Table I. Formation[a] of Mesylate Esters with "Easy Mesyl"[7] (6d)

Alcohol	% conversion of alcohol With 1.2 equiv of 6d	With 2.0 equiv of 6d
Ethanol[b]	64	98
Cyclohexanol	83	98
Menthol	100	*c*
1-Octanol	82	100
Borneol	89[d,e]	*c*
5α-Cholestan-3β-ol	100	*c*
5α-Cholestan-3α-ol	~80	84[f]
Phenol	100	*c*
Allyl alcohol	75	92
Benzyl alcohol	85	100

[a] For reaction conditions, see text. [b] In the absence of base there is only very slow reaction. [c] Not tried. [d] Bornyl "mesylmesylate" (11%) also formed; see text. [e] With 1.5 equiv 6d used. [f] The "mesylmesylate" (14%) also formed; see text.

were variable; this made it possible to determine some of the factors which lead to optimal yields. The best yield (89%) was obtained with **6d** using a catalytic amount of DMAA; with **6a** or **6b** with DMAA or pyridine the yields of bornyl mesylate were as high as 30–50%, whereas with stronger bases (e.g., triethylamine) yields of the mesylate were negligible with **6a, 6b,** or **6d.** Table I shows the results of experiments using **6d** in a standard procedure (addition of a solution of **6d** in CH_3CN at 0° to a solution of 1 mmol of the alcohol and 0.1 mmol of DMAA in CH_2Cl_2 at 0°, and letting the mixture stand at 0° for 10 min). The yields given are estimated from the weight and NMR spectra of the products following conventional extraction and washing; except where otherwise indicated the products were evidently substantially pure (>95%). This mode of reporting the yield was necessitated by the instability of some of these esters, since the yield of the product after further purification would give little information about the efficiency of the esterification itself.

In addition to the mesylate, another product, viz, the "mesylmesylate" ($CH_3SO_2CH_2SO_2OR$), was also formed in the reactions with the less reactive alcohols, e.g., borneol. A mesylmesyl derivative can also be formed in other ways, e.g., when **6a** is mixed with trimethylamine and *p*-toluidine added 30 sec later, or with **6a** and *p*-toluidine with triethylamine. The mesylmesyl products very likely arise from the stabilized zwitterion[8] $CH_3SO_2^-CHSO_2NR_3^+$ (**7**), formed via the sequence **2** + **3** → $[^-CH_2SO_2CH_2SO_2NR_3^+]$ → **7.** Formation of mesylmesyl derivatives relative to mesylates are thus predicted—and found—to be minimized by (a) the presence of reactive sulfene traps and (b) factors favoring a low concentration of **3,** e.g., (i) having the R groups in **3** relatively large, (ii) using a weak base, and (iii) minimizing the concentration of NR_3.

Because the quaternary methylsulfonylammonium salts (a) require only a catalytic (rather than stoichiometric) quantity of base and (b) react quickly and in high yield, even at low temperatures, these species appear to us to be the reagents of choice for many mesylations, especially those leading to highly sensitive mesylate esters. Experiments designed to explore the selectivity of these reagents are now in progress.

"Easy Mesyl" (**6d**) was prepared as follows. *N,N*-Diethylmethanesulfonamide (10 g) was dissolved in methyl fluorosulfonate (Aldrich, "Magic Methyl") (20 ml) in a two-necked, round-bottomed flask equipped with an inlet tube for dry nitrogen and a condenser fitted with a drying tube of indicating silica gel. The contents of the flask were heated to 50° for 3 days under dry nitrogen, then diluted with dry methylene chloride (50 ml) and cooled in a Dry Ice–acetone bath. When crystallization appeared complete, the diethylmethylammonium salt was collected and washed with dry methylene chloride in a drybox under nitrogen, yield 11.15 g (64%), mp ~115 dec. The product was used for reactions without further purification. The NMR spectrum showed (CD_3CN): δ 1.40 (6 H, triplet, J = 7 Hz), 3.11 (3 H, singlet), 3.60 (4 H, quartet, J = 7 Hz), and 3.70 (3 H, singlet). An analytical sample was recrystallized from acetonitrile–methylene chloride solution at −78°.[9]

Supplementary Material Available. Further experimental details will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, Americal Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2566.

References and Notes

(1) J. F. King, E. A. Luinstra, and D. R. K. Harding, *J. Chem. Soc., Chem. Commun.* 1313 (1972).

(2) Trialkyl(*aryl*sulfonyl)ammonium salts were first described many years ago,[3] but to the best of our knowledge credit for the first preparation of a quaternary *alkyl*sulfonylammonium salt belongs to R. W. Alder and M. H. Ahmed (University of Bristol), who found that **5a** and methyl fluorosulfonate give a crystalline product which was assigned structure **6a** on the basis of its NMR spectrum. We learned of this experiment before beginning our work from Professor M. C. Whiting (with further data provided subsequently by Dr. Alder); we thank Professor Whiting and Dr. Alder most cordially for this invaluable information.

