in water, a small fraction of the solid was insoluble in water, in contrast with the tetramer and form II polymer which were both quite soluble in water. Thus, it is probable that the pentamer as originally supplied had both forms I and II present, the latter predominating. This proposition is supported by solubility, Raman scattering lines at 360, 540, and 960 cm^{-1}, and finally the strong scattering of the carbonyl band.

In the discussion of the spectra obtained from the polymers, the assignment of the lines at 1315, and 1337 cm^{-1} was deferred. If the spectra of the three oligomers in Figure 5 are compared with the spectrum of L-proline in Figure 2, it is seen that the monomer has a line occurring at 1294 cm^{-1}, the trimer at 1288 cm^{-1}, the pentamer and the polymer both at 1307 cm^{-1}. Since pyrrolidine has a CH_2 twisting mode at 1287 cm^{-1},[13] the line at 1315 cm^{-1} for the polymer is assigned to a CH_2 twisting mode. The assignment of the 1347-cm^{-1} line is less clear; however, the monomer has a line at 1369 cm^{-1} which may be identified with the CN-stretching mode seen at 1424 cm^{-1} for pyrrolidone and 1369 cm^{-1} for *N*-bromopyrrolidone. Based on this assignment, the 1337-cm^{-1} line of the polymer may be seen to arise from the C–N stretching mode.

A feature of the spectra of the two forms of the polymer was the variation in the ratio of the scattering at 1650 cm^{-1} to the scattering at 1446 cm^{-1}. All three oligomers have a similar ratio to that found for form II. Likewise, the intensities of the scatterings at 1266 and 1240 cm^{-1} are indicative of form II rather than form I. The multiple lines in the carbonyl region may be assigned to ester carbonyls, internal carbonyls, and free carboxyl groups as in the infrared;[7] however, the change in intensities is interpreted as being due to a simple increase in the number of internal carbonyls over end group carbonyls as the chain lengthens. The 1650-cm^{-1} line is interpreted as the vibration of an imino acid peptide-linked carbonyl; however, the persistence of a weak band at 1686 cm^{-1} is confusing.

Finally, it is worth noting a couple of additional changes in the spectra as the oligomer is progressively lengthened from 3 to 5 units. A line at ~476 cm^{-1} is seen to be diminished in intensity and since this line is absent both from L-proline and poly-L-proline I or II, it is assigned to a skeletal mode of the *tert*-amyloxycarbonyl group blocking the terminal nitrogen of these oligomers.

If the spectra in Figure 5 are compared, it is evident that the trimer has a weak line at ~880 cm^{-1} whereas the tetramer has two lines in this region, one at ~880 cm^{-1} and the other at 871 cm^{-1}. Finally, the pentamer has only one line at 869 cm^{-1} with a slight shoulder at 880 cm^{-1}. For comparison, form II of the polymer has a line at 869 cm^{-1} and is similar to the pentamer and since there are no corresponding bands in the spectra of the monomer, they are likely to be skeletal vibrations.

Conclusion

The Raman spectrum of poly-L-proline I is seen to have a line at 957 cm^{-1} which corresponds to the 960-cm^{-1} band in the infrared spectrum. In addition, lines at 781, 662, and 363 cm^{-1} are unique to the Raman spectrum and sensitive to conformation. Finally, comparison of the spectra obtained for form I and form II shows a reduction in the carbonyl scattering at 1650 cm^{-1} for the latter and a reversal of the intensities of the lines at 1264 and 1239 cm^{-1}.

From the Raman spectra of a series of proline oligomers, it is concluded that in aqueous solution and lyophilized solids, the oligomers from the trimer upward are capable of existing in a helical form similar to poly-L-proline II. However, the spectra from dried solids indicate that the tetramer is the first to have a stable helical form and this is in agreement with the conformational calculations done on these oligomers. The failure to obtain any oligomers in the cis form, as solids, is also in agreement with these calculations. Recent solution studies[20] indicate, however, that the cis structure may be possible for DP $\geq$ 3 if no imino blocking group is present.

