π-Complexed β-Arylalkyl Derivatives. I. The Preparation and Acetolysis of 3-[π-(Phenyl)chromium tricarbonyl]-2-butyl and 2-[π-(Phenyl)chromium tricarbonyl]-3-pentyl Methanesulfonates[1]

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Abstract: The π-(arene)chromium tricarbonyl complexes of D-, L-, DL-*threo*-, DL-*erythro*-3-phenyl-2-butyl, and DL-*erythro*-2-phenyl-3-pentyl methanesulfonates have been prepared and their acetolysis rates and products compared with those of the noncomplexed compounds. Data are presented which indicate that π complexation prior to acetolysis inhibits phenyl and hydrogen migration, prevents racemization in the *threo* case, reduces the extent of direct displacement by solvent while enhancing the sensitivity of the rate to added acetate ion, and decreases the extent of elimination while increasing the proportion of nonconjugated olefin which is formed. These effects are more pronounced in the *threo* than in the *erythro* cases. The net effect of π complexation upon the acetolysis rates of the 3-phenyl-2-butyl methanesulfonates is small: a fivefold decrease in the *erythro* case; no change in the *threo* derivative. Using the acetolysis rates of *threo*- and *erythro*-3-(*p*-nitrophenyl)-2-butyl *p*-toluenesulfonates as models for those of the complexed methanesulfonates in the *absence* of participation suggests that the reactivity of the complexed methanesulfonates may be enhanced by factors of 33 in the case of the *threo* and 6.8 in the *erythro* derivative. Steric buttressing and inhibition of phenyl migration, $\sigma-\pi$ type delocalization, or d-orbital participation are considered as possible causes for the observed effects of π complexation.

Several years ago, Cram in a now classic series of papers[9] reported the solvolytic behavior of some diastereomeric β-phenylalkyl tosylates. He found that the acetolysis of optically pure L-*threo*-3-phenyl-2-butyl *p*-toluenesulfonate yields essentially racemic *threo*-3-phenyl-2-butyl acetate and shows little diastereomeric crossover to the *erythro* series, while under similar conditions the optically pure D-*erythro*-tosylate produces *erythro*-3-phenyl-2-butyl acetate with almost complete retention of configuration but again with little crossover to a diastereoisomeric acetate. These steric consequences were later shown to be even more pronounced in formolysis. Cram demonstrated that phenyl migration occurs in both diastereomeric tosylates by showing that appropriate pairs of stereoisomeric 2-phenyl-3-pentyl and 3-phenyl-2-pentyl *p*-toluenesulfonates produce the same mixture of 2-phenyl-3-pentyl and 3-phenyl-2-pentyl acetates, and that their stereochemistries in each case are predictable by analogy with the behavior of the diastereomerically appropriate 3-phenyl-2-butyl system. Kinetic measurements[10] indicate that during acetolysis at 75° L-*threo*-3-phenyl-2-butyl *p*-toluenesulfonate racemizes about 3.4 times as rapidly as it dissociates although its actual ionization rate under these conditions is only 3 times greater than that of 2-butyl *p*-toluenesulfonate. When correction was made for the anticipated rate-retarding inductive effect of the phenyl group it appeared that the ionization of *threo*-3-phenyl-2-butyl *p*-toluenesulfonate in acetic acid is enhanced about 24 times by phenyl participation. Cram suggested that these experimental observations were incompatible with classical "open" carbonium ion theory but could easily be understood on the basis of phenyl-bridged intermediates.

Since its original postulation the concept of the phenonium ion as a discrete intermediate in the solvolysis of β-arylalkyl derivatives has received support from many other lines of investigation. Winstein, Lindegren, Marshall, and Ingraham[11] and more recently Nordlander and Deadman[12] for example have shown that the increased rate enhancements relative to ethyl *p*-toluenesulfonate which are observed as β-phenyl-

(1) (a) Portions of this work were presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967; Abstract 008S. (b) There appear to be no generally accepted conventions for naming π-complexed arenes. For example, the chromium tricarbonyl complex of benzene itself has been variously referred to as: benzene chromium tricarbonyl,[2] benzenechromium tricarbonyl,[3] π-benzene-chromium-tricarbonyl,[4] benzene-tricarbonyl-chromium(0),[5] or tricarbonylbenzene-chromium.[6] When the π-complexed arene carries functional substituents on the ring the situation becomes even more confusing.[7,8] Believing as we do that investigators who are carrying out transformations on the organic ligands of π complexes will find names such as (DL-*threo*-3-phenyl-2-butyl methanesulfonate)chromium tricarbonyl or tricarbonyl(DL-*threo*-3-phenyl-2-butanol)chromium(0) to be awkward, to place undue emphasis on either the metal or the inorganic ligand, and occasionally even to be ambiguous, we have chosen to treat the entire π-complexed aryl group in such compounds as a substituent whose position on the organic backbone is indicated by number in the usual manner. Thus the foregoing compounds would be referred to as DL-*threo*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl methanesulfonate and DL-*threo*-3-[π-(phenyl)chromium tricarbonyl]-2-butanol. For convenience and simplicity we will employ this system thoughout this paper.

(2) (a) M. L. H. Green in "Organometallic Compounds," Vol. 2, 3rd ed, G. E. Coates, M. L. H. Green, and K. Wade, Ed., Methuen and Co., Ltd., London, 1968, p 180 ff. (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 558.

(3) (a) W. McFarlane and S. O. Grim, *J. Organometal. Chem.*, **5**, 147 (1966); (b) this name is used by *Chemical Abstracts*.

(4) G. E. Herberich and E. O. Fischer, *Chem. Ber.*, **95**, 2803 (1962).

(5) H. Zeiss, P. J. Wheatley, and H. J. S. Winkler, "Benzenoid Metal Complexes, Structural Determinations and Chemistry," The Ronald Press Co., New York, N. Y., 1966, and in particular the Nomenclature Appendix, pp 93–94.

(6) D. A. Brown, *J. Chem. Soc.*, 4389 (1963).

(7) G. Klopman and K. Noack, *Inorg. Chem.*, **7**, 579 (1968).

(8) G. Klopman and F. Calderazzo, *ibid.*, **6**, 977 (1967).

(9) (a) D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3863 (1949); (b) *ibid.*, 71, 3875 (1949); (c) *ibid.*, 74, 2129 (1952); (d) *ibid.*, 74, 2137 (1952); (e) *ibid.*, 74, 2159 (1952); (f) for a condensed summary of these papers see D. J. Cram, *ibid.*, **86**, 3767 (1964).

(10) S. Winstein and K. C. Schreiber, *ibid.*, 74, 2165 (1952).

(11) (a) S. Winstein and H. Marshall, *ibid.*, 74, 1120 (1952); (b) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

(12) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968).

ethyl-1,1-d_2 *p*-toluenesulfonate is solvolyzed in a series of solvents of decreasing nucleophilicity but increasing electrophilicity is paralleled by an increase in the extent of phenyl migration, implying that a greater portion of the reaction occurs *via* the phenyl-bridged ion in the less nucleophilic but more solvolyzing solvents. Winstein and Heck[13] have demonstrated that both the rate and the extent of aryl migration in the acetolysis of a series of *meta*- and *para*-substituted neophyl tosylates at 75° are well correlated by the linear free-energy relation, $\log k_1^Z - \log k_1^H = -2.959\sigma^+$, indicating that charge is extensively delocalized into the ring during the ionization.

Some of the underlying assumptions on which the concept of bridged phenyl cations is based have recently been questioned and reexamined. In particular, Brown[14] has focused attention on the relatively small rate enhancements which accompany the acetolysis and formolysis of many β-arylalkyl derivatives and has suggested that they are not consistent with aryl participation in the ionization step. He proposes that the high stereospecificities which are observed in these cases may be due to a rapidly equilibrating pair of "open" cations or weakly interacting π-type complexes. Collins, Benjamin, and Lietzke[15] have calculated the expected product yields in the solvolysis of 3-phenyl-2-butyl derivatives using an equilibrating open carbonium ion model and have concluded that this alternative cannot be refuted on the basis of Cram's observations.

In view of the renewed and continuing interest in the related questions of aryl participation and aryl-bridged cations in solvolytic reactions, we felt that it would be interesting and perhaps informative to parallel some of the earlier solvolytic studies using β-arylalkyl derivatives in which the aromatic π electrons had been "tied down" by prior complexation and thus rendered less available for the stabilization of developing positive charge at a nonadjacent or α position. When we started our investigation, no solvolytic studies of π-complexed aryl derivatives had been reported but, because of their apparent stability, their ease of preparation and their crystalline character, we chose the π-arenechromium tricarbonyls[16] for our initial studies.

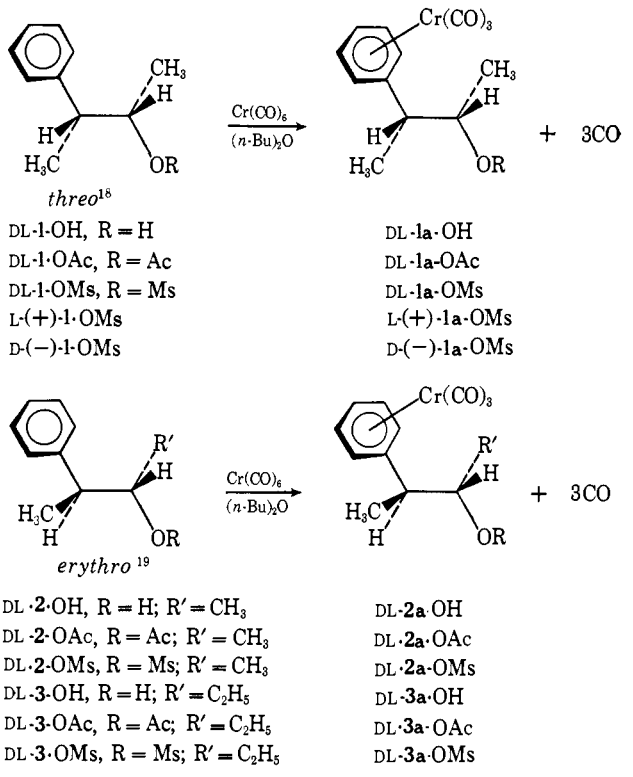
In this first paper of the series we report the synthesis and solvolytic behavior of chromium tricarbonyl complexed *threo*- and *erythro*-3-phenyl-2-butyl and *erythro*-2-phenyl-3-pentyl methanesulfonates. Later papers in this series will present similar studies with π-complexed β-phenylethyl, 2-phenylpropyl, and substituted neophyl methanesulfonates.

Methods and Results

Starting Materials. The required alcohols DL-*threo*- and -*erythro*-3-phenyl-2-butanol (DL-**1**- and -**2**-OH) were prepared as described by Cram.[9a] The DL-*threo* was resolved to yield L-(+)-*threo*-3-phenyl-2-butanol (L-(+)-**1**-OH) and D-(−)-*threo*-3-phenyl-2-butanol (D-(−)-**1**-OH) of 97.2 and 56% enantiomeric purity, respectively, based on the rotations of their corresponding acid phthalates. DL-*erythro*-2-Phenyl-3-pentanol (DL-**3**-OH) was obtained by fractional recrystallization of a mixture of the DL-*threo*- and -*erythro*-pentanols (DL-**3**- and -**15**-OH, respectively) prepared according to Cram's procedure.[9e] Each of the alcohols was converted to the acetate (DL-**1**-OAc) and/or methanesulfonate (L-(+)-, D-(−)-, and DL-**1**-OMs; DL-**2**- and -**3**-OMs, respectively) in the usual manner.[9a]

The π-arenechromium tricarbonyl complexes shown in Chart I were prepared in a Strohmeier apparatus[17] by

Chart I



heating the noncomplexed compounds with a slight excess of chromium hexacarbonyl in refluxing, peroxide-free *n*-butyl ether. The highest yields (*cf.* Table VII) were obtained in relatively dilute solutions, *e.g.*, about 1 g of the compound to be complexed per 100 ml of solvent. The complexes are yellow, crystalline solids which, when dry, are apparently stable in air at temperatures up to their melting points.

Product Studies. Acetolyses were conducted as detailed in the Experimental Section under conditions identical with those used in the rate determinations. Deoxygenated solvents were employed with the complexes and their solutions were protected from light to prevent decomposition.[20]

Products from the noncomplexed methanesulfonates were analyzed as alcohols by gas–liquid partition chromatography (glpc) of the reduced acetolysis extracts and were identified from their spectra or, where possible, by comparison with authentic samples.

(13) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, 79, 3432 (1957).
(14) (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, 87, 2137 (1965); (b) H. C. Brown, R. Berńheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, 89, 370 (1967).
(15) C. J. Collins, B. M. Benjamin, and M. H. Lietzke, *Ann. Chem.*, 687, 150 (1965).
(16) For reviews see: (a) G. R. Dobson, I. W. Stoltz, and R. K. Sheline, *Advan. Inorg. Radiochem.*, 8, 1 (1966); (b) *cf.* ref 5, pp 44–92.
(17) W. Strohmeier, *Chem. Ber.*, 94, 2490 (1961).
(18) The diastereomer represented here is that of the L series.
(19) The diastereomer(s) represented here is that of the D series.
(20) Although the course of this decomposition is not clear it apparently results in the initial formation of a Cr(II) species (yellow orange) which is rapidly converted to a Cr(III) complex (green) by the dissolved oxygen in the solvent.

The reduced products from the acetolysis at 85° of DL-*threo*- and DL-*erythro*-3-phenyl-2-butyl and DL-*erythro*-2-phenyl-3-pentyl methanesulfonates (DL-**1**-, **2**-, and **3**-OMs, respectively) are depicted in Charts II and III and are compared quantitatively with the reduced products from the acetolysis at 75° of the corresponding tosylates DL-**1**-, **2**-, and **3**-OTs[9a-e] in Tables I and II.

