/mol. The nmr spectrum of VI underwent irreversible changes rapidly at 35°.

---

(2) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, 90, 6085 (1968).

(3) J. M. Bollinger, J. M. Brinich, and G. A. Olah, *ibid.*, 92, 4025 (1970).

(4) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, 85, 299 (1963).

(5) L. M. Jackman, T. E. Kavanagh, and R. C. Haddon, *Org. Magn. Resonance*, 1, 109 (1969).

(6) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 9, 219 (1970).

(7) R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, 40, 2426 (1964).

(8) This coupling was not considered in ref 2 and 3.

(9) C. H. DePuy, *Accounts Chem. Res.*, 1, 33 (1968); P. von R. Schleyer, G. W. van Dine, U. Schollkopf, and J. Paust, *J. Amer. Chem. Soc.*, 88, 2688 (1966).

(10) N. Deno and C. U. Pittman, Jr., *ibid.*, 86, 1871 (1964); N. Deno, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, 87, 2153 (1965).

(11) T. S. Sorensen, *ibid.*, 87, 5075 (1965); *Can. J. Chem.*, 42, 2768 (1964).

(12) Using a bond distance of 1.39 Å for C=C (as in benzene) and 120° angles about trigonal carbons.

(13) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 261.

Protonated 3-methyl-2-butenal and protonated 4-methyl-3-penten-2-one can be regarded as hydroxyallyl cations. Their nmr spectra in HO$_3$SF were unchanged from 25 to 112° and 25 to 88°, respectively.

Acknowledgment. Grateful acknowledgment is made to both the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

* Address correspondence to this author.

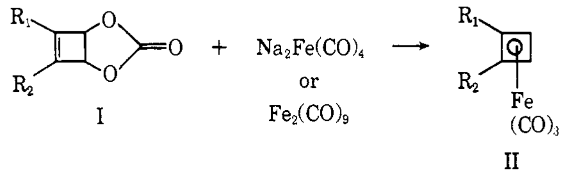
N. C. Deno,* Robert C. Haddon, Edward N. Nowak
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

Received April 22, 1970

Cyclobutadieneiron Tricarbonyl Complexes

Sir:

Treatment of *cis*-3,4-carbonyldioxycyclobutenes (I) with reducing iron carbonyl complexes gives cyclobutadieneiron tricarbonyl complexes (II) in good yields.

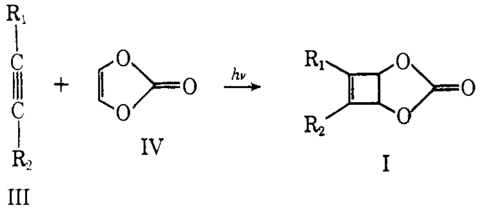


I

II

a, R$_1$ = R$_2$ = H
b, R$_1$ = H; R$_2$ = butyl
c, R$_1$ = R$_2$ = CH$_3$

The hitherto unknown *cis*-3,4-carbonyldioxycyclobutenes (I) can be prepared in reasonable yields by the photolysis of vinylene carbonate (IV) with the appropriate acetylene (III). This procedure represents a simple



III

IV

I

and convenient route to a wide variety of previously unavailable cyclobutadiene complexes. In particular, monosubstituted complexes not available by alkylation of the parent system and 1,2-disubstituted complexes which cannot be made by alkylation of the monosubstituted complexes can be prepared by this method. Also this procedure provides the unsubstituted complex in reasonable yields from readily available starting materials.

The cyclobutadiene complexes that have been previously prepared have proved very useful as synthetic intermediates and as convenient precursors for the study of the chemistry and electronic structure of cyclobutadiene.[1] However, published procedures require the use of materials that are not readily available,[2,3] or are not suited for the preparation of complexes with a variety of substituents.[2-4]

In the most useful reported preparations, 3,4-dihalocyclobutenes[2,4,5] are reduced with iron carbonyl complexes. It was thought that the *cis*-3,4-carbonyldioxycyclobutenes (I) would yield cyclobutadiene complexes and iron carbonates under reducing conditions and should be easy to prepare with a variety of substituents. A key feature of these bicyclic compounds should be their resistance to the well-known cyclobutene ring-opening reactions. Consequently, photolysis[6] of vinylene carbonate[7] (IV) in acetone with an excess of the appropriate acetylene was attempted, and gave the *cis*-3,4-carbonyldioxycyclobutene in 20–40% yields along with vinylene carbonate dimer. All the derivatives were thermally stable and were easily isolated by fractional distillation at reduced pressure.[8]

Treatment of the *cis*-3,4-carbonyldioxycyclobutenes (Ia–c) with either the disodium salt of iron tetracarbonyl dianion[5] (1.3 equiv) in tetrahydrofuran for 2 hr, or with excess diiron enneacarbonyl in cyclohexane at 55° gave the corresponding cyclobutadiene complexes (IIa–c) in good yields.[9] All of the complexes showed the characteristic carbonyl stretching frequencies in the infrared near 1980 and 2050 cm^{-1},[2,4] and their mass spectra were characterized by a large parent peak followed by peaks for the successive loss of the three CO groups.[2,4] The unsubstituted complex (IIa), obtained in 37% yield, showed a single nmr signal at τ 6.05 (lit.[2] 6.09) and gave infrared spectra and retention times on the gas chromotograph identical with an authentic sample.[10] The butyl derivative (IIb) (bp 70–72° (1 mm)), obtained in 50% yield, gave nmr signals at τ 6.08 (singlet), 6.12 (singlet), 8.02 (quartet), 8.65 (multiplet), and 9.12 (triplet). The ratio of the peak areas was 2:1:4:8:6. There was no detectable coupling between the two different types of cyclobutadiene ring protons.[4,11] The dimethyl derivative (IIc), obtained in 30% yield, showed two singlets at τ 8.22 and 6.12, in the ratio of 3:1 (lit.[11] 8.24 and 6.10).

Studies are presently under way to extend this procedure to the preparation of other synthetically useful and theoretically interesting cyclobutadiene complexes.

Acknowledgments. We gratefully acknowledge the support of a National Science Foundation Institutional grant administered by Michigan State University for partial support of this project.

---

[1] R. Reeves, T. Devon, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5890 (1969), and references therein.

[2] G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965); this procedure requires cyclooctatetraene as a starting material.

[3] M. Rosenblum and G. Gatsonis, *ibid.*, **89**, 5074 (1967).

[4] B. W. Roberts, A. Wissner, and R. A. Rimerman, *ibid.*, **91**, 6208 (1969); also, this reaction gives low yields (7–9%) of the desired compounds.

[5] R. G. Amiel, P. C. Reeves, and R. Pettit, *Chem. Commun.*, 1208 (1967).

[6] W. Hartman, *Chem. Ber.*, 101, 1643 (1968).

[7] Available from Aldrich Chemical Co. or easily prepared from ethylene carbonate by the procedure of M. S. Newman and R. W. Addor (*J. Amer. Chem. Soc.*, 75, 1264 (1953)) or from chloroethylene which is commercially available.

[8] A report of the preparation and chemistry of these compounds will be presented at a later date.

[9] The anion procedure is the preferred route since 4–5 equiv of diiron eneacarbonyl added over a 24-hr period was required to complete the reaction.

[10] Samples prepared by the method given in ref 2 were obtained from Professors H. Hart and E. LeGoff.

[11] H. A. Brune, W. Eberius, and H. P. Wolff, *J. Organometal. Chem.*, 17, 485 (1968); H. Huther, *Chem. Ber.*, 101, 1485 (1968).

Robert H. Grubbs
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

Received July 25, 1970