Finally, this work has emphasized the usefulness of comparing band intensities as well as the more commonly treated band frequencies, since it has been shown that the relative intensities of the carbonyl stretching modes and the various CH modes are sensitive to the conformation of the polypeptide chain.

Acknowledgment. The authors are pleased to acknowledge the financial support of the National Institutes of Health, Program/Project No. DE 02587.

Communications to the Editor

π-Complexed β-Arylalkyl Derivatives. III. The Acetolysis of Some Chromium Tricarbonyl Complexed 2-Benzonorbornenyl Methanesulfonates[1]

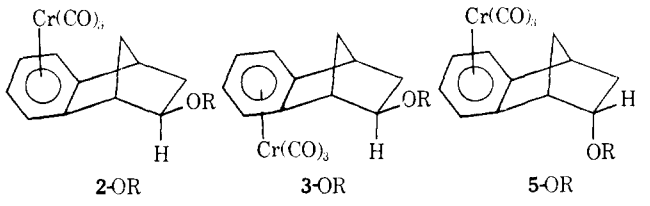
Sir:

The acetolyses of chromium tricarbonyl complexed neophyl-type methanesulfonates are enhanced and yield π-arylchromium tricarbonyl migrated products.[2] In order that we might infer whether the π-bonded metal moiety prefers to precede or to follow[3] the migrating aryl to which it is bonded in these acylic derivatives, we have examined the relative acetolysis rates and products of the isomeric *endo*- and *exo*-chromium tricarbonyl

(1) Portions of this work were presented at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, Abstract ORGN 133.

(2) R. S. Bly, R. C. Strickland, R. T. Swindell, and R. L. Veazey, *J. Amer. Chem. Soc.*, **92**, 3722 (1970).

(3) We use the terms "precede" and "follow" in the geometric sense only and do not intend them to imply anything about the electronic nature of the process.

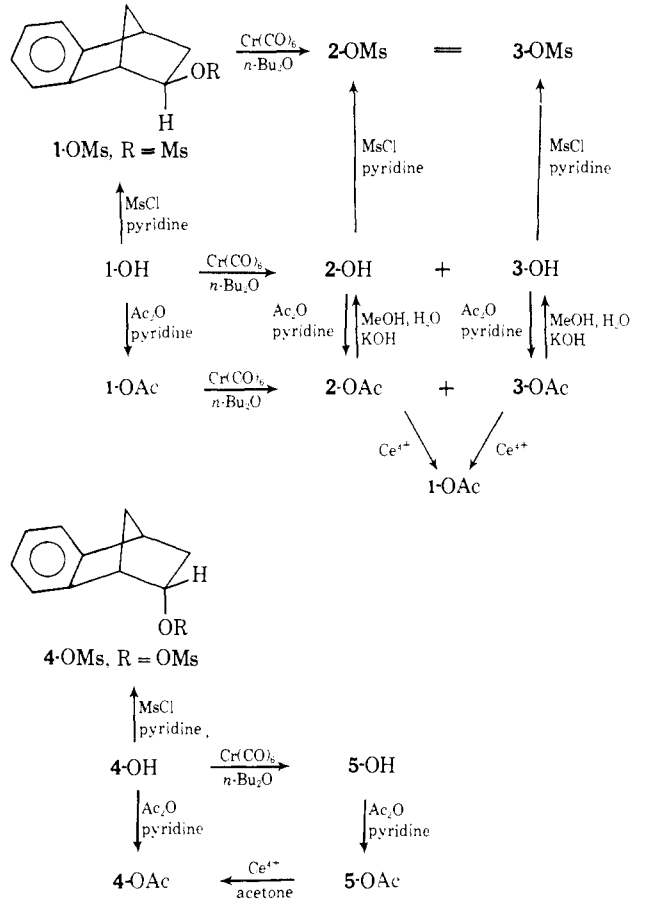


R = H, Ac, Ms, or Bs

complexed *exo*-2-benzonorbornenyl methanesulfonates in which the chromium is constrained by the geometry of the system either to precede (3-OMs) or to follow (2-OMs) the migrating benzo group.