Chart II

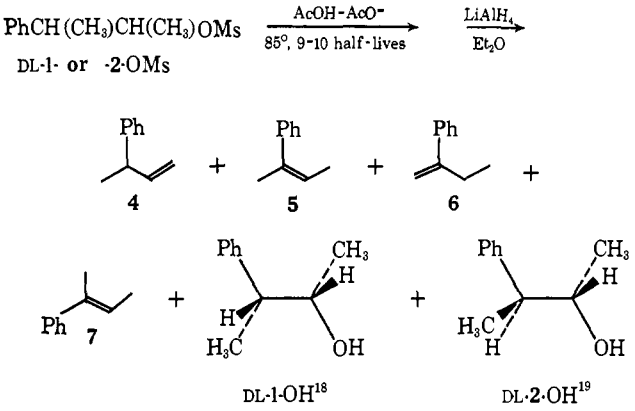
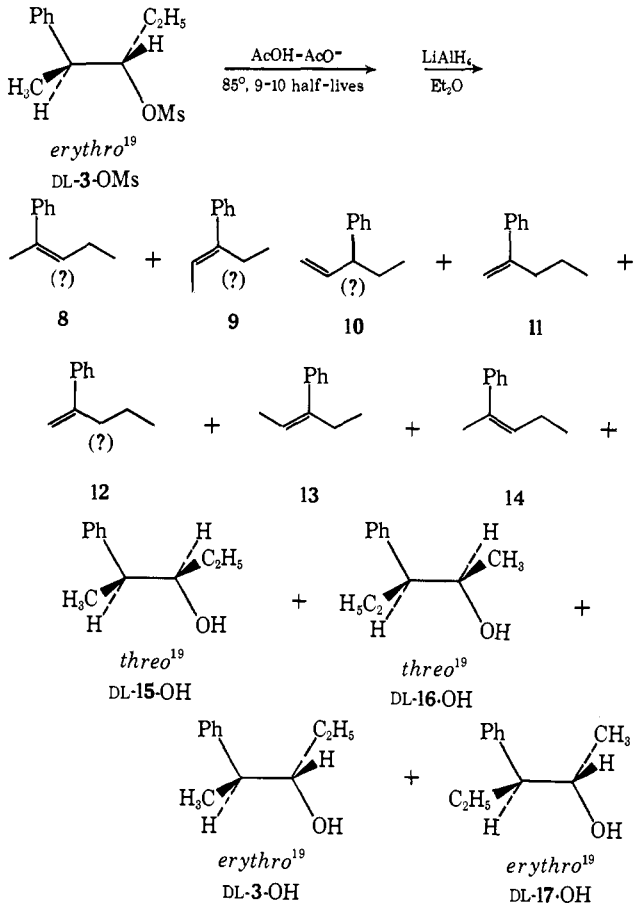


Chart III



Products from the acetolysis of the π-complexed methanesulfonates were determined as uncomplexed acetates by glpc of dry, acetic acid free, pentane–ether extracts of the solvolysis mixtures[21] or as uncomplexed alcohols by glpc of oxidatively decomplexed[22] and reduced ethereal extracts. The structures of the products

(21) *Cf.* D. J. Cram and D. I. Wilkinson, *J. Amer. Chem. Soc.*, **82**, 5721 (1960).

(22) G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, 87, 131 (1965).

Table I. Reduced Products from the Acetolysis of the DL-3-Phenyl-2-butyl-Type Sulfonates[a]

Compd	Relative abundance, %[b,c] 4	5	6	7	18-OH	1-OH	2-OH
1-OTs[d]	2.6	11.4	9.5	16.3		50.9	2.1
1-OMs	3.7	6.6	8.9	16.5		62.4	1.9
1a-OMs	3.4	0.3	0.4	0.7	Trace[e]	94.5	0.4
2-OTs[d]	3.3	2.1	5.8	14.0		3.7	71.1
2-OMs	3.0	2.8	5.2	9.5		2.2	77.3
2a-OMs	20.9	1.0	1.8	4.8	1.2[e]	1.9	68.4

[a] From an ~0.02 *M* solution of the sulfonate in anhydrous acetic acid buffered with 1.5–2.0 equiv of sodium acetate and heated for nine to ten half-lives at 85° unless otherwise specified. [b] In order of elution from a Carbowax 20M column. [c] Averaged relative glpc peak areas of duplicate determinations uncorrected for differences in thermal conductivity and normalized to 100%. [d] At 75° for 33 hr; *cf.* ref 9c and 9d. [e] Identification is tentative, see text.

Table II. Reduced Products from the Acetolysis of DL-*erythro*-2-Phenyl-3-pentyl-Type Sulfonates[a]

Compd	Relative abundance, %[b,c] 11	15- and 16-OH	17-OH	3-OH
3-OTs[d]	14	2	41	30
3-OMs[e]	19.0	Trace[f]	39.1	33.8
3*a*-OMs	74.4	1.0[f]	1.6[f]	23.0

[a] Table I, footnote *a*. [b] Table I, footnote *b*. [c] Table I, footnote *c*. [d] At 75° for 30 hr; also may contain 9% **8** and/or **12** and/or **14**, 4% **9** and/or **10** and/or **13**; *cf.* ref 9e. [e] Also contains 1.8% **8**[f] + **9**,[f] 1.3% **10**,[f] 1.4% **12**,[f] 1.0% **13**, and 1.7% **14**. [f] Table I, footnote *e*.

determined in this manner from the acetolyses at 85° of DL-**1a**-OMs, DL-**2a**-OMs, and DL-**3a**-OMs are summarized in Charts IV and V and compared quantitatively in Tables I and II with the acetolysis products from the noncomplexed methanesulfonates.

Chart IV

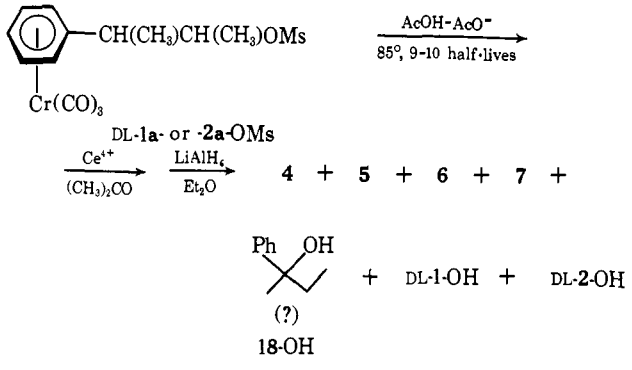
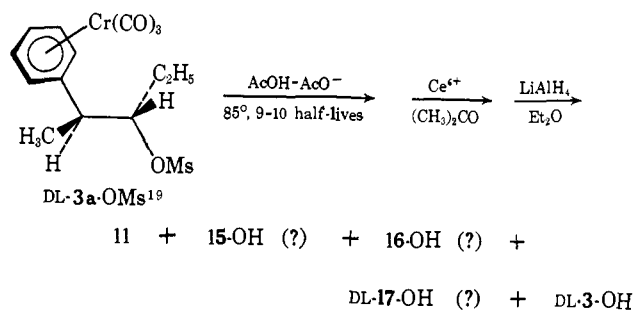


Chart V



The acetolysis of L-(+)-*threo*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl methanesulfonate (L-(+)-**1a**-OMs) in buffered acetic acid yields the corresponding acetate

Table III. Apparent First-Order Acetolysis Constants of the 3-Phenyl-2-butyl-Type Methanesulfonates

Run	Compd[a]	Temp,[b] °C	[NaOAc], *M*	$10^6 k_t$, sec^{-1}	$10^6 k_\alpha$, sec^{-1}
1,2	DL-**1**-OMs	69.2	0.0478	27.2 ± 0.05	
3,4		85.0	0.0478	160 ± 2	
5			0.0194	138	
6			0.0478	309[c]	
7			0.0194	149[d]	
8				136	
9, 10		100.9	0.0478	774 ± 3	
11, 12	D-(−)-**1**-OMs[e,f]	55.5	0.0461		26.65 ± 0.75
13, 14		85.0	0.0461		644 ± 10
15, 16	DL-**1a**-OMs	69.2	0.0478	31.2 ± 0.25	
17, 18		84.9	0.0478	168 ± 4	
19			0.0154	87.8	
20			0.0478	249[g]	
21			0.0357	146	
22			0.0264	119[h]	
23			0.0478	147[i]	
24				52.1	
25				66.6[j]	
26, 27		100.9	0.0478	688.5 ± 1.5	
28, 29	D-(−)-**1a**-OMs[e]	85.0	0.0468		193.5 ± 16[k,l]
30					75.3[k,l]
31, 32		97.4	0.0468		579 ± 21[k,l]
33, 34	DL-**2**-OMs	69.2	0.0461	33.3 ± 0.1	
35		85.0	0.0492	185	
36			0.0492	188[m]	
37				169	
38		101.4	0.0492	995	
39		101.5	0.0492	1000	
40, 41	DL-**2a**-OMs[n]	69.5	0.0492	7.59 ± 0.07	
42		85.0	0.0469	37.0	
43			0.0156	31.9	
44			0.0469	47.3[d]	
45				18.7[o]	
46				17.7	
47, 48		87.4	0.0492	50.7 ± 0.6	
49, 50		101.1	0.0492	181 ± 0.5	
51			0.0492	215[p]	
52	DL-**3**-OMs	85.0	0.0468	405	
53	DL-**3a**-OMs		0.0478	140[q]	

[a] Contains 0.0185–0.0216 *M* ROMs unless otherwise specified. [b] Controlled to ±0.03°. [c] Contains 0.0510 *M* lithium perchlorate. [d] Contains 0.0304 *M* sodium methanesulfonate. [e] Enantiomeric purity is 56%, see text. [f] Rotations read at 365 mμ; infinity reading is 0.00 ± 0.02°. [g] Contains 0.0500 *M* lithium perchlorate. [h] Contains 0.0230 *M* sodium methanesulfonate. [i] Contains 0.0403 *M* ROMs. [j] Contains 0.0528 *M* sodium methanesulfonate. [k] Rotations read at 546 mμ. [l] Corrected for the 18–20% residual rotation in the infinity samples, see text. [m] Contains 0.0438 *M* ROMs. [n] Plots of ln [ROMs] *vs.* time show slight upward drift (*i.e.*, rate decreases after 50% reaction); rate constants reported are for first 50% reaction.[23] [o] Contains 0.0212 *M* sodium methanesulfonate. [p] Contains 0.0399 *M* ROMs. [q] Based on a single determination.

of retained configuration, *e.g.*, L-(+)-**1a**-OAc. When this product is subjected to the oxidative decomplexation–hydride reduction–glpc collection sequence described earlier, the resulting alcohol, L-(+)-**1**-OH, has an enantiomeric purity of 81.0%. However, when the π-complexed acetate is first isolated by column chromatography on alumina and then subjected to the decomplexation–reduction–collection procedure, the enantiomeric purity of the resulting alcohol is 92.0%.

Since the enantiomeric purity of the starting methanesulfonate is ~97%, *vide supra*, the acetolysis apparently occurs with at least 94% retention of optical activity.

There is little doubt but that the acetolysis of the π-complexed methanesulfonates actually produces π-complexed products in all cases. In each instance the major olefin(s) and acetate(s) can be isolated as yellow chromium tricarbonyls by chromatography of the reaction mixture on neutral alumina. It has been shown that the relatively poor product balances attained in this manner are due to decomplexation during the chromatography rather than during the acetolysis proper. Finally, control experiments demonstrate that the complexes do not undergo ligand interchange during the acetolysis and that they are not isomerized during the work-up and isolation. We have not been able to detect or isolate any of the minor acetolysis products as complexes but feel that this simply reflects the limitations of our analytical and isolation techniques rather than their absence in the product mixtures.

Kinetic Studies. Apparent first-order titrimetric (k_t) and polarimetric (k_α) rate constants were determined as described in the Experimental Section and are summarized in Table III.

The effect of added sodium acetate, sodium methanesulfonate, and lithium perchlorate—expressed as the customary *b* values[24] on the titrimetric acetolysis

(23) Although we have no explanation for this deviation from linearity, it is apparently not due to competing decomplexation, ion-pair return, or impure starting material.

(24) (a) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *Chem. Ind.* (London), 664 (1954); *J Amer. Chem. Soc.*, 76, 2597 (1954); (b) A. H. Fainberg and S. Winstein, *ibid.*, 78, 2763 (1956); (c) A. H. Fainberg, G. C. Robinson, and S. Winstein, *ibid.*, 78, 2777 (1956); (d) A. H. Fainberg and S. Winstein, *ibid.*, 78, 2780 (1956);

Table IV. Dependence of Apparent First-Order Titrimetric Acetolysis Constants of the 3-Phenyl-2-butyl Sulfonates upon Added Salts

Compd	Temp,[a] °C	10^6k_t, sec^{-1} [b]	Values of b for added NaOAc	NaOMs	$LiClO_4$
DL-**1**-OMs	85.0	160	6.2	3.0	24
DL-**1**-OTs[c]	75.0	52.0	2.6	0.1[d]	31
DL-**1a**-OMs	85.0	168	47[e]	3.3	30.7
DL-**2**-OMs	85.0	185	1.9		
DL-**2a**-OMs	85.0	37.0	5.7[f]	2.2	24

[a] Table III, footnote *b*. [b] Contains 0.048 *M* sodium acetate, see Table III for data on the individual runs. [c] Extrapolated value; *cf.* ref 10. [d] Determined with sodium tosylate. [e] Determination based on four points. [f] $k_{ext}^0 = 1.6k_t^{0.24c}$

rates are summarized in Table IV. Because the π complexes are less stable in unbuffered acetic acid—especially in the presence of lithium perchlorate—the b values in these cases were determined in the presence of acetate ion and calculated using the equation: $k_t = k_t^0(1 + b_1[\text{salt 1}] + b_2[\text{salt 2}])$.[24b]

The activation parameters, computed as described previously[25] from duplicate determinations of the rate constants at three temperatures, are recorded in Table V.

Table V. Activation Parameters and Apparent First-Order Acetolysis Constants at 85° for the 3-Phenyl-2-butyl-Type Sulfonates

Compd	10^6k, sec^{-1} [a]	ΔH^*, kcal/mol	ΔS^*, eu
DL-**1**-OMs	158	26.2	−3.13
DL-**1**-OTs[b]	155	26.3	−2.85
D-(−)-**1**-OMs	644	24.6	−4.83
L-(+)-**1**-OTs[b]	672	26.0	−8.97
DL-**1a**-OMs	160	24.2	−8.71
D-(−)-**1a**-OMs	193	22.9	−12.1
DL-**2**-OMs	191	26.2	−2.83
DL-**2**-OTs[c]	178	26.5	−2.18
DL-**2a**-OMs	39.0	24.9	−9.61

[a] In the presence of 0.048 *M* sodium acetate. [b] Reference 10. [c] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952).

Since some green color formation[20] during the acetolysis of the π-complexed compounds was evident after ten half-lives at 85° in even the deoxygenated solutions, it was deemed important to establish the approximate rate of the decomposition under these conditions. Accordingly, samples of DL-*erythro*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl acetate (DL-**2a**-OAc) in buffered oxygen-free acetic acid were thermostated at 86° and the rate of disappearance of the band at 315 mμ—due to the chromium tricarbonyl complexed arene[26]—and/or appearance of the 592-mμ band—due to Cr(III)[27]—was measured spectrophotometrically as described in the Experimental Section. In this manner, apparent first-order rate constants for the decomplexation, *viz.*

$$\text{DL-2a-OAc} \xrightarrow[86°]{\text{HOAc}} \text{DL-2-OAc} + \text{Cr(III)} + \text{CO (?)}$$

of $k_{316\ m\mu} \simeq 3.4 \times 10^{-7}$ sec^{-1} and $k_{592\ m\mu} \simeq 2.0 \times 10^{-7}$ sec^{-1} were determined. The 592-mμ band reached a constant extinction after about 10% reaction, and hence is thought to provide a less precise estimate of the actual decomposition rate. By assuming that all of the complexed 3-phenyl-2-butyl derivatives decomplex in an irreversible first-order manner[20] with similar rate constants of $k_d = 3.4 \times 10^{-7}$ sec^{-1}, and by treating the data as described in the kinetic protion of the Experimental Section, it can be estimated that, after ten half-lives at 85°, less than 0.2% of the total methanesulfonate anion produced in the acetolysis of DL-**1a**-OMs originates from the acetolysis of previously decomplexed starting material, and that less than 1.2% of the total acetolysis products are decomplexed during the acetolysis. A similar calculation applied to the acetolysis of DL-**2a**-OMs at this temperature yields values of 0.7 and 5.3%, respectively. These estimates corroborate the conclusions inferred from the product studies, *vide supra*, namely, that in each case the process being studied is truly the acetolysis of a chromium tricarbonyl complexed derivative, and that the decomplexed products are formed during the work-up rather than in the acetolysis itself.