(3) (a) D. Vorländer and M. Kauffmann, *Ber.*, **43,** 2735 (1910); cf. L. Horner and H. Nickel, *Justus Liebigs, Ann. Chem.*, **597,** 20 (1955) and also C. R. Gambill, T. D. Roberts, and H. Shechter, *J. Chem. Educ.*, **49,** 287 (1972), and references cited; (b) T. Oishi, K. Kamata, and Y. Ban, *Chem. Commun.*, 777 (1970).

(4) Compounds **6a** and **6b** crystallize from the reaction mixture, the first while the reaction proceeds, the second upon subsequent cooling. With **6c** and **6d** the crystalline product was obtained after addition of CH_2Cl_2 and cooling to −70°. The salts were recrystallized for analysis from CH_3CN–CH_2Cl_2.

(5) Cf. G. R. Chalkley, D. J. Snodin, G. Stevens, and M. C. Whiting, *J. Chem. Soc. C*, 682 (1970).

(6) The reaction conditions and analysis were as previously described.[1]

(7) The systematic name for **6d,** diethylmethyl(methylsulfonyl)ammonium fluorosulfonate, is sufficiently inconvenient to prompt us to offer something shorter. Our personal choice is "Easy Mesyl", but for those who prefer the sobriety of an acronym we offer (rather half-heartedly) "DEMMSAF" or perhaps "$DEMMSA^+$ FSO_3^-".

(8) G. Opitz, M. Kleeman, D. Bücher, G. Walz, and K. Rieth, *Angew. Chem., Int. Ed. Engl.*, **5** 594 (1966); G. Opitz and D. Bücher, *Tetrahedron Lett.*, 5263 (1966); J. S. Grossert and M. M. Bharadwaj, *J. Chem. Soc., Chem. Commun.*, 144 (1974).

(9) Further experimental details regarding the preparation and use of these reagents appear in the microfilm edition. See paragraph at end of paper regarding supplementary material.

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Asymmetric Hydrogenation with a Complex of Rhodium and a Chiral Bisphosphine

Sir:

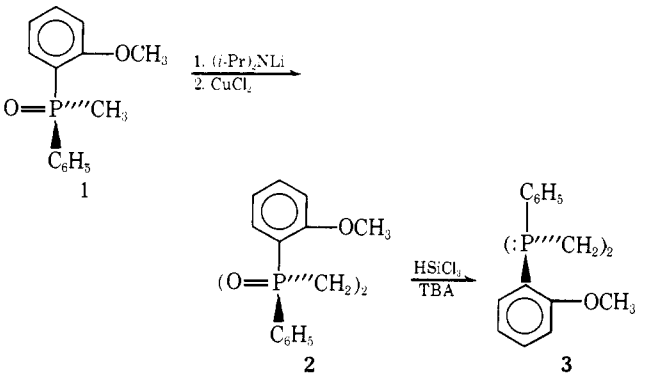
We have previously reported asymmetric hydrogenations[1] with efficiencies of 85–90% using a rhodium–chiral *o*-anisylcyclohexylmethylphosphine complex.[1e] In this update, we wish to report further improvements in the selectivity of these catalysts. Enantiomeric excesses of 95–96% were achieved in the reduction of α-acylamidoacrylic acids using a chiral bisphosphine[2] [1,2-bis(*o*-anisylphenylphosphino)ethane], **3,** as a ligand. The resulting amino acid intermediates have thus been prepared by a synthetic route which rivals the stereospecificity observed with enzymes. The bisphosphine was made by the sequence shown in Scheme I. Oxidative coupling of *o*-anisylmethylphenylphos-

Table I. Asymmetric Reduction of α-Acetamidoacrylic Acids[a]

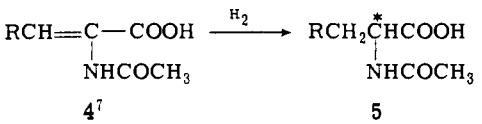
Substrate	Solvent	Temp, °C	Abs press, atm	Reaction time, hr	%c,d ee
4a	88% *i*-PrOH	25	3.5	3	92.8
4a	88% *i*-PrOH	50	3.5	0.8	93.6
4a	88% *i*-PrOH	25	27	0.8	91.8
4a	50% MeOH[e]	25	4	4	95.7
4a	50% MeOH[e]	50	4	1.3	95.2
4a	50% MeOH[e]	25	27	1.0	95.5
4b	MeOH[b]	50	3.5	1	89.4
4b	MeOH	50	3.5	1.5	89.5
4b	MeOH	25	3.5	4	90.9
4b	88% *i*-PrOH	50	3.5	0.7	94.0
4c	MeOH	50	4.0	0.75	93.5