The complexes were prepared[4] and their configurations related to that of 2-OAc[5] as shown in Scheme I.

Scheme I[a]



[a] Series 1, noncomplexed, exo OR (R = H, Ac, Ms); 2, *exo*-tricarbonylchromium, exo OR; 3, *endo*-tricarbonylchromium, exo OR; 4, noncomplexed, endo OR; 5, *exo*-tricarbonylchromium, endo OR.

Acetolyses were conducted and products determined as described previously.[2,6] Product composition was estimated by inspection of analytical thin-layer plates and by integration of nmr spectra of reaction mixtures; *cf.* Table I. Equilibration and control experiments reveal that 3-OAc slowly isomerizes to 2-OAc but oxidatively decomplexes more rapidly than the latter during the reaction. The product ratios of Table I are thus only approximate but clearly indicate that 3-OAc is the dominant kinetic product from the acetolysis of both 2- and 3-OMs, and that the acetolysis of 3-OMs is accompanied by internal return to 2-OMs. Titrimetic acetolysis constants[2] are summarized in Table II.[7]

Table I. Acetolysis Products of Chromium Tricarbonyl Complexed 2-Benzonorbornenyl Methanesulfonates at 86°

Compd	Reaction time, half-lives	Ratio of 2-:3-OAc in product mixture[a]
2-OMs	0.5	~1:5–1:10[b]
	4.0	~1:1
3-OMs	1.3	~1:5[b]
	5.3	~1:4[b,c]
5-OMs	4 days[d]	No detectable reaction[e]

[a] Yields of recovered complexed products range from 20 to 50% depending upon reaction and isolation conditions. [b] Some starting material observed. [c] Some internally returned 2-OMs observed. [d] Sufficient for complete reaction of 2-OMs. [e] Trifluoroacetolysis at 70° converts 5-OMs to 2-$OCOCF_3$.

Table II. Apparent First-Order Acetolysis Constants and Activation Parameters for 2-Benzonorbornenyl Methanesulfonates

Compd	Temp, °C	10^6k, sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
1-OMs	39.70	14.9 ± 0.05	24.0	−3.93
	54.52	92.2 ± 0.1		
	69.04	447 ± 14		
	100.00	9,220[a]		
2-OMs	69.30	5.37 ± 0.17	23.0	−15.9
	86.64	25.4		
	86.72	25.2		
	99.43	91.1 ± 1.3		
	100.00	90.5[a]		
3-OMs	39.73	87.6	20.6	−11.2
	54.51	544		
	69.24	1,580		
	69.35	1,920		
	100.00	24,100[a]		
4-OMs	99.95	3.35 ± 0.07	27.5	−10.3
	115.30	15.4 ± 0.2		
	130.78	61.6 ± 2.1		
	100.00	3.38[a]		
5-OMs	99.87	<0.24[b]	~26.8	~−17
	115.80	<1.1[b]		
	131.00	<4.2[b]		
	100.00	≤0.24[a,b]		

[a] Calculated from data at other temperatures. [b] Accompanied by decomplexation to the more reactive 4-OMs. Rate constants, determined from the first 2–5% reaction, represent upper limits to the true value.

The acetolysis of 4-OMs is known to be unassisted;[8] hence the 3.38/≤0.24 ≃ 14 times retardation of 5-OMs must reflect the electron-withdrawing inductive effect of the tricarbonylchromium.[9] The greater retardation, 9220/90.5 ≈ 100 times, experienced by 2-OMs relative to 1-OMs even though dipole–dipole interactions in the transition state of the complex are expected to be less unfavorable in this isomer, confirms that arene participation is indeed important in the acetolysis of

(4) Satisfactory spectral and elemental analyses were obtained for each new compound.