Discussion

The effects of complexing the π electrons of the phenyl ring in the 3-phenyl-2-butyl and 2-phenyl-3-pentyl systems prior to solvolysis may be summarized as follows.

(1) In contrast to L-*threo*-3-phenyl-2-butyl methane- and *p*-toluenesulfonates (L-(+)-**1**-OMs and -OTs) which yield racemic products upon acetolysis,[9a,f] the chromium tricarbonyl complexed derivative, L-*threo*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl methanesulfonate (L-(+)-**1a**-OMs), solvolyses with 94% retention of configuration. The π-complexed acetate from the solvolysis of L-(+)-**1a**-OMs, when decomplexed and reduced, gives an L-(+)-*threo*-3-phenyl-2-butanol (L-(+)-**1**-OH) of 97.3% optical purity.

This conclusion is confirmed by the polarimetric rate runs. After ten half-lives the absolute rotation of the acetolysis mixture from D-(−)-**1a**-OMs has decreased to about 20% of its original value at zero time. When the polarimetric readings are corrected to allow for this 20% residual rotation in the infinity sample, both the titrimetric and polarimetric rate constants are approximately equal, *i.e.*, $k_\alpha \simeq k_t$ (Table III).

In contrast to the results with the complexed derivative, the acetolysis mixture from D-(−)-*threo*-3-phenyl-2-butyl methanesulfonate (D-(−)-**1**-OMs) shows no detectable rotation after ten half-lives and the polarimetric rate exceeds the titrimetric by 4.1 times at 85°.

Our results with this noncomplexed methanesulfonate are similar to those of Cram and Winstein with the enantiomeric L-(+)-*threo*-3-phenyl-2-butyl *p*-toluenesulfonate at 75°.[9a,f,10] They found that the products were about 95% racemic, and the polarimetric rate exceeded the titrimetric by 4.3 times.

(2) π complexation greatly reduces or completely eliminates aryl migration during the acetolysis. In contrast to the noncomplexed tosylate which solvolyses to yield *erythro*-3-phenyl-2-pentyl acetate and *erythro*-

(e) S. Winstein, B. Appel, R. Baker, and A. Diaz, "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 109.

(25) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Amer. Chem. Soc.*, **89**, 880 (1967).

(26) R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).

(27) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

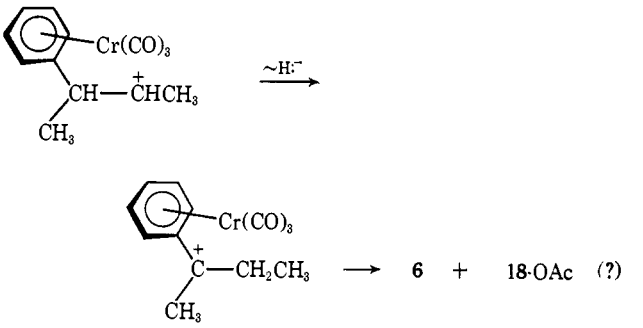
2-phenyl-3-pentyl acetate in almost equal amounts,[9e] *erythro*-2-[π-(phenyl)chromium tricarbonyl]-3-pentyl methanesulfonate (DL-**3a**-OMs) produces, after decomplexation and reduction, *erythro*-2-phenyl-3-pentanol (DL-**3**-OH) almost exclusively (Chart III, Table II). By inference then, no aryl migration occurs during the acetolysis of the 3-phenyl-2-butyl complexes.

(3) π complexation decreases the amount of direct backside displacement that occurs during the acetolysis of DL-*threo*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl methanesulfonate (DL-**1a**-OMs). Such displacement causes a crossover from the *threo* to the *erythro* series. This occurs to the extent of about 0.4% (Table I), clearly less than the 3% which we observe with the noncomplexed methanesulfonate DL-**1**-OMs or the 5% reported by Cram in the case of the tosylate (DL-**1**-OTs).[9a,f]

On the other hand, complexation appears to have but a slight effect on the extent of direct displacement which is observed with the *erythro* methanesulfonates. Acetolysis of either DL-**2a**- or DL-**2**-OMs produces about 2% of the *threo* acetate DL-**1a**- or -**1**-OAc, respectively (Table I). Cram observed 3.7% crossover in the acetolysis of the noncomplexed tosylate DL-**2**-OTs at 75°.[9a,f] The acetolysis of DL-*erythro*-2-[π-(phenyl)chromium tricarbonyl]-3-pentyl methanesulfonate apparently produces a little more (~1.0%) of the *erythro* acetate DL-**15a**-OAc than does that of the noncomplexed derivative DL-**3**-OMs (Table II). Crossover is evidently slightly less with each of the noncomplexed methanesulfonates than with the corresponding tosylates.[9e]

(4) π complexation has a pronounced effect upon both the relative amount and nature of the olefins produced in these acetolyses. Less than 5% of the decomplexed and reduced products from the complexed *threo*-3-phenyl-2-butyl methanesulfonate (DL-**1a**-OMs) are hydrocarbons in contrast to the ~36% produced in the acetolysis of the noncomplexed derivative DL-**1**-OMs (Table I). Furthermore, of the olefins produced from DL-**1a**-OMs, less than a third are conjugated, while well over half of those formed from DL-**1**-OMs are of the conjugated or styrene type. In contrast to the *threo* diastereomer, the *erythro*-3-phenyl-2-butyl methanesulfonate produces a larger proportion of olefins (~29%) when complexed than when not complexed (~20%), *cf.* Table I. Thus DL-**2a**-OMs yields six times more hydrocarbon upon acetolysis than does DL-**1a**-OMs. However, again of the olefins produced by the complexed *erythro* methanesulfonate, DL-**2a**-OMs, less than a fourth are conjugated while more than eight-tenths of those from the noncomplexed derivative DL-**2**-OMs are of the styrene type. In the case of the *erythro*-2-phenyl-3-pentyl methanesulfonate (Table III), π complexation causes a large increase in the proportion of hydrocarbons produced in the acetolysis. Although some additional olefin is to be expected in view of the large decrease in the extent of aryl migration caused by the complexation, the product mixture actually contains less of even the unrearranged acetate, DL-**3a**-OAc. Here, as in the other complexed methanesulfonates, the nonconjugated olefin (**11a**) is by far the major hydrocarbon. Though it is clear in all cases that the complexed olefins are not formed by decomposition of the acetates either during the solvolysis or subsequently in the isolation and analysis, it is not known whether their relative abundance in the product mixtures is kinetically or thermodynamically determined.

(5) π complexation seems to decrease the extent of hydride migration during the acetolysis but to stabilize the small amounts of hydride-migrated acetates which are produced. Both the 2-phenyl-1-butene (**6**) and the 2-phenyl-2-butanol (**18**-OH) which appear to be present in the decomplexed and reduced mixture from the acetolysis of the π-complexed 3-phenyl-2-butyl methanesulfonates are products of a hydride migration. It is likely that this migration occurs during the acetolysis and that both these products are formed initially from the rearranged cation, methylethyl[π-(phenyl)chromium tricarbonyl]carbonium ion, *e.g.*



Since the total amount of **6** + **18**-OH (?) is less in the case of the π-complexed methanesulfonates (DL-**1a**- or -**2a**-OMs) than in the products which result from the noncomplexed derivatives (DL-**1**- or -**2**-OMs), it appears that π complexation suppresses hydride migration to some extent.

Surprisingly some of the π-complexed, hydride-migrated acetate, 2-[π-(phenyl)chromium tricarbonyl]-2-butyl acetate (**18a**-OAc), apparently survives the acetolysis at 85° while none of the noncomplexed acetate, **18**-OAc, is found under these conditions.[9d] Cram has demonstrated that **18**-OAc is stable in acetic acid at relatively low temperatures (30°) but that it undergoes elimination to produce the isomeric phenylbutenes **5**, **6**, and **7** at higher temperatures,[9d] *viz.*

$$\textbf{18}\text{-OAc} \xrightarrow[75°,\ 26\ hr]{HOAc} \textbf{4}\ (0\%) + \textbf{5}\ (3\%) + \textbf{6}\ (43\%) + \textbf{7}\ (54\%)$$

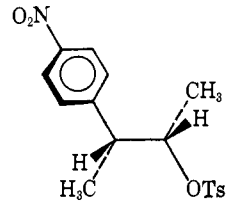
If it is assumed that the gross proportions of the olefins produced by elimination from the π-complexed acetate, **18a**-OAc, do not differ appreciably from those observed by Cram in the noncomplexed acetate, **18**-OAc, then a crude estimate of the extent of hydride migration accompanying the acetolysis of the complexed 3-phenyl-2-butyl methanesulfonates may be made. Thus, hydride migration apparently accounts for >0.5 but <1.4% of the products formed from DL-**1a**-OMs and >3.5 but <8.8% of those arising from DL-**2a**-OMs. Both values are clearly less than the 29% hydride migration observed by Cram for the acetolysis of DL-**1**-OTs.[9d]

Although some hydride-migrated product (**12**) may be formed in the acetolysis of DL-*erythro*-2-phenyl-3-pentyl methanesulfonate, DL-**3**-OMs, we can detect none in the case of the π-complexed counterpart, DL-**3a**-OMs.

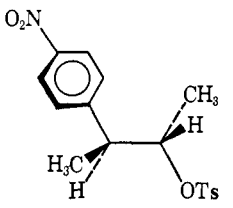
(6) π complexation causes a small decrease in the reactivity of the *erythro*-3-phenyl-2-butyl derivative and an inversion in the relative reactivities of the diastereo-

isomeric *threo*- and *erythro*-methanesulfonates. At 85° and similar base concentration, DL-**2a**-OMs reacts with acetic acid about 4.9 times more slowly than does the noncomplexed derivative DL-**2**-OMs (Table III). The reactivities of the complexed and noncomplexed *threo* compounds are similar. The result that the π-complexed *erythro*-3-phenyl-2-butyl methanesulfonate is now four times less reactive at this temperature than its π-complexed diastereomer, DL-**1a**-OMs, was unexpected. By way of comparison, earlier work on the noncomplexed tosylates[10] had shown that the *erythro* compound DL-**2**-OTs is slightly more reactive than the *threo*, DL-**1**-OTs.

(7) π complexation may increase slightly the extent of participation which occurs in the acetolysis of the 3-phenyl-2-butyl methanesulfonates. In order to estimate the additional enhancement provided by the chromium tricarbonyl group, it is necessary to correct for its inductive effect. Since the reported pK_a's of [π-(phenyl)chromium tricarbonyl]acetic and *p*-nitrophenylacetic acids in 50% aqueous ethanol at 25° are experimentally identical (5.02 and 5.01, respectively)[28] and considerably lower than that of phenylacetic acid itself under these conditions (5.64),[28] the inductive effects of the π-(phenyl)chromium tricarbonyl and *p*-nitrophenyl groups appear to be similar.[7,8,29] If the assumption is made that there exists a Hammett-type linear free-energy relation which relates the ionization constants of these phenylacetic acids with the unassisted acetolysis rates of the 3-phenyl-2-butyl methanesulfonates, then the ratio of the apparent first-order titrimetric acetolysis constants of DL-*threo*-3-(*p*-nitrophenyl)-2-butyl and DL-*threo*-3-phenyl-2-butyl tosylates (DL-**19**- and **-1**-OTs, respectively) at 85° may be taken as a measure of the *expected* ratio of rate constants for the DL-*threo*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl and DL-*threo*-3-phenyl-2-butyl methanesulfonates (DL-**1a**- and **-1**-OMs, respectively) *in the absence of participation.*[30] This value, interpolated from Cram's data at 75 and 100° is 0.0308 in the *threo* case and 0.0298 for the diastereomeric *erythro* derivative.[31] The *observed* titrimetric reactivity ratios for the complexed and noncomplexed methanesulfonates at this temperature (Table V) are 1.02 and 0.204 in the *threo* and *erythro* series, respectively. Thus, it appears that the acetolysis of the π-complexed *threo*-3-phenyl-2-butyl methanesulfonate (DL-**1a**-OMs) may be enhanced over that of the noncomplexed by 1.02/0.0208 or about 33 times. In the *erythro* case, the extent of participation is apparently 0.204/0.0298 or 6.8 times. Note that these are *dissociation* rather than *ionization* rates.



threo[18]
DL-19-OTs



erythro[19]
DL-20-OTs

(8) π complexation causes an unusual rate dependence on added acetate ion (Table IV). The dependence of an apparently first-order solvolysis reaction on added salts, including the conjugate base of the solvent itself, is usually reported as a *b* value calculated from the equation $k_t = k_t^0(1 + b_1[\text{salt 1}] + b_2[\text{salt 2}])$.[24b] The *b* value for added acetate ion normally lies in the range of 0 to 20 for most acetolyses.[24] Small acetate *b* values reflect only slight variations in rate with added conjugate base and are usually taken to indicate that the rate-limiting step of the solvolysis is predominately unimolecular.[24] The acetate ion *b* values associated with the acetolysis of the noncomplexed *threo*- and *erythro*-3-phenyl-2-butyl methanesulfonates at 85°, 6.1 and 1.9, respectively, fall into this category and are similar to those reported by Winstein for the acetolysis of the corresponding tosylates at 75°.[10]

In contrast, the apparent first-order titrimetric acetolysis constant of the π-complexed *threo* derivative, DL-**1a**-OMs, shows a very large dependence on added acetate ion. We calculate a *b* value of 47, larger than those reported for many biomolecular nucleophilic displacement reactions.[24] This is quite unusual in view of the fact that the first-order plots are linear to 80% reaction, and that less than 0.4% of the product results from direct displacement with inversion of configuration at C-2. The complexed *erythro* methanesulfonate, DL-**2a**-OMs, also exhibits an enhanced *b* for added acetate ion compared to that found in the noncomplexed derivative, but its magnitude, 5.7, is still well within the range of that expected for a normal first-order acetolysis.

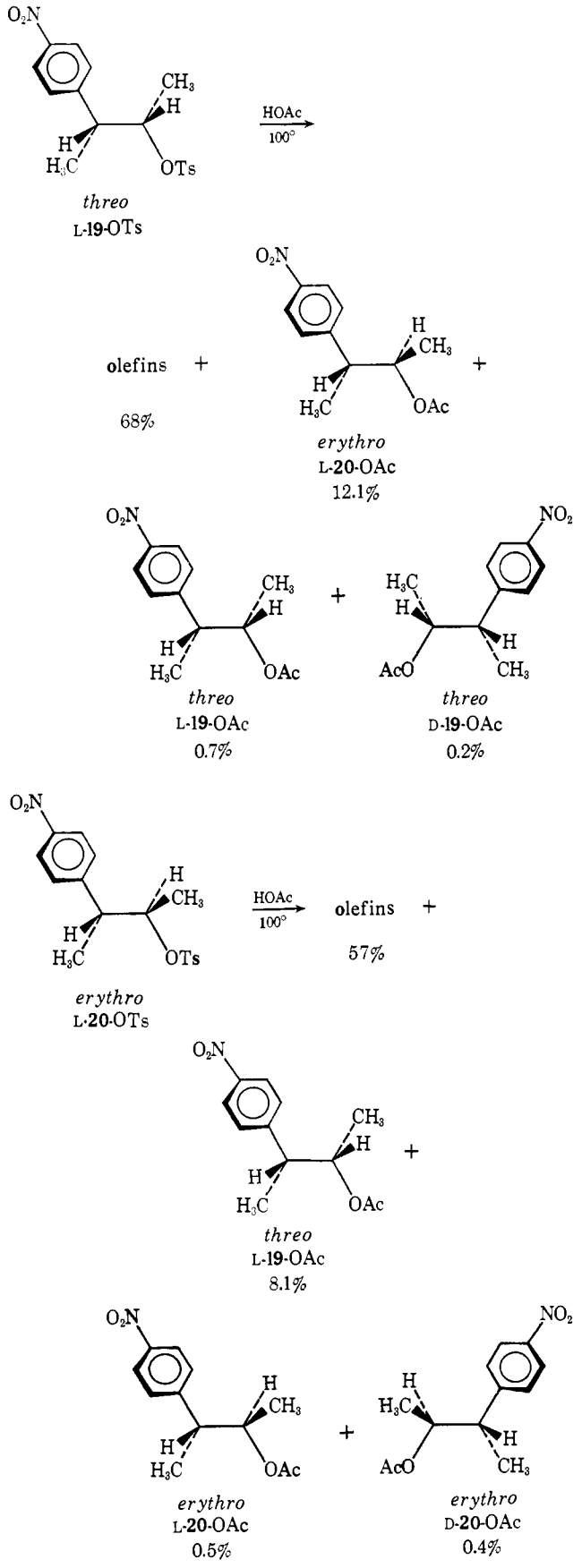
The *b* values for added sodium methanesulfonate and lithium perchlorate are somewhat larger in the complexed methanesulfonates than they are in the noncomplexed cases. Again the change is greater in the case of *threo* diastereomer.