[a] All hydrogenations were run with 0.05% metal levels based on substrate and at concentrations of 2×10^{-4} *M*. [b] In this run, an in situ catalyst was employed while, in all other examples, the crystalline complex [Rh(COD) (bisphosphine)]$^+$ BF_4^- was used. [c] Enantiomeric excess. [d] All rotations were measured without isolation by diluting to volume and comparing with a blank, taking for pure **5a** {$[\alpha]^{20}D$ + 47.5° (*c* 1.0, 95% EtOH)}, **5b** {$[\alpha]^{20}D$ + 40.8° (*c* 1.0, MeOH)}, and **5c** {$[\alpha]^{20}D$ + 35.1° (*c* 0.5, MeOH)}. In the case of the basic solutions, an additional 0.55 equiv of NaOH was added before dilution to volume. In no case was the catalyst contribution in the blank more than 2%. [e] Run as sodium carboxylate with 0.95 equiv of NaOH.

Scheme I



phine oxide (**1**) {$[\alpha]^{20}D$ +25.9° (*c* 1.0, MeOH)} to 1,2-bis(*o*-anisylphenylphosphinyl)ethane (**2**) {$[\alpha]^{20}D$ −44.9° (*c* 1.0, MeOH)} was achieved using a modification of Mislow's procedure.[3] Metallation with lithium diisopropylamide[4] at 5° in place of butyllithium at −70° significantly improved the yields. The bisoxide **2** was reduced to **3** {$[\alpha]^{20}D$ −85.0° (*c* 1.0, $CHCl_3$)}, employing a combination of trichlorosilane and tri-*n*-butylamine in acetonitrile at 70°.[5] Less meso-**3** and higher conversions were obtained with tributylamine than with the more commonly used triethylamine. Oxidation of (−)-**3** to (+)-**2** with H_2O_2 established that there was inversion at both asymmetric centers during the silane reduction of **2** to **3**. A solid complex[6] of (−)-**3**, of the type [Rh(1,5-cyclooctadiene)(bisphosphine)]$^+$ BF_4^-, was prepared from $[Rh(COD)Cl]_2$ and **3**. Hydrogenations were run with either the complex or with an in situ catalyst formed from **3** and $[Rh(COD)Cl]_2$. Table I shows the enantiomeric excess of substituted alanines obtained under a variety of conditions for the following hydrogenation reaction. In all cases, (−)-**3** gives derivatives of L-amino acids. Several points in the table merit discussion. As in our previous experience, the hydrogenation can be run on either the free acid or the carboxylate anion,[1b,c,e] however, with ligand **3**, better results are observed with the anion. The high optical yields obtained with the bisphosphine **3** were not sensitive to temperature and pressure,[1e] and excellent results could be obtained without a rate penalty.



4[7] **5**

4a, 5a, R = phenyl
4b, 5b, R = 3-methoxy-4-acetoxyphenyl
4c, 5c, R = 3-(1-acetyl-indolyl)-

This nonsensitivity to variables as well as the superior optical yields may be attributed to the rigid, five-membered ring possible between **3** and the rhodium, which prevents rotation around the metal-phosphorus bonds. The modest results (40% ee) obtained with α-phenylacrylic acid support our contention[1b,e] that the methoxyl group is improving the selectivity by hydrogen bonding with the amide substrate.

References and Notes

(1) (a) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968); (b) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Ann. N.Y. Acad. Sci.*, 172, 232 (1970); 119, 214 (1973); (c) *J. Chem. Soc., Chem. Commun.*, 10 (1972); (d) *Chem. Technol.*, 590 (1972); (e) "Homogeneous Catalysis II", *Adv. Chem. Ser.*, **No. 132**, 274 (1974).
(2) Good results have been obtained using a bisphosphine derived from tartaric acid. T. P. Dang and H. B. Kagan, *Chem. Commun.*, 481 (1971); *J. Am. Chem. Soc.*, **94**, 6429 (1972).
(3) C. A. Maryanoff, B. E. Maryanoff, R. Tang, and K. Mislow, *J. Am. Chem. Soc.*, **95**, 5839 (1973).
(4) T. Kauffmann and M. Schoenfelder, *Justus Liebigs Ann. Chem.*, **731**, 37 (1970).
(5) This reaction is very solvent dependent. A mixture of acetonitrile and tributylamine kept the silane complexes in solution.
(6) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 2397 (1971).
(7) The α-acetamidoacrylic acids were made by a base condensation via the azlactone, a method which gives only the stable isomer. X-ray evidence indicates that this stable isomer is the *Z* form or the one related to *trans*-cinnamic acid. K. Brocklehurst, *J. Chem. Soc. D*, 632–633 (1971), and references therein.

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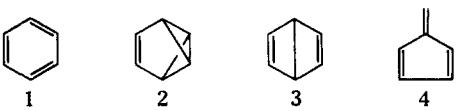
Energy Storage and Release. Direct and Sensitized Photoreactions of Benzvalene. Evidence for a Quantum Chain Process, an Adiabatic Photorearrangement, a Degenerate Photovalence