(5) The exo stereochemistry of the tricarbonylchromium group in 2-OAc was established by a three-dimensional single-crystal X-ray diffraction study: E. L. Amma, H. Lüth, and I. F. Taylor, Jr., to be published.

(6) R. S. Bly and R. L. Veazey, *J. Amer. Chem. Soc.*, 91, 4221 (1969).

(7) In an accompanying communication (*ibid.*, 92, 7461 (1970)) D. K. Wells and W. S. Trahanovsky report similar results for the hydrolyses of 2-, 3-, and 5-OBs. We thank these authors for disclosing the results of their work prior to its publication.

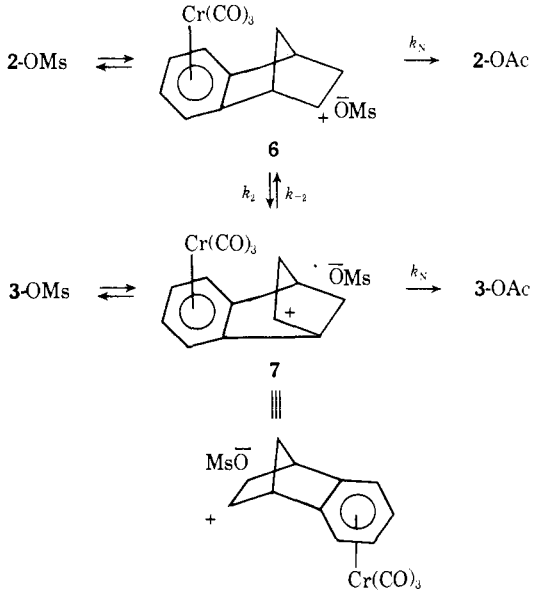
(8) J. P. Dirlam, A. Diaz, S. Winstein, W. P. Giddings, and G. C. Hanson, *Tetrahedron Lett.*, 3133 (1969), and references cited therein.

(9) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

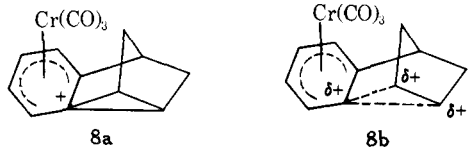
noncomplexed *exo*-2-benzonorbornenyl derivatives.[10] The 24,100/90.5 = 266 times rate enhancement of **3**-OMs relative to **2**-OMs indicates that *the endo-tricarbonylchromium provides an additional driving force over that due to the ring itself.*[11] We are unable to estimate the extent to which the additional rate enhancement is attributable to a steric effect, but the preferential formation of the more hindered and less stable product (**3**-OAc) clearly implies that electronic factors are important.

These data confirm that the metal moiety exhibits a strong tendency to precede[3] the ring during the migration and to stabilize that intermediate (**7**) in which the positive charge is concentrated in the vicinity of the metal;[12] *cf.* Scheme II.[13] Pseudosymmetric cat-

Scheme II



ionic intermediates such as **8** are excluded as are diastereomeric structures which by rapid equilibration achieve such symmetry prior to attack by acetate.[14]



8a **8b**

We cannot distinguish between direct metal bridging[15] or $\sigma-\pi$ type homoconjugation[16] as the mode of stabilization of **7**, for either interpretation would appear to be compatible with our data.[17,18]

Acknowledgment. We are indebted to the Directorate of Chemical Sciences of the Air Force Office of Scientific Research (Grant No. 991-67) for their generous support of this work, and to Professor E. L. Amma and his group for the single-crystal X-ray diffraction study of **2**-OAc.[5]

(10) (a) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963); (c) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, **90**, 1901 (1968), and references cited therein; (d) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushimi, *ibid.*, **90**, 4512 (1968).

(11) This compares favorably with the factor of 280 observed by Wells and Trahanovsky[7] for the hydrolysis of **3**-OBs in 70% acetone at 80° and implies that a major portion of the observed enhancement of **3**-OMs relative to **5**-OMs, 24,100/0.24 = 100,000, may be due to some type of metal participation.