(9) π complexation causes a decrease in the magnitude of the calculated activation parameters in both 3-phenyl-2-butyl series (Table V). The ΔH^* decreases about 2 kcal/mol upon complexation of either diastereomer while the ΔS^* is lowered by 5.5 in the *threo* and 8.8 eu in the *erythro* series. These results are consistent with the idea of increased participation in the complexed cases.[11]

Interpretation of these effects is hampered by our present uncertainty regarding the true electronic and steric effect of the chromium tricarbonyl group. Our estimations of the rate enhancements which attend π complexation, if they are correct, indicate that the effects are small at best. Also it is clear from the nmr spectra of the complexed diastereomers, DL-**1a**- and **-2a**-OMs, that they do not adopt the same equilibrium conformation in deuteriochloroform solution,[32] *cf.* Table VIII, Experimental Section. Doubtless some of the obvious differences in the solvolytic behavior of these two methanesulfonates are due to such conformational effects. In spite of these uncertainties, however, it is likely that the observed effects of π complexation must be attributed to either a decrease in the extent of phenyl participation caused by the steric and/or electron-withdrawing effect of the chromium tricarbonyl group accompanied by a steric buttressing and shielding effect or

(28) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).
(29) *Cf.* D. A. Brown and J. R. Raju, *ibid.*, *A*, 40 (1966).
(30) Assuming of course that the *ratios* are not affected by the difference in the leaving groups.
(31) D. J. Cram and J. A. Thompson, *J. Amer. Chem. Soc.*, **89**, 6766 (1967).
(32) *Cf.* C. A. Kingsbury and W. B. Thornton, *J. Org. Chem.*, **31**, 1000 (1966).

Chart VI



some sort of direct nucleophilic participation by the complex itself.

Cram and Thompson[31] have recently demonstrated that phenyl rings substituted with a strong electron-withdrawing group exhibit decreased participation. They found that the acetolysis of each of the diastereoisomeric 3-*p*-nitrophenyl-2-butyl *p*-toluenesulfonates is retarded with respect to that of the unsubstituted compound and the major acetate produced in each case is the crossover product of inverted configuration at C-2 and retained configuration at C-3. The minor acetates of the same diastereomeric series as the starting material are partially racemic, *cf.* Chart VI. Thus the pattern of minimum crossover and complete racemization which Cram had observed earlier with the active *erythro*- and *threo*-3-phenyl-2-butyl *p*-toluenesulfonates,[9a] respectively, is no longer evident in the *p*-nitro-substituted compounds. Clearly, when aryl participation is minimized, the predominant reaction is direct displacement with inversion, and much of the aryl migration which does occur is nonstereospecific.

Thus if the electron-withdrawing ability of a chromium tricarbonyl group is comparable to that of a *p*-nitro some decrease in the extent of phenyl participation and migration is to be expected. Further, if as Nicholls and Whiting have suggested the steric bulk of the chromium tricarbonyl is equivalent to that of a "large ortho substituent,"[28] such migration might be completely inhibited by the inability of the aromatic ring to achieve a favorable conformation for electron delocalization. Finally, it is not unreasonable to expect that such a large group might also enhance somewhat the ionization rate of the methanesulfonate through its buttressing effect on the hydrogen and methyl at C-2 while it shields the backside of the developing cation from attack by solvent. Under such circumstances, dissociation of the resulting ion pair could well be assisted by attack of acetate from the front side.[33] This would account for the large acetate *b* values which accompany the acetolysis of the complexes as well as the formation of products of retained configuration.

There may be a parallel between the solvolytic behavior of α- and β-[π-(phenyl)chromium tricarbonyl]-alkyl derivatives and the corresponding π-cyclopentadienyl compounds. Pettit, Holms, and Jones have reported that the hydrolysis rate of [π-(phenyl)-chromium tricarbonyl]carbinyl chloride exceeds that of benzyl chloride by $\sim 10^5$ times.[35] McEwen, Manning, and Kleinberg have suggested that some participation may also occur during the ethanolysis of α-[π-(cyclopentadienyl)manganese tricarbonyl]benzyl acetate.[36] Similarly, α-metallocenyl derivatives are also much more reactive than their phenyl analogs[37] and give products of retained configuration.[37] Although as in the

(33) Several other cases of solvolytic reactions which take place with net retention of configuration have recently been found.[34] Although the conjugate base effects have not always been reported, it is possible that these reactions involve frontside nucleophilic displacements on tight ion pairs.

(34) (a) H. L. Goering and S. Chang, *Tetrahedron Lett.*, 3607 (1965); (b) B. L. Murr and C. Santiago, *J. Amer. Chem. Soc.*, 88, 1826 (1966); (c) K. Okamoto, H. Yamada, I. Nitta, and H. Singu, *Bull. Chem. Soc. Jap.*, **39**, 299 (1966); (d) K. Okamoto, M. Hayashi, and H. Shingu, *ibid.*, **39**, 408 (1966); (e) T. G. Traylor and C. L. Perrin, *J. Amer. Chem. Soc.*, 88, 4934 (1966); (f) P. G. Gassman and J. M. Hornback, *ibid.*, **89**, 2487 (1967); (g) F. M. Miles, *ibid.*, **89**, 2488 (1967).

(35) J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.*, 4, 324 (1965).

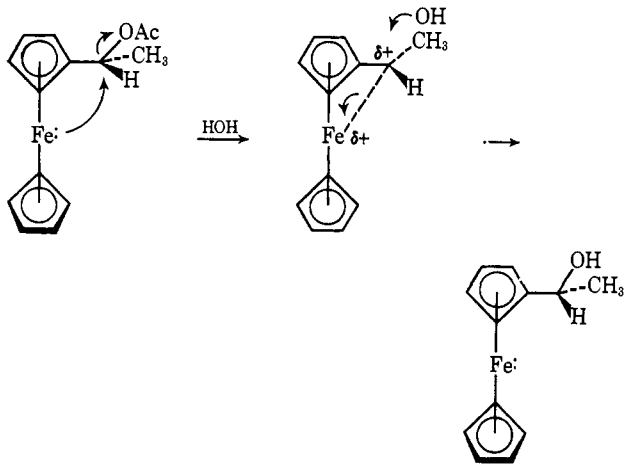
(36) W. E. McEwen, J. A. Manning, and J. Kleinberg, *Tetrahedron Lett.*, 2195 (1964).

(37) (a) J. H. Richards and E. A. Hill, *J. Amer. Chem. Soc.*, 81, 3484 (1959); (b) *ibid.*, **83**, 3840 (1961); (c) *ibid.*, **83**, 4216 (1961). For sum-

chromium tricarbonyl complexed arenes, the extent of participation is greatly reduced when the reaction site is not directly conjugated with the cyclopentadienide ring, β-ferrocenylethyl *p*-toluenesulfonate is still about 500 times as reactive as the β-phenylethyl derivative.[38] Interestingly, large conjugate base effects have also been observed in the hydrolyses of [π-(phenyl)chromium tricarbonyl]carbinyl chloride[35] and α-methylferrocenylcarbinyl acetate.[37a,b]

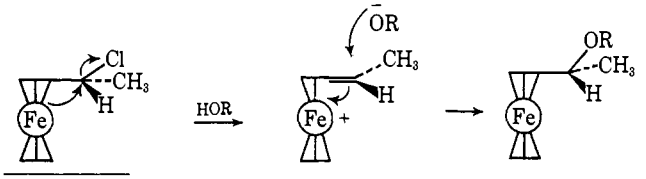
Two different hypotheses have been advanced to explain the enhanced solvolytic rates and stereospecificity of these ferrocene derivatives. Richards and Hill, who were the first to observe these effects in α-ferrocenyl compounds, have suggested that they result from the direct interaction of an appropriate, filled d orbital on the iron with the developing empty p orbital of the cation in the transition state and intermediate of the reaction, *viz.*[37a,c] Chart VII.

Chart VII



Alternatively, Traylor and Ware[37d,e,39]—following an idea developed by Nesmeyanov[40] to explain some of the chemical and spectroscopic properties of ferrocenes and other organometallics—have proposed that the formation of α-ferrocenyl cations is aided by, and the intermediates themselves stabilized by, metal–carbon hyperconjugation (σ–π delocalization) through the cyclopentadienide ring. This type of interaction is depicted schematically for the solvolysis of α-ferrocenylethyl chloride in Chart VIII. The observed stereospecificity

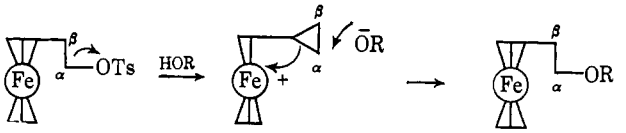
Chart VIII



of such reactions is attributed to the fact that the leaving group departs and the nucleophile attacks from the top or "outside" of the cyclopentadienide moiety where the electron density is lowest. The σ–π formulation of Traylor and Ware differs from that of Richards and Hill in that it does not involve direct or bridging d orbital participation.[39a,b]

The concept of σ–π-type delocalization has also been extended by Traylor and Ware to account for the enhanced solvolytic reactivity of β-ferrocenylethyl *p*-toluenesulfonate.[39b] They envision the intermediate as being formed through an SE2 attack by the developing cationic center on the cyclopentadienyl ring. The intermediate itself is pictured as being similar to a phenonium ion, but with the important difference that the "inside" or interior bond is broken much more readily than the exterior or "outside" one so that the attacking nucleophile becomes attached exclusively to the α-carbon in the second step of the reaction as shown in Chart IX.

Chart IX



Although the rate effects are less dramatic, it may be that the chromium tricarbonyl group acts in an analogous manner to enhance the reactivity of complexed β-arylalkyl derivatives. The alternant formulations of d-orbital or σ–π-type participation in the active *threo*-3-phenyl-2-butyl complex are shown in Charts X and XI,

Chart X

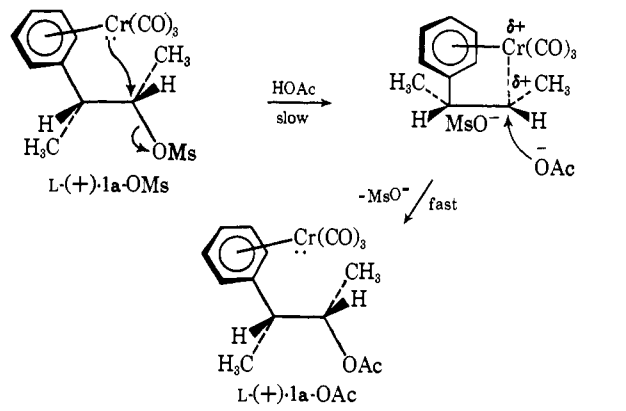
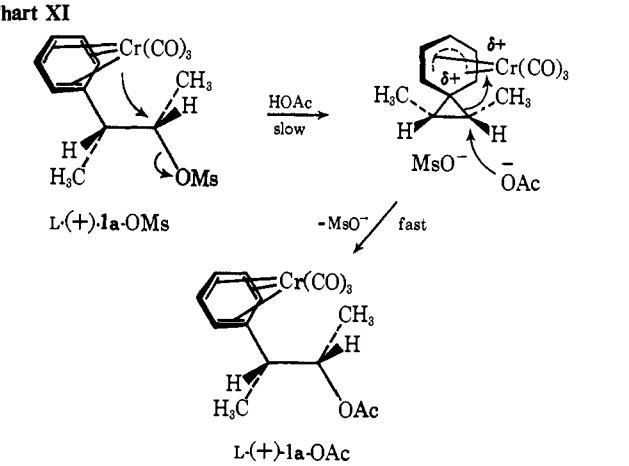


Chart XI



maries see: (d) M. Cais, *Organometal. Chem. Rev.*, 1, 435 (1966); (e) M. Cais, *Rec. Chem. Progr.*, 27, 177 (1966).

(38) D. S. Trifan and R. Bacskai, *Tetrahedron Lett.*, No. 13, 1 (1960).

(39) (a) T. G. Traylor and J. C. Ware, *ibid.*, 1295 (1965); (b) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, 89, 2304 (1964); (c) W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 4451 (1967); (d) J. A. Mangravite and T. G. Traylor, *ibid.*, 4457, 4461 (1967); (e) T. T. Tidwell and T. G. Traylor, *J. Amer. Chem. Soc.*, 88, 3442 (1966).

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respectively. Since each of these interpretations suggests that the chromium tricarbonyl should be positioned at the backside of the α (or C-2) carbon, either is compatible with the decreased crossover (*i.e.*, direct displacement with inversion at C-2) which is observed in these acetolyses.

We are extending our studies to other chromium tricarbonyl complexed β-arylalkyl derivatives in an attempt to distinguish these mechanistic possibilities.

Experimental Section[41]

Preparation of DL-*threo*- and DL-*erythro*-3-phenyl-2-butanols (DL-1-OH and DL-2-OH) was followed as described by Cram.[9a]

Resolution of DL-*threo*-3-Phenyl-2-butanol (DL-1-OH). The procedure described in ref 9a was followed. The brucine salt was recrystallized nine times from acetone. The phthalate half-ester obtained from hydrolysis of the brucine salt had the following properties: mp 100.5–102°; $[\alpha]^{25}D$ +24.5° (*c* 6.07, ethanol) [lit.[9a] mp 101–102°, $[\alpha]^{25}D$ +25.2° (*c* 3.7, ethanol)]. Hydrolysis of the phthalate ester gave the butanol: $[\alpha]^{25}D$ +20.40° (*c* 6.09, ethanol) [lit.[9a] $[\alpha]^{25}D$ +30.9° (neat)]. When concentrated, the acetone filtrates from the first recrystallization yielded an oil which was hydrolyzed, to give the phthalate half-ester enriched in the (−) isomer: $[\alpha]^{25}D$ −16.6° (*c* 5.83, ethanol) [lit.[9a] $[\alpha]^{25}D$ −30.2° (neat)].

DL-*erythro*- and DL-*threo*-2-phenyl-2-pentanols were prepared by adding ethylmagnesium iodide to 2-phenylpropionaldehyde as described by Cram.[9b] The pure *erythro*-pentanol was separated from the mixture of diastereomeric alcohols by seeding the pentane solution with pure DL-3-OH. The precipitate that formed was recrystallized from pentane until none of the *threo* isomer could be detected by glpc. The yield of DL-3-OH, mp 41–42°, was 58%.

Preparation of the Methanesulfonates. To a cold (0 to −10°) solution containing 0.0200 mol of the alcohol in 30 ml of dry pyridine was added 0.0210 mol of methanesulfonyl chloride in one portion. The reaction mixture was immediately stoppered and maintained at −10° for about 12 hr. The reaction mixture, containing a white precipitate, was added to a large separatory funnel with about 200 g of ice. About 200 ml of chloroform was added, and the mixture was vigorously shaken. The chloroform layer was separated, washed twice with cold, dilute sulfuric acid, once with an excess of cold, saturated sodium carbonate, twice with ice-cold water, and dried over anhydrous magnesium sulfate. The chloroform was removed under vacuum to leave a residue of light tan oil. This oil was dissolved in dry ether, filtered through charcoal, and crystallized from a pentane–ether mixture. Seed crystals were added to induce crystallization. Yields range from 48 to 92%. The methanesulfonates were recrystallized from a pentane–ether mixture before being used in the rate, product, or complexation studies. Melting points and yields are reported in Table VI.

Table VI. Melting Points and Yields of the 3-Phenyl-2-butyl and 2-Phenyl-3-pentyl Methanesulfonates

Compd	Mp, °C	Yield, %
DL-1-OMs	Liquid	65.7
L-1-OMs	41.5–42	92.0
DL-2-OMs	46–47	73.9
DL-3-OMs	42–43	48.0

(41) Melting and boiling points are uncorrected. Microanalyses were performed by Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany, or Galbraith Laboratories, Knoxville, Tenn. Spectra were determined on a Perkin-Elmer Model 202 ultraviolet-visible spectrometer, a Perkin-Elmer Model 337, grating infrared spectrophotometer, and a Varian A60A nmr spectrometer. Tetramethylsilane (δ 0.00) and/or chloroform (δ 7.31) were employed as internal standards. Optical rotations were measured on an O. C. Rudolph and Sons, Model 80 polarimeter equipped with an oscillating polarizer, a photoelectric readout and a filtered mercury or sodium light source. Gas chromatographic analyses employed 12 or 16 ft × 0.25 in. copper columns packed with 20% Carbowax 20M on 60–80 mesh Gas-Chrom CL (Applied Science Laboratories) or 10% diisododecyl phthalate on 60–80 mesh Chromosorb W (Johns-Manville) and an 8 ft × 0.25 in. copper tube packed with silver nitrate in propylene glycol coated Chromosorb P in an F & M Model 500 equipped with a thermal conductivity detector or a 300 ft × 0.02 in. stainless steel capillary coated with water-insoluble Ucon in an F & M Model 1609 equipped with a flame detector.

DL-*threo*-3-Phenyl-2-butyl methanesulfonate (DL-1-OMs): ir (CCl_4) 3030 (CH phenyl), 2980 and 2940 (CH aliphatic), 1370 and 1172 ($-OSO_2-$), 980 and 911 (CO), and 702 cm^{-1} (monosubstituted phenyl);[42] nmr (CCl_4) δ 7.21, slightly perturbed singlet (5 C_6H_5–); 4.75, an ~1:4:6:4:1 pentet, $J_{BA} \simeq J_{BC} \simeq 6.7$ Hz (1 $>CH^{C}CH^{B}(CH_3^{A})O-$);[43] 2.98, an ~1:4:6:4:1 pentet, $J_{CB} \simeq J_{CD} \simeq 7.3$ Hz (1 $PhCH^{C}(CH_3^{D})CH^{B}<$); 2.41, singlet (3 $-OS(O)_2CH_3$); 1.36, doublet, $J_{AB} = 6.2$ Hz (3 $>CH^{B}CH_3^{A}$); 1.33, doublet, $J_{CD} = 6.3$ Hz (3 $>CH^{C}CH_3^{D}$).

Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.07; O, 21.02; S, 14.04. Found: C, 58.04; H, 6.94; O, 21.12; S, 13.86.

D-(−)-*threo*-3-Phenyl-2-butyl methanesulfonate (D-1-OMs): $[\alpha]^{25}_{365}$ 105.1° (*c* 4.61, chloroform).

L-(+)-*threo*-3-Phenyl-2-butyl methanesulfonate (L-1-OMs): $[\alpha]^{25}D$ +19.30° (*c* 2.19, ethanol).

DL-*erythro*-3-Phenyl-2-butyl methanesulfonate (DL-2-OMs): ir (CCl_4) 3080, 3070, and 3030 (CH phenyl); 2980 and 2940 (CH aliphatic); 1610 and 1590 (phenyl nucleus); 1370 and 1170 ($-OSO_2-$); 960 (CO); and 700 cm^{-1} (monosubstituted phenyl); nmr (CCl_4) δ 7.22, singlet (5 C_6H_5–); 4.77, an ~1:4:6:4:1 pentet, $J_{BA} \simeq J_{BC} \simeq 6.8$ Hz (1 $>CH^{C}CH^{B}(CH_3^{A})O-$);[43] 2.91, an ~1:4:6:4:1 pentet, $J_{CB} \simeq J_{CD} \simeq 7.4$ Hz (1 $PhCH^{C}(CH_3^{D})CH^{B}<$) superimposed on a singlet at 2.69 (3 $-OS(O)_2CH_3$); 1.39, doublet, $J_{AB} = 6.2$ Hz (3 $>CH^{B}CH_3^{A}$) superimposed on a doublet, $J_{CD} = 6.3$ Hz, at 1.28 (3 $>CH^{C}CH_3^{D}$).

Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.07; O, 21.02; S, 14.04. Found: C, 57.75; H, 6.91; O, 21.10; S, 13.89.

DL-*erythro*-2-Phenyl-3-pentyl methanesulfonate (DL-3-OMs): ir (CCl_4) 3090, 3060, and 3030 (CH phenyl); 2960 and 2940 (CH aliphatic); 1610 and 1590 (phenyl nucleus); 1350 and 1170 ($-OSO_2-$); 969 and 911 (CO); and 701 cm^{-1} (monosubstituted phenyl); nmr ($DCCl_3$) δ 7.16, singlet (5 C_6H_5–); 4.70, an ~1:3:3:1 broad quartet, $J_{BC} \simeq 6.3$ Hz, $J_{BA} \simeq 5.5$ Hz (1 $>CH^{C}CH^{B}(CH_2^{A}-)O-$);[43] 3.09, an ~1:4:6:4:1 broad pentet, $J_{CB} \simeq J_{CD} \simeq 7.0$ Hz (1 $PhCH^{C}(CH_3^{D})CH^{B}<$); 2.64, singlet (3 $-OS(O)_2CH_3$); 1.84–0.70, complex mutiplet (~2 $>CH^{B}CH^{A'}H^{A}CH_3^{E}$) superimposed on a doublet, $J_{DC} = 7.0$ Hz (3 $>CH^{C}CH_3^{D}$); 0.94, asymmetric triplet $J_{BA} \simeq 6.0$ Hz (~3 $>CH^{C}CH_3^{D}$); 0.94, asymmetric triplet, $J_{EA} \simeq 6.0$ Hz (~3 $-CH^{A}H^{A'}CH_3^{E}$). (Apparently the nonequivalent methylene hydrogens A and A′ are sufficiently similar that the over-all appearance of the resonances due to E still superficially resemble those of a normal ethyl group of the A_2B_3 type.[43])

Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.47; H, 7.49; O, 19.81; S, 13.23. Found: C, 59.30; H, 7.40; O, 19.83; S, 13.14.

Preparation of the π-Complexed Methanesulfonates. To 125 ml of *n*-butyl ether (freshly distilled from sodium) and 20 ml of heptane was added 0.044 mol of the methanesulfonate and 0.050 mol of chromium hexacarbonyl. The reaction mixture was heated in the dark in a Strohmeier[17] apparatus at an oil bath temperature of 155–160°. At this temperature any chromium hexacarbonyl which sublimes is automatically returned to the reaction flask by the refluxing solvent. Optimum yields were obtained when the reaction was allowed to proceed for about 25 hr. The hot reaction mixture was then filtered through charcoal, concentrated to about 50 ml by distillation of the solvent at reduced pressure, cooled to 0°, and diluted with pentane until crystallization occurred. The crystals were collected, dryed under vacuum, dissolved in ether, filtered through charcoal, and recrystallized from 1:1 pentane–ether. Yields and melting points are reported in Table VII.

Table VII. Melting Points and Yields of the π-Complexed Methanesulfonates

Compd	Mp, °C	Yield, %
DL-1a-OMs	85–86.5	48.3
L-1a-OMs	80.5–81.5	48.3
DL-2a-OMs	104–105	56.0
DL-3a-OMs	128.5–129.3	75.6

(42) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 26.

(43) We recognize that this resonance is a portion of a more complex system and hence should not be subject to a simple intuitive interpretation. In fact, however, a simple analysis seems to provide a reasonably satisfactory explanation of the observed multiplicity in this case and has been included for this reason. *Cf.* L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1959, pp 90–92.

DL-*threo*-**3-[π-(Phenyl)chromium tricarbonyl]-2-butyl methanesulfonate** (DL-**1a-OMs**): ir (CCl_4) 3020 (CH phenyl); 2985 (CH aliphatic); 1980 and 1920 (C≡O); 1375, 1350, and 1171 ($-OSO_2-$); 970 and 910 (CO); 661, 632, and 535 cm^{-1} (CrC);[44] nmr ($DCCl_3$) δ 5.33, singlet (5 $Cr(CO)_3C_6H_5-$); 4.74, an ~1:4:6:4:1 pentet, $J_{AB} \simeq J_{BC} \simeq 6.4$ Hz (1 >$CH^CCH^B(CH_3^A)O-$);[43] 2.91, singlet (3 $-OS(O)_2CH_3$) superimposed on an ~1:4:6:4:1 pentet (?), $J_{CB} \simeq J_{CD} \simeq 6.6$ Hz, at 2.73 (1 $PhCH^C(CH_3^D)CH^B<$); 1.43, doublet, $J_{AB} \simeq 6.3$ Hz (3 >$CH^BCH_3^A$) superimposed on a doublet, $J_{DC} \simeq 6.9$ Hz, at 1.35 (3 >$CH^CCH_3^D$)[3a,45] (see Table VIII).

Anal. Calcd for $C_{14}H_{16}O_5SCr$: C, 46.15; H, 4.43; O, 26.35; S, 8.80. Found: C, 46.25; H, 4.57; O, 26.14; S, 8.62.

L-(+)-*threo*-**3-[π-(Phenyl)chromium tricarbonyl]-2-butyl methanesulfonate** (L-**1a-OMs**): $[\alpha]^{25}D$ +16.6° (*c* 2.92, ethanol).

D-(−)-*threo*-**3-[π-(Phenyl)chromium tricarbonyl]-2-butyl methanesulfonate** (D-**1a-OMs**): $[\alpha]^{25}_{546}$ −24.7° (*c* 2.23, chloroform).

Anal. Calcd for $C_{14}H_{16}O_6SCr$: C, 46.15; H, 4.43; O, 26.35; S, 8.80. Found: C, 46.34; H, 4.55; O, 26.09; S, 8.73.

DL-*erythro*-**3-[π-(Phenyl)chromium tricarbonyl]-2-butyl methanesulfonate** (DL-**2a-OMs**): ir ($HCCl_3$) 3030 (CH phenyl); 2980 and 2940 (CH aliphatic); 1980 and 1900 (C≡O); 1370, 1340, and 1170 ($-OSO_2-$); 910 (CO); 660, 630, and 532 cm^{-1} (CrC); nmr ($DCCl_3$) δ 5.35, singlet (5 $Cr(CO)_3C_6H_5-$); 4.86, an ~1:1:3:3:3:3:1:1:1 octet, $J_{BA} \simeq 6.7$ Hz, $J_{BC} \simeq 3.8$ Hz (1 >$CH^CCH^B(CH_3^A)O-$);[43] 2.89, singlet (3 $-OS(O)_2CH_3$) superimposed on an octet (?) at ~2.80 (1 $PhCH^C(CH_3^D)CH^B<$); 1.41, doublet, $J_{AB} \simeq 6.7$ Hz (3 >$CH^BCH_3^A$) superimposed on a doublet, $J_{DC} = 7.2$ Hz, at 1.38 (3 >$CH^CCH_3^D$); uv (C_2H_5OH) 213.5 (ε 21,900), 255 (ε 6300), and 319 mμ (ε 9100).[26,46]

Anal. Calcd for $C_{14}H_{16}O_6SCr$: C, 46.15; H, 4.43; O, 26.35; S, 8.80. Found: C, 46.07; H, 4.35; O, 26.14; S, 8.55.

DL-*erythro*-**2-[π-(Phenyl)chromium tricarbonyl]-3-pentyl methanesulfonate** (DL-**3a-OMs**): ir ($HCCl_3$) 3030 (CH phenyl); 2970 and 2940 (CH aliphatic); 1980 and 1900 (C≡O); 1370, 1340, and 1170 ($-OSO_2-$); 912 (CO); 660, 631, and 529 cm^{-1} (CrC); nmr ($DCCl_3$) δ 5.38, singlet (5 $Cr(CO)_3C_6H_5-$); 4.73, an ~1:1:3:3:1:1 sextet, $J_{BC} \simeq 6.8$ Hz, $J_{BA} \simeq 3.3$ Hz (1 >$CH^CCH^B(CH_2^A-)O-$);[43] 2.98, singlet (3 $-OS(O)_2CH_3$) superimposed on a broad complex multiplet at 3.15–2.70 (~1 $PhCH^C(CH_3^D)CH^B<$); 1.78, an ~1:1:3:3:3:3:3:1:1 (?) octet, $J_{AB} \simeq 1.5$ Hz, $J_{AE} \simeq 6.7$ Hz (~2 >$CH^BCH^AH^{A'}CH_3^E$); 1.41, doublet, $J_{DC} \simeq 7.1$ Hz (3 >$CH^CCH_3^D$); 1.14, slightly perturbed 1:3:1 triplet, $J_{EA} \simeq 7.5$ Hz (~3 $-CH^AH^{A'}CH_3^E$). (Apparently the nonequivalent hydrogens of the methylene group are sufficiently similar that the methyl-hydrogen resonances still resemble superficially those of a normal ethyl group.[43])

Anal. Calcd for $C_{12}H_{18}O_6SCr$: C, 47.62; H, 4.79; O, 26.37; S, 8.47. Found: C, 47.86; H, 4.85; O, 26.15; S, 8.21.