(12) Although we represent **6** and **7** as charge localized for convenience and simplicity, we do not intend to imply that delocalization may not be substantial, especially in the latter case.

(13) If in fact more **3**-OAc is produced from **2**-OMs than from **3**-OMs, **7** clearly cannot be the only intermediate which yields **3**-OAc. It may be that the nucleophile prefers to attack that site of positive charge in the diastereomeric tight ion pairs **6** and **7** which is least shielded by the methanesulfonate counterion.

(14) *I.e.*, the following condition cannot obtain: $k_2 \approx k_{-2} \gg (k_N + k_{N'})$.

(15) (a) J. H. Richards and E. A. Hill, *J. Amer. Chem. Soc.*, **81**, 3484 (1959); **83**, 3840, 4216 (1961); (b) M. Cais, *Organometal. Chem. Rev.*, 1, 435 (1966).

(16) (a) T. G. Traylor and J. C. Ware, *Tetrahedron Lett.*, 1295 (1965); *J. Amer. Chem. Soc.*, **89**, 2304 (1967); (b) J. A. Mangravite and T. G. Traylor, *Tetrahedron Lett.*, 4461 (1967); (c) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970).

(17) Implicit in the concept of $\sigma-\pi$ type homoconjugation,[16a] though perhaps not explicity stated in the case of cationic intermediates, is the expectation that in a π-complexed "bridged" intermediate, *cf.* ref 6, Charts IX and XI, the "inside" bridging bond adjacent to the metal will be more rapidly broken by an attacking nucleophile than the "outside" one,[19] hence even a pseudosymmetric structure such as **8a** or **8b** could be expected to react with acetate in an asymmetric fashion.

(18) *Cf.* M. J. Nugent, R. Kummer, and J. H. Richards, *J. Amer. Chem. Soc.*, **91**, 6141 (1969), for a similar conclusion in the ferrocene series.

(19) Private communication from T. G. Traylor to the senior author dated July 7, 1967.

(20) NSF Trainee, 1968–1970.

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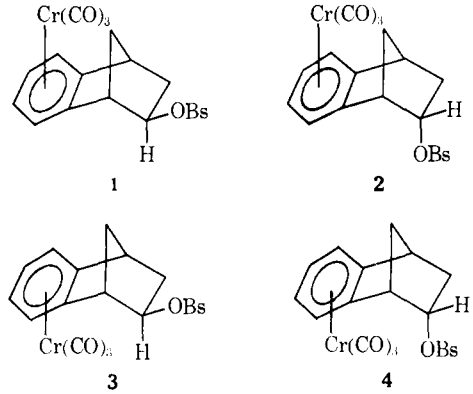
Arene–Metal Complexes. III. Solvolysis of the anti-exo-2, anti-endo-2, and syn-exo-2 Isomers of (Benzonorbornen-2-yl)tricarbonylchromium *p*-Bromobenzenesulfonates[1]

Sir:

There are four possible isomers of (benzonorbornen-2-yl)tricarbonylchromium *p*-bromobenzenesulfonates, anti-exo-2 (**1**), anti-endo-2 (**2**), syn-exo-2 (**3**), and syn-



endo-2 (**4**). We now report the solvolysis study of the first three isomers. Attempts to synthesize the fourth isomer have met with failure, undoubtedly because of the severe steric interactions of the *syn*-tricarbonylchromium and the endo-2 substituent that would exist.

The *anti*-tricarbonylchromium complex of benzonorbornen-2-*exo*-yl acetate was prepared and reduced

(1) (a) II: D. K. Wells and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **91**, 5871 (1969). (b) This work was partially supported by Public Health Service Grant No. GM 13799 from the National Institute of General Medical Sciences and Grant No. 5261-AC from the Petroleum Research Fund administered by the American Chemical Society. We thank these organizations for their support. (c) Based on work by D. K. W. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.