Preparation of DL-*erythro*-**3-[π-(Phenyl)chromium tricarbonyl]-2-butyl Acetate** (DL-**2a-OAc**). This and the following complexes were prepared by the method described previously. The yield in this case was 76%. This compound has the following properties: mp 64.5–65.5°; ir ($HCCl_3$) 3020 (CH phenyl); 2980 and 2940 (CH aliphatic); 1970 and 1850 (C≡O), 1720 (ester C=O); 1235 and 1016 (ester CO); 660, 630, and 530 cm^{-1} (CrC); nmr ($DCCl_3$) δ 5.39, singlet, (5 $Cr(CO)_3C_6H_5$) superimposed on an ~1:1:3:3:3:3:1:1:1 octet, $J_{BA} \simeq 6.3$ Hz, $J_{BC} \simeq 4.1$ Hz, at 5.09 (1 >$CH^CCH^B(CH_3^A)O-$);[43] 2.77, an ~1:1:3:3:3:3:3:1:1:1 octet, $J_{CB} \simeq 4.3$ Hz, $J_{CD} \simeq 7.0$ Hz (1 $PhCH^C(CH_3^D)CH^B<$); 2.12, singlet (3 $-OCOCH_3$); 1.36, doublet, $J_{DC} \simeq 7.0$ Hz (3 >$CH^DCH_3^C$); 1.27, doublet, $J_{AB} \simeq 6.4$ Hz (3 >$CH^BCH_3^A$).

Anal. Calcd for $C_{15}H_{16}O_5Cr$: C, 54.88; H, 4.91; O, 24.37. Found: C, 54.90; H, 4.91; O, 24.13.

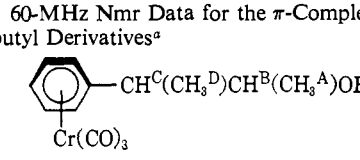
DL-*threo*-**3-[π-(Phenyl)chromium tricarbonyl]-2-butanol** (DL-**1a-OH**). The yield was 50%. This compound had the following properties: mp 82.8–83.8°; ir ($HCCl_3$) 3590 and 3440 (OH); 3020 (CH phenyl); 2970 and 2930 (CH aliphatic); 1960 and 1870 (C≡O); 1100 (CO); 660, 631, and 530 cm^{-1} (CrC); nmr ($DCCl_3$) δ 5.40, singlet (5 $Cr(CO)_3C_6H_5-$); 3.84, an ~1:4:6:4:1 pentet, $J_{BA} \simeq J_{BC} \simeq 6.0$ Hz (1 >$CH^CCH^B(CH_3^A)O-$);[43] 2.53, an ~1:4:6:4:1 pentet, $J_{CB} \simeq J_{CD} \simeq 6.6$ Hz (1 $PhCH^C(CH_3^D)CH^B<$); 1.73, a concentration-dependent singlet (1 $-OH$); 1.37, doublet, $J_{DC} \simeq 6.9$ Hz (3 >$CH^CCH_3^D$); 1.31, doublet, $J_{AB} \simeq 6.2$ Hz (3 >$CH^BCH_3^A$).

Anal. Calcd for $C_{13}H_{14}O_4Cr$: C, 54.56; H, 4.89. Found: C, 54.48; H, 4.65.

DL-*erythro*-**3-[π-(Phenyl)chromium tricarbonyl]-2-butanol** (DL-**2a-OH**). The yield was 32.4%. This compound exhibited the following properties: mp 51.2–52.5°; ir ($HCCl_3$) 3600 and 3440 (OH); 3030 (CH phenyl); 2970 and 2900 (CH aliphatic); 1950 and 1850 (C≡O); 1105 (CO); 658 and 632 cm^{-1} (CrC); nmr ($DCCl_3$) δ 5.40, broad singlet (5 $Cr(CO)_3C_6H_5-$); 4.03, an ~1:1:3:3:3:3:1:1:1 octet, $J_{BA} \simeq 7.0$ Hz, $J_{BC} \simeq 3.7$ Hz (1 >$CH^CCH^B(CH_3^A)O-$);[43] 2.62, an ~1:1:1:3:3:3:3:1:1:1 octet, $J_{CB} \simeq 3.8$ Hz, $J_{CD} \simeq 6.4$ Hz (1 $PhCH^C(CH_3^D)CH^B<$); 1.83, concentration dependent singlet (1 $-OH$); 1.32, doublet, $J_{AB} \simeq 7.0$ Hz (3 >$CH^BCH_3^A$); 1.28, doublet, $J_{DC} \simeq 6.3$ Hz (3 >$CH^CCH_3^D$).

Anal. Calcd for $C_{13}H_{14}O_4Cr$: C, 54.56; H, 4.89. Found: C, 54.54; H, 4.66.

Table VIII. 60-MHz Nmr Data for the π-Complexed 3-Phenyl-2-butyl Derivatives[a]



Compd[c]	J_{BC}, Hz[d]	Chemical shift,[b] δ (multiplicity) A	B	C	D
DL-**1a**-OH	~6.3	1.31 (2)	3.84 (5)	2.53 (5)	1.37 (2)
DL-**1a**-OMs	6.5	1.43 (2)	4.74 (5)	2.73 (5)	1.35 (2)
DL-**1a**-OAc	~6.3	1.28 (2)	4.97 (5)	2.71 (5)	1.35 (2)
DL-**2a**-OH	3.8	1.32 (2)	4.03 (8)	2.62 (8)	1.28 (2)
DL-**2a**-OMs	3.8	1.41 (2)	4.86 (8)	2.80 (8?)	1.38 (2)
DL-**2a**-OAc	4.2	1.27 (2)	5.09 (8)	2.77 (8)	1.36 (2)

[a] Data for noncomplexed alcohols is given in ref 32. [b] As 5–10% solutions in $CDCl_3$ at ambient probe temperature (30–35°). Solutions were filtered through charcoal to remove paramagnetic Cr(III) prior to analysis. [c] Refer to Chart I. [d] Mean for those listed under individual samples.

Kinetic Studies. Titrimetric acetolysis rates were determined in the usual manner on ~0.02 *M* solutions of the methanesulfonates in acetic acid buffered with sodium acetate and containing about 1% acetic anhydride.[10,47] In the presence of light and/or oxygen the complexed methanesulfonates are unstable under these conditions and their initially yellow solutions turn green long before the solvolysis is complete.[20] The extent of decomposition during acetolysis can be greatly reduced, though apparently not completely eliminated, *vide infra*, by conducting the reaction in the dark in deoxygenated acetic acid under a dry nitrogen atmosphere. Dry, oxygen-free (Fieser's solution[48]) nitrogen was passed for ~10 min through a hot (70–80°) solution of sodium acetate and acetic anhydride in acetic acid and the solution was allowed to cool to room temperature under the nitrogen atmosphere. For the kinetic runs, each ampoule was also deoxygenated in this manner at 25° before being sealed under dry oxygen-free nitrogen. Each was wrapped in aluminum foil to protect it from light during the kinetic determination. After control experiments had demonstrated that the acetolysis rates of the noncomplexed methanesulfonates were not significantly affected by the deoxygenation procedure, *cf.* runs 3 (oxygen-free) and 4, Table III, it was omitted in these cases. With the exception of DL-*erythro*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl methanesulfonate (DL-**2a-OMs**), the acetolysis of each of the 3-phenyl-2-butyl compounds is kinetically first order to greater than 65% reaction and exhibits a measured infinity titer at ten half-lives which is within 5% of the calculated value based on the starting methanesulfonate. In contrast, plots of ln [DL-**2a-OMs**] *vs.* time begin to deviate appreciably from linearity at about 50% reaction and after ten half-lives (based on the initial rate constants) only 85–92% of the theoretical amount of methanesulfonate has been liberated.[23]

Polarimetric acetolysis rates for the active methanesulfonates were determined as described previously.[10] Deoxygenated solvent was used in the case of the π-complexed derivative, D-(−)-**1a-OMs**. Rotations were measured by filling a thermostated (25°), 2-dm polarimeter tube with the contents of an ampoule which had been

(44) (a) R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960); (b) R. E. Humphrey, *Spectrochim. Acta*, **17**, 93 (1961).

(45) (a) D. A. Brown and J. R. Raju, *J. Chem. Soc., A*, 1617 (1966); (b) W. Strohmeier and H. Hellmann, *Chem. Ber.*, **97**, 1877 (1964).

(46) E. O. Fischer and H.-P. Fritz, *Angew. Chem.*, **73**, 353 (1961).

(47) R. S. Bly and R. T. Swindell, *J. Org. Chem.*, **30**, 10 (1965).

(48) L. F. Fieser, *J. Amer. Chem. Soc.*, **46**, 2639 (1924).

removed from a thermostated bath (±0.03°) after a measured period of time. The actual rotations determined in this manner ranged from about −0.660 to −0.002° for the D-(−)-**1**-OMs and from about −0.639 to 0.116° for D-(−)-**1a**-OMs throughout the individual rate runs.

The apparent first-order polarimetric (k_α) and/or titrimetric (k_t) acetolytic rate constants for the 3-phenyl-2-butyl methanesulfonates are summarized in Table III. Although we have made no attempt to determine them precisely, crude estimates of the titrimetric acetolysis constants of the noncomplexed and complexed *erythro*-2-phenyl-3-pentyl methanesulfonates (DL-**3**- and -**3a**-OMs, respectively) are included for purposes of comparison, *cf.* runs 52 and 53.

Acetolysis Products of DL-*erythro*-3-Phenyl-2-butyl Methanesulfonate (DL-2-OMs). The procedure described here for the isolation of products was used in all subsequent acetolysis runs on the noncomplexed methanesulfonates. **Run A.** To 10 ml of a solution of 0.0478 *M* sodium acetate in the anhydrous rate solvent was added 36.7 mg (0.168 mmol) of the methanesulfonate. The solution was heated at 85° for 12 hr (ten half-lives), cooled to room temperature, poured over about 50 ml of crushed ice, and extracted with three 50-ml portions of pentane. The combined pentane extract was washed twice with 50-ml portions of cold saturated sodium carbonate solution, twice with cold water, and dried over anhydrous magnesium sulfate. The dried pentane extract was then concentrated to about 25 ml by slow distillation through a 20-cm wire-spiral-packed column and treated with lithium aluminum hydride in the usual manner.[2a] Analysis by glpc on the 12-ft Carbowax column at 155° of the dried ethereal solution after reduction showed, in addition to the solvent, five components whose relative retention times (peak areas, %) were 3.2 (5.8), 4.1 (5.0), 5.8 (9.4), 21.0 (2.1), and 24.3 (77.7). In duplicate **run B** the same five components were observed. Relative areas were 5.9, 5.4, 9.5, 2.4, and 76.8%, respectively. This procedure was found to give better results than the direct glpc analysis of the acetates because the *threo*- and *erythro*-alcohols are well separated on a Carbowax column whereas the isomeric esters are not. Runs A and B were combined and the individual components were collected for spectral analysis.

The *first component* proved to be a mixture of two compounds which were separated by glpc on the silver nitrate column at 70°. Their relative peak areas on this column were 52.4 and 47.6%, respectively. The *first peak* had an infrared spectrum identical with that of authentic *trans*-2-phenyl-2-butene (**5**);[9d] the *second peak* with that of authentic 3-phenyl-1-butene (**4**).[9d]

The *second, third, fourth,* and *fifth components* were identified as 2-phenyl-1-butene (**6**), *cis*-2-phenyl-2-butene (**7**), DL-*threo*-3-phenyl-2-butanol (DL-**1**-OH), and *erythro*-3-phenyl-2-butanol (DL-**2**-OH), respectively, by comparison of the infrared spectra of collected samples with those of authentic compounds.[9c,d]

Acetolysis Products of DL-*threo*-3-Phenyl-2-butyl Methanesulfonate (DL-1-OMs). Run C. To a solution of 0.0468 *M* sodium acetate in 10 ml of rate solvent was added 45.8 mg (0.203 mmol) of DL-**1**-OMs. The solution was heated at 85° for 12 hr (ten half-lives), cooled to room temperature, and the products were isolated as in run A. Analysis by glpc on the 12-ft Carbowax column at 155° revealed the presence of five components whose relative retention times were identical with those reported for the acetolysis products of DL-**2**-OMs. The relative peak areas were 10.2, 9.0, 17.8, 61.1, and 1.9%, respectively. In a duplicate **run D** the relative areas were 10.5, 8.8, 15.2, 63.5, and 1.9%. Runs C and D were combined and the components were collected for spectral examination.

The *first component* when analyzed on the 300-ft Ucon-coated capillary column at 90° was separated into two compounds whose relative retention times and peak (areas) were 17 (35.7%) and 18 (64.3%), respectively. The *first peak* had a retention time under these conditions identical with that of authentic *trans*-2-phenyl-2-butene (**5**), and the *second peak* with that of authentic 3-phenyl-1-butene (**4**).

Other components were identified as **6**, **7**, DL-**1**-OH, and DL-**2**-OH, respectively, by comparison of their relative glpc retention times on the 16-ft Carbowax column and the infrared spectra of collected samples with those of the authentic compounds.

Acetolysis Products of DL-*erythro*-2-Phenyl-3-pentyl Methanesulfonate (DL-3-OMs). Run E. To a solution of 0.0478 *M* sodium acetate in 250 ml of anhydrous acetic acid was added 2.416 g (9.970 mmol) of the methanesulfonate. The solution was heated at 85° for 285 min (ten half-lives), cooled to 25°, and the products were isolated as described in run A. Analysis on the 16-ft Carbowax column at 155° showed nine components present in addition to the solvent. Their relative retention times (peak areas, %) were 3.8 (1.9), 4.2 (1.3), 4.8 (19.7), 5.6 (1.5), 6.2 (1.1), 7.4 (1.7), 2.43 (trace), 28.2 (38.9), and 29.2 (34.1). In duplicate **run F** the relative peak areas were 1.8, 1.2, 20.1, 1.3, 0.9, 1.7, trace, 39.4, and 33.5%, respectively. The components were collected for spectral analysis from the 16-ft Carbowax column at 120°. The last three components were re-collected from the 16-ft diisododecyl phthalate column at 155°.

The *first component* is thought to be a mixture of ~43% *trans*-2-phenyl-2-pentene (**8**) and ~57% *cis*-3-phenyl-2-pentene (**9**); nmr (CCl_4) δ 7.02, singlet (5 C_6H_5–); ~5.29, complex multiplet (0.43 =C*H*CH_2– + 0.57 =C*H*CH_3); 2.4–1.8, complex multiplet (0.86 =CH$C_2H_2CH_3$ + 1.14 =C(—)CH_2CH_3 + 1.3 =C(—)CH_3); 1.50, doublet, $J \simeq 6.5$ Hz (1.7 =CHCH_3); 0.92, slightly perturbed 1:2:1 triplet, $J \simeq 6.5$ Hz (1.3 = $CHCH_2CH_3$ + 1.7 =C(—)CH_2CH_3). These two olefins could not be separated by glpc on the silver nitrate impregnated column.

The *second component* exhibited the following spectra: ir (CCl_4) 3080, 3060, and 3030 (CH phenyl and vinyl); 2970, 2930, and 2870 (CH aliphatic); 1650 (vinyl); 1610 and 1590 (phenyl nucleus); 1460 and 1380 (CC aliphatic); 990 and 912 (vinyl); and 699 cm^{-1} (monosubstituted phenyl); nmr (CCl_4) δ 7.01, singlet (5 C_6H_5–); ~6.0–5.5, complex multiplet (~1 >CHC*H*=CHH); 5.1–4.6, complex multiplet (2 –CH=C*HH*); 3.27–2.87, complex multiplet (~1 PhC*H*(CH_2—)CH=); 2.09–1.38, complex multiplet (2 >CH-CH_2CH_3); 0.83, distorted 1:2:1 triplet, $J \simeq 6.8$ Hz (3 –CH_2CH_3). This component is believed to be 3-phenyl-1-pentane (**10**).

The *third component* has the following spectral properties: ir (CCl_4) 3080, 3060, and 3030 (CH phenyl and olefinic); 2970, 2930, and 2920 (CH aliphatic); 1610 and 1590 (phenyl nucleus); 1460 and 1380 (CC aliphatic); 970 and 960 (*trans* CH=CH); 718 and 698 cm^{-1} (monosubstituted phenyl); nmr (CCl_4) δ 7.02, singlet (5 C_6H_5–); 5.53–5.27, complex multiplet (2 –CH_2CH=C*H*CH_3); 3.46–2.98, complex multiplet (1 PhC*H*(CH_2—)CH=); 1.62, finely split doublet, J = 4.4 Hz (3 CH_3CH=CH–); and 1.28, doublet, J = 6.1 Hz (3 >CHCH_3).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.33; H, 9.70.

This compound is *trans*-4-phenyl-2-pentene (**11**).

The *fourth component* has the following spectral properties: ir (CCl_4) 3080, 3060, and 3030 (CH phenyl and olefinic); 2960, 2930, and 2880 (CH aliphatic); 1645 (C=C olefinic); 895 (terminal methylene); and 703 cm^{-1} (monosubstituted phenyl); nmr (CCl_4) δ 7.12, perturbed singlet (5 C_6H_5–); 5.09, slightly perturbed singlet (1 PhC(–)=C*H*H); 4.88, slightly perturbed singlet (1 PhC(—)=CH*H*); 2.40, slightly distorted and perturbed triplet, $J \simeq 7.3$ Hz (2 =C(—)CH_2CH_2–); 1.68–1.08, complex multiplet (2 –$CH_2CH_2CH_3$); 0.88, distorted triplet, $J \simeq 6.4$ Hz (3 –CH_2CH_3). This component is believed to be 2-phenyl-1-pentene (**12**).

The *fifth component* has an infrared spectrum identical with that of 3-phenyl-*trans*-2-pentene (**13**):[49a] nmr (CCl_4) δ 7.07, singlet (5 C_6H_5–); 5.53, a 1:3:3:1 quartet, J = 7.0 Hz (1 >CH=CHCH_3); 2.46, a 1:3:3:1 quartet, J = 7.5 Hz (2 =C(—)CH_2CH_3); 1.74, doublet, J = 7.0 Hz (3 =CHCH_3), and 0.96, a 1:2:1 triplet, J = 7.5 Hz (3 –CH_2CH_3).

The *sixth component* has an infrared spectrum identical with that of authentic 2-phenyl-*cis*-2-pentene (**14**):[49b] nmr (CCl_4) δ 7.07, singlet (5 C_6H_5–); 5.58, perturbed 1:2:1 triplet, $J \simeq 6.2$ Hz (1 >C=C*H*CH_2–), 2.10, a 1:3:3:1 quartet, J = 7.4 Hz (2 =C(—)CH_2CH_3) superimposed on a singlet at 1.95 (3 =C(—)CH_3); 1.04, a 1:2:1 triplet, J = 7.2 Hz (3 –CH_2CH_3).

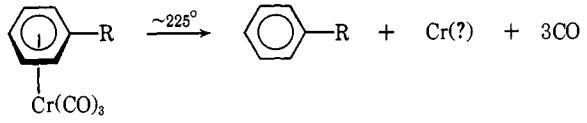
The *seventh component* has a glpc retention time on the 16-ft Carbowax column identical with that of the *threo*-pentanols, DL-**15**-OH and DL-**16**-OH.

The *eighth component* has an infrared spectrum identical with that of authentic *erythro*-3-phenyl-2-pentanol (DL-**17**-OH):[9e] nmr (CCl_4) δ 7.03, singlet (5 C_6H_5–); 3.72, an ~1:4:6:4:1 pentet, $J_{BA} \simeq J_{BC} \simeq 6.6$ Hz (1 >CH^C(CH^B(CH_3^A)O–);[43] 2.52–2.00, complex multiplet (1 PhC*H*^{C}(CH_2^D—)CH^E<) superimposed on a concentration-dependent singlet at 2.25 (1 –O*H*); 2.04–1.46, complex multiplet (~2 >CH^CC*H*^{D}*H*$^{D'}$$CH_3^E$); 0.95, doublet, $J_{AB} \simeq 6.4$ Hz (3 –CH^A(CH_3^B)O–) superimposed on an asymmetric triplet, $J_{ED} \simeq 6.5$ Hz, at 0.75 (~3 –CH^DH$^{D'}$$CH_3^E$). (Apparently the nonequivalent methylene hydrogens of the ethyl group are sufficiently similar that the resonance of the methyl hydrogens (E) still superficially resembles that of a normal ethyl group.[43])

(49) Sadtler Standard Spectra, Sadtler Research Laboratories, Philadelphia, Pa.: (a) Infrared No. 1615; (b) No. 1620.

The *ninth component* has an infrared spectrum identical with that of authentic DL-*erythro*-2-phenyl-3-pentanol (DL-**3**-OH);[9e] nmr (CCl_4) δ 7.03, slightly perturbed singlet (5 C_6H_5–); 3.42, broad ~1:1:2:2:1:1 sextet, $J_{BA} \simeq 4.9$ Hz, $J_{BC} \simeq 6.7$ Hz (1 >CH^C-$CH^B(CH^AH^{A'}$–)O–);[43] 2.63, an ~1:4:6:4:1 pentet, $J_{CB} \simeq J_{CD} \simeq 6.8$ Hz (1 Ph$CH^C(CH_3^D)CH^B$<) superimposed on a concentration-dependent singlet at 2.47 (1 –O*H*); 1.6–0.7, complex multiplet (5 >$CH^BCH^AH^{A'}CH_3^E$) superimposed on a doublet, $J_{DC} \simeq 6.7$ at 1.26 (3 >$CH^CCH_3^D$). (Apparently the methylene hydrogens A and A′ are sufficiently nonequivalent that the resonance of the ethyl hydrogens can no longer be analyzed in a simple manner.[50]).

Acetolysis Products of the Chromium Tricarbonyl Complexed Methanesulfonates. Products from the acetolysis of the π-complexed methanesulfonates were determined by the use of the two complimentary procedures. The structures of the organic moieties could be established by direct glpc analysis of the acetic acid free, dried pentane–ether extracts from each acetolysis mixture, since control experiments had demonstrated that the π-complexed olefins and acetates which are produced could be decomposed to unrearranged arene, chromium (?), and carbon monoxide in the heated (225°) injection port of a gas chromatograph,[21] *viz.*



However, it was found that more reproducible results could be obtained by oxidatively decomplexing then reducing the π-complexed products prior to glpc. Accordingly, the procedure described below was used in all subsequent acetolysis runs on the π-complexed methanesulfonates. Control experiments established that this procedure does not isomerize the organic portion of a π-complexed olefin or acetate.

Acetolysis Products of DL-*erythro*-3-[π-(Phenyl)chromium tricarbonyl]-2-butyl Methanesulfonate (DL-2a-OMs). Run G. To a solution of 0.0468 *M* sodium acetate in 8 ml of dry oxygen-free acetic acid was added 59.1 mg (0.205 mmol) of the π-complexed methanesulfonate. The solution was heated under anhydrous deoxygenated nitrogen in the dark at 85° for ten half-lives (12.0 hr), cooled to room temperature, poured over about 50 ml of crushed ice, and extracted with three 50-ml portions of 1:1 pentane–ether. The yellow extract was washed with two 25-ml portions of cold saturated sodium carbonate solution, two 50-ml portions of cold water, and transferred to a 300-ml erlenmeyer flask. To the rapidly stirred solution was slowly added 10 ml of freshly prepared ceric ammonium nitrate in acetone. The mixture was stirred at room temperature until no yellow color remained in the pentane–ether layer (about 10 min). The pentane–ether layer was then poured over ice and washed with four 75-ml portions of cold water. The decomplexed reaction products were isolated as described previously in run A. Analysis by glpc on the 16-ft Carbowax column at 155° revealed the presence of six components whose relative retention time (peak areas; %) were 4.6 (24.1), 5.4 (1.7), 7.9 (4.8), 28.0 (1.7), 30.0 (1.8), 35.6 (65.9), respectively. In duplicate **run H** the relative peak areas were 19.7, 1.9, 4.8, 0.8, 1.9, and 70.8%, respectively. Runs G and H were combined, and the components were collected for spectral identification.

The *first component* was subjected to glpc analysis on the 8-ft silver nitrate column at 75°. Two peaks were observed. The first compound had a relative retention time of 13.8—identical with that of authentic *trans*-2-phenyl-2-butene (**5**)—and a relative peak area of 4.4%. The second material, which had a relative retention time of 17.4 and a relative peak area of 95.6%, was collected. It had an infrared spectrum identical with that of authentic 3-phenyl-1-butene (**6**).

The *second, third, fifth,* and *sixth components* were collected and identified as **6**, **7**, DL-**1**-OH, and DL-**2**-OH, respectively, by comparison of their infrared spectra with those of the authentic compounds.

The *fourth component* was tentatively identified as 2-phenyl-2-butanol (DL-**18**-OH) by comparison of its glpc retention time with that of an authentic sample on the 16-ft Carbowax column.

Acetolysis Products of DL-*threo*-3-[π-(Phenyl)chromium tricarbonyl]-2-butyl Methanesulfonate (DL-1a-OMs). Run I. To a solution of 0.0468 *M* sodium acetate in 8 ml of deoxygenated anhydrous acetic acid was added 58.0 mg (0.199 mmol) of the methanesulfonate. The solution was heated under dry oxygen-free nitrogen in the dark for ten half-lives (49.4 hr) at 85°. The reaction products were isolated as described in run G. Analysis by glpc on the 16-ft Carbowax column at 155° showed the presence of six components whose relative retention times were identical with those of the products obtained in the acetolysis of the *erythro* π complex, DL-**2a**-OMs. Relative peak areas were 4.1, 0.4, 0.9, trace, 94.3, and 0.4%, respectively. In duplicate **run J** the relative peak areas were 3.8, 0.4, 0.7, trace, 94.9, and 0.3%. The *first, second, third, fourth, fifth,* and *sixth components* were identified as **4** (3.5%) and **5** (0.3%), **6**, **7**, DL-**18**-OH, DL-**1**-OH, and DL-**2**-OH, respectively, by comparison of their relative glpc retention times with those of the authentic compounds. The *first* and *fifth components* were collected and identified as 3-phenyl-1-butene (**4**) and DL-**1**-OH by comparison of their infrared spectra with those of the authentic samples.

Acetolysis Products of L-(—)-*threo*-3-[π-(Phenyl)chromium tricarbonyl]-2-butyl Methanesulfonate (L-1a-OMs). Run K. To a solution of 0.0468 *M* sodium acetate in 25 ml of deoxygenated anhydrous rate solvent was added 182 mg (0.499 mmol) of the methanesulfonate. The solution was protected from light and heated under nitrogen at 85° for ten half-lives (12.0 hr). The reaction products were isolated as described in run G. The isolated *threo* alcohol had the following rotation: $[\alpha]^{25}D$ +17.3° (*c* 1.61, ethanol); in duplicate **run L**: $[\alpha]^{25}D$ +16.7° (*c* 2.09, ethanol).

Acetolysis Products of DL-*erythro*-2-[π-(Phenyl)chromium tricarbonyl]-3-pentyl Methanesulfonate (DL-3a-OMs). run M. To a 5-ml solution of 0.0468 *M* sodium acetate in deoxygenated acetic acid was added 0.0462 g (0.122 mmol) of the methanesulfonate. The solution was sealed in an ampoule under nitrogen and heated at 85° for 14 hr in the dark. Acetolysis products were isolated as described in run G. Analysis by glpc on the 16-ft diisododecyl phthalate column revealed the presence of four components whose relative retention times were the same as those of authentic **11**, DL-**15**-OH and DL-**16**-OH, DL-**17**-OH, and DL-**3**-OH. Peak areas were 72.9, 1.1, 2.1, and 23.9%, respectively. In duplicate **run N** the relative peak areas were 75.9, 0.9, 1.1, and 22.1%. Products from the two runs were combined and collected for spectral identification. The *first* and *fourth components* were identified as **11** and DL-**3**-OH, respectively, by comparison of their infrared spectra with those of the authentic samples. The *second component* was identified as a mixture of DL-**15**-OH and/or DL-**16**-OH, and the *third* as DL-**17**-OH by comparison of their relative glpc retention times on the 16-ft Carbowax column with those of the known compounds.

π-Complexed Products from the Acetolysis of DL-*erythro*-3-[π-(Phenyl)chromium tricarbonyl]-2-butyl Methanesulfonate (DL-2a-OMs). Run O. To 100 ml of a solution of 0.0468 *M* sodium acetate in deoxygenated, anhydrous acetic acid was added 0.719 g (1.97 mmol) of the methanesulfonate. The solution was heated under oxygen-free nitrogen in the dark for ten half-lives (53 hr) at 85°. The reaction mixture was poured over about 200 ml of crushed ice and extracted three times with 75-ml portions of 1:1 pentane–ether. The extracts were combined and washed twice with 50-ml portions of cold saturated sodium carbonate solution, twice with cold water, and dried over anhydrous magnesium sulfate. The volume of the dry pentane extract was reduced to about 5 ml of slow distillation at atmospheric pressure through a 20-cm wire spiral packed column. Chromatographic analysis over neutral alumina (Woelm, activity grade I) revealed the presence of two bands. The first was eluted with 1:9 ether–pentane, the second with 1:1 ether–pentane. Each component was collected and the solvent evaporated under reduced pressure.

The *first component* was a yellow oil. Analysis by nmr showed that this oil was mostly 3-[π-(phenyl)chromium tricarbonyl]-1-butene (**4a**): nmr (CCl_4) δ 5.80–4.70, complex multiplet (~3 >$CHCH$=CHH) superimposed on a singlet at 5.10 (~5 Cr-$(CO)_3C_6H_5$–); 3.10, complex multiplet (~1 Ph$CH(CH_3)CH$=); 1.32, doublet, J = 6.7 Hz (~3 >$CHCH_3$). A yield of 85 mg (16%) was obtained.

The *second component* was a yellow solid (mp 64.5–66.5°). The infrared and nmr spectra were identical with those of authentic DL-*erythro*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl acetate (DL-**2a**-OAc). The yield was 0.283 g (43.8%).

When a pure sample of DL-*erythro*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl acetate (DL-**2a**-OAc) was chromatographed in a similar fashion, a green band—presumably Cr_2O_3—developed at the top of the alumina column (as it in fact did in all cases), and only 42% of the acetate could be recovered as the complex. It could also be demonstrated that the extent of decomplexation which occurred

(50) *Cf.* K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, pp 21–27.

was roughly proportional to the length of time required to elute the complex from the column. Since no isomeric π-complexed olefins or acetates could be detected, it is evident that the organic portion of the complex is not isomerized under these conditions.

π-Complexed Products from the Acetolysis of DL-*threo*-3-[π-(Phenyl)chromium tricarbonyl]-2-butyl Methanesulfonate (DL-1a-OMs). Run P. To a solution of 0.0478 *M* sodium acetate in 50 ml of deoxygenated, anhydrous acetic acid was added 0.365 g (1.00 mmol) of the methanesulfonate. The solution was heated under oxygen-free nitrogen in the dark at 85° for 12 hr (ten half-lives), and the reaction products were isolated as described in run O.

The *first component*, a yellow oil, was present in such a small amount that it was not collected, but since it was eluted with 1:9 ether–pentane, it is suspected to be a mixture of π-complexed olefins.

The *second component* was a yellow solid which was identified as (DL-1a-OAc) by comparison with an authentic sample: mp 72.5–73.5°; ir ($HCCl_3$) 3030 (CH phenyl); 2980 (CH aliphatic); 1970 and 1910 (C≡O); 1737 (ester C=O); 1380 (CC aliphatic); 1244 and 1074 (ester CO); 663, 635, and 538 cm^{-1} (CrC); nmr ($DCCl_3$) δ 5.36, singlet (5 $Cr(CO)_3C_6H_5$–); 4.97, an ~1:4:6:4:1 pentet, $J_{BA} \simeq J_{BC} \simeq 6.4$ Hz (1 >CH^{C}CH^B(CH_3^A)O–);[43] 2.71, an ~1:4:6:4:1 pentet, $J_{CB} \simeq J_{CD} \simeq 6.8$ Hz (1 PhCH^C(CH_3^D)CH<); 2.08, singlet (3 –OCOCH_3); 1.35, doublet, $J_{DC} \simeq 7.3$ Hz (3 >CH^{C}CH_3^D) superimposed on a doublet, $J_{AB} \simeq 6.1$ Hz, at 1.28 (3 >CH^{B}CH_3^A). The yield of recovered material was 200 mg (59%).

Anal. Calcd for $C_{15}H_{16}O_5Cr$: C, 54.88; H, 4.91; O, 24.37. Found: C, 54.73; H, 5.10; O, 23.14.

π-Complexed Products from the Acetolysis of DL-*erythro*-2-[π-(Phenyl)chromium tricarbonyl]-3-pentyl Methanesulfonate (DL-3a-OMs). Run Q. To a solution of 0.0468 *M* sodium acetate in 75 ml of anhydrous oxygen-free acetic acid was added 1.143 g (3.020 mmol) of the methanesulfonate. The sample was allowed to react under anhydrous deoxygenated nitrogen for ten half-lives at 85°, and the products were isolated as described in run O. Two bands were observed. Each was collected, and the solvent was removed by distillation under vacuum at room temperature.

The *first component* was a yellow oil (0.605 g, 71.3%) which was identified from spectral data as *trans*-4-[π-(phenyl)chromium tricarbonyl]-2-pentene (**11a**): ir (CCl_4) 3030 (CH phenyl); 2960, 2940, and 2910 (CH aliphatic); 1980 and 1910 (C≡O); 1460 and 1380 (CC aliphatic); 965 (*trans* CH=CH); 660, 630, and 530 cm^{-1} (CrC); nmr (CCl_4) δ 5.54–5.27, complex multiplet (2 >CHCH=CHCH_3) superimposed on a singlet at 5.13 (5 $Cr(CO)_3C_6H_5$–); 3.12–2.78, broad complex multiplet (1 PhCH(CH_3)CH=CH–); 1.71, broad perturbed doublet, $J \approx 3.4$ Hz (3 –CH=CHCH_3); 1.31, doublet, $J \approx 6.9$ Hz (3 >CHCH_3).

Anal. Calcd for $C_{14}H_{14}O_3Cr$: C, 59.55; H, 5.00; O, 17.00. Found: C, 59.77; H, 5.23; O, 17.20.

The *second component* was a yellow solid which had the following properties: mp 66.5–67.5°; ir (CCl_4) 3020 (CH phenyl); 2970, 2940, and 2880 (CH aliphatic); 1970 and 1900 (C≡O); 1740 (ester C=O); 1470 and 1380 (CC aliphatic); 1240 (ester CO); 663, 634, and 537 cm^{-1} (CrC); nmr ($DCCl_3$) δ 5.33, singlet (5 $Cr(CO)_3C_6H_5$–) superimposed on a complex multiplet at ~5.3–4.7 (~1 >CHCH(CH_2–)O–); 2.96–2.54, complex multiplet (~1 PhCH(CH_3)CH<); 2.11, singlet (3 –OCOCH_3); 1.85–1.4, complex multiplet (~2 >CHCHHCH_3); 1.38, doublet, $J \approx 7.3$ Hz (~3 >CHCH_3); 1.00, asymmetric, perturbed triplet, $J \approx 7.0$ Hz (~3 –CHHCH_3).

Anal. Calcd for $C_{16}H_{18}O_5Cr$: C, 56.14; H, 5.30; O, 23.37. Found: C, 56.09; H, 5.59; O, 22.61.

The yield was 121.9 mg (11.8%) of DL-3a-OAc.

Although our analytical procedures are not sufficiently sensitive to have revealed their presence in the reaction mixture, it is likely that the complexed counterparts of most, if not all, of the uncomplexed products shown in Charts IV and V are actually formed as initial products in the acetolysis of the π-complexed methanesulfonates DL-1a-, -2a-, and -3a-OMs, respectively. The relatively low yields of π-complexed products isolated from the acetolyses of these π-complexed methanesulfonates apparently result from decomplexation during the alumina chromatography.

Stability of Acetolysis Products of DL-*threo*-3-Phenyl-2-butyl Methanesulfonate (DL-1-OMs) to Decomplexation and Isolation Procedures. Reaction products from run D were isolated by the procedure described for run G. Analysis by glpc showed no change in product composition compared to that found in run C.

Stability of Uncomplexed Reaction Products to Vapor Phase Chromatographic Analysis. A pure sample of each of the uncomplexed products, dissolved in carbon tetrachloride, was injected into the glpc under normal operating conditions. Only one peak was observed in each case whose relative retention time was identical with that of the authentic compound.

Stability of DL-*erythro*-3-[π-(Phenyl)chromium tricarbonyl]-2-butyl Acetate (DL-2a-OAc) to Acetolysis Conditions. Run R. To a 5 ml solution of anhydrous deoxygenated acetic acid containing 0.0468 *M* sodium acetate was added 65.8 mg (0.194 mmol) of the acetate. The solution was heated in the dark under dry, oxygen-free nitrogen for 53 hr at 85°. Reaction products were isolated as described in run G. Analysis by glpc on the 16-ft Carbowax column at 155° revealed the presence of only one peak whose relative retention time was identical with that of DL-*erythro*-3-phenyl-2-butanol (DL-2-OH). Identical results were obtained in duplicate run S. This experiment suggests that each of the π-complexed acetates is stable under the acetolysis conditions.

Stability of π-Complexed Olefins to Acetolysis Conditions. Run T. To a solution of 0.0468 *M* sodium acetate in 75 ml of dry, oxygen-free acetic acid was added 0.0789 g (0.217 mmol) of DL-*erythro*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl methanesulfonate (DL-2a-OMs). The sample was heated at 87° for 42 hr (ten half-lives), and the products were isolated as described in run O. The solvent from the first eluted component (π-complexed olefins) was evaporated under reduced pressure at room temperature. The resulting yellow oil was pumped at 0.5 mm for 2 hr, and then redissolved in 5 ml of the acetolysis solvent, *vide supra*. The sample was sealed under nitrogen and heated at 87° for 44 hr, cooled, extracted with pentane, washed with cold sodium carbonate solution and cold water, and dried. Decomplexation was accomplished as described in run G. Analysis by glpc on the 16-ft Carbowax column at 155° revealed the presence of three components whose relative retention times were the same as **4** and **5**, **6**, and 7. The relative peak areas were similar to those observed when in run G, *i.e.*, 82.6, 4.1, and 13.3%, respectively. This experiment suggests that the π-complexed olefins are also stable under the reaction conditions.

π-Complexed Acetate from the Acetolysis of L-(+)-*threo*-3-[π-(Phenyl)chromium tricarbonyl]-2-butyl Methanesulfonate (L-1a-OMs). Run U. To a solution of 0.0468 *M* sodium acetate in 50 ml of deoxygenated, dry acetic acid was added 0.344 g (0.946 mmol) of the methanesulfonate. The sample was sealed under oxygen-free dry nitrogen and solvolyzed at 87° for 12 hr in the dark. The sample was allowed to cool and then poured over 200 ml of ice. The acetolysis products were extracted into 1:1 pentane–ether. The organic layer was washed with excess sodium carbonate solution and water and was then removed over anhydrous magnesium sulfate. The solution was filtered and concentrated to about 20 ml by slow distillation of the solvent at atmospheric pressure. Pentane was added to the boiling solution until crystallization occurred. The crystals were collected and dried under vacuum (0.5 mm). The yield was 0.193 g (62.3%). The acetate was then decomplexed, reduced, and the alcohol was collected from the 16-ft Carbowax column at 155°; $[\alpha]^{25}D$ +19.30° (*c* 2.41, ethanol). No attempt was made to isolate any other π-complexed products from this acetolysis mixture, though presumably it also contains 3-[π-(phenyl)chromium tricarbonyl]-1-butene (**4a**) and *erythro*-3-[π-(phenyl)chromium tricarbonyl]-2-butyl acetate (**2a**-OAc) which should both be optically active.

Attempted Chromium Tricarbonyl Exchange between 2-[π-(Phenyl)-chromium tricarbonyl]propane and Anisole. Run V. To a 50-ml solution of 0.0486 *M* sodium acetate in anhydrous deoxygenated acetic acid was added 0.216 g (2.00 mmol) of anisole and 0.510 g (1.99 mmol) of 2-[π-(phenyl)chromium tricarbonyl]propane. The solution was sealed in an ampoule under dry, oxygen-free nitrogen, protected from light, and heated at 87.45° for 36 hr. The ampoule was removed from the rate bath, allowed to cool, cleaned, and opened. Its contents were poured over about 250 g of ice. This solution was then extracted with three 75-ml portions of a 1:1 pentane–ether mixture. The combined extract was washed twice with excess cold saturated sodium carbonate solution and twice with two 100-ml portions of cold water. The yellow solution was dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated to about 20 ml by slow distillation of the solvent at atmospheric pressure. Thin layer chromatographic analysis on silica gel (Mallinckrodt SilicAR TLC-7GF) using a 1:10 ether–pentane eluent revealed the presence of two components whose R_f factors were identical with those of anisole and/or cumene, and of the π-complexed cumene. No π-complexed anisole, which had an R_f factor of approximately one-half that of the π-complexed cumene, could be detected.

The inference here is that none of the π-complexed products

formed during the acetolyses of DL-**1a**-, **2a**-, or **3a**-OMs arise from ligand interchange during the solvolysis.

Rate of Decomplexation of DL-*erythro*-3-[π-(Phenyl)chromium tricarbonyl]-2-butyl Acetate (DL-2a-OAc). Run W. A 0.165-g (0.500 mmol) sample of the complex was dissolved in 25 ml of a 0.0486 *M* solution of sodium acetate in dry, oxygen-free acetic acid. Four-milliliter aliquots of the resulting solution were pipetted into six ampoules which were sealed under nitrogen, protected from light, and placed in a 86.83 ± 0.03° bath. Tubes were removed at predetermined times, cooled in ice to quench the reaction, cleaned, and cracked, and the contents transferred to a quartz cell. The ultraviolet spectrum was measured at 316 mμ and an approximate first-order rate constant for the disappearance of this band was calculated in the usual manner to be 3.43×10^{7} sec^{-1}. The magnitude of the 592-mμ band in the visible spectrum for the formation of Cr(III) remained approximately constant after 10% reaction. The rate of formation of Cr(III) during the first 10% reaction approximately equaled the rate of disappearance of the 316-mμ band.

Kinetic Treatment. Decomplexation accompanies the acetolysis of π-complexed β-arylalkyl methanesulfonates. The fraction of the total acetolysis products after ten half-lives which are decomplexed may be calculated in the following manner.

Assume

$$\begin{array}{ccc} A & \xrightarrow{k_1} & B + MsO^- \\ \downarrow{\scriptstyle k_2} & & \downarrow{\scriptstyle k_4} \\ C & \xrightarrow{k_3} & D + MsO^- \\ + & & + \\ Cr(III) & & Cr(III) \end{array}$$

where A = DL-**1a**- or **2a**-OMs, B = π-complexed olefins and acetates, C = DL-**1**- or **2**-OMs (*i.e.*, decomplexed starting material), and D = decomplexed olefins and acetates. This scheme may be described mathematically by eq i–iii, *viz.*

$$d[A]/dt = -(k_1 + k_2)[A] \quad \text{(i)}$$

$$d[B]/dt = k_1[A] - k_4[B] \quad \text{(ii)}$$

$$d[C]/dt = k_2[A] - k_3[C] \quad \text{(iii)}$$

which integrate to eq iv–vi when $t = 0$, $[A] = [A]_0$, $[B] = [C] = [D] = 0$, *viz.*

$$[A] = [A]_0 \exp(-k_1 t - k_2 t) \quad \text{(iv)}$$

$$[B] = \{k_1[A]_0/(k_1 + k_2 - k_4)\}\,[\exp(-k_4 t) - \exp(-k_1 t - k_2 t)] \quad \text{(v)}$$

$$[C] = \{k_2[A]_0/(k_1 + k_2 - k_3)\}\,[\exp(-k_3 t) - \exp(-k_1 t - k_2 t)] \quad \text{(vi)}$$

If it is assumed that $k_2 \simeq k_4$, *i.e.*, that the rate of decomplexation is not affected by changes in the structure remote from the aromatic ring, then (v) can be simplified to

$$[B] = [A]_0\,[\exp(-k_2 t) - \exp(-k_1 t - k_2 t)] \quad \text{(vii)}$$

From the stoichiometry and initial conditions it follows that

$$[D] = [A]_0 - [A] - [B] - [C] \quad \text{(viii)}$$

For the acetolysis of DL-**1a**-OMs at 87°: $k_1 = 1.95 \times 10^{-4}$ sec^{-1} (from titrimetric data on DL-**1a**-OMs), $k_2 = 3.4 \times 10^{-7}$ sec^{-1} (from uv data on DL-**2a**-OAc), $k_3 = 1.94 \times 10^{-4}$ sec^{-1} (from titrimetric data on DL-**1**-OMs), and $10t_{1/2} = 6.93/k_1 = 3.55 \times 10^{4}$ sec. Substituting these values into eq iv and vi–viii, it may be calculated that after ten half-lives the concentrations of A–D in the acetolysis mixture are: $[A] = 0.00088[A]_0$, $[B] = 0.987[A]_0$; $[C] \simeq 0$, and $[D] = 0.012\,[A]_0$. In other words about 1.2% of the total products have been decomplexed during the reaction and about $(3.4 \times 10^{-7})/(2.0 \times 10^{-4})$ or 0.2% of the total methanesulfonate anion produced is formed from decomplexed starting material.

A similar calculation in the case of the acetolysis of DL-**2a**-OMs at 87°, where $k_1 = 4.76 \times 10^{-5}$ sec^{-1}, $k_2 = 3.4 \times 10^{-7}$ sec^{-1}, $k_3 = 2.35 \times 10^{-4}$ sec^{-1}, and $10t_{1/2} = 1.60 \times 10^{5}$ sec, reveals that after ten half-lives $[A] = 0.00047[A]_0$, $[B] = 0.947[A]_0$, $[C] \simeq 0$, and $[D] = 0.053[A]_0$ or that 5.3% of the total products are decomplexed and that about 0.7% of the total methanesulfonate anion arises from the solvolysis of previously decomplexed material.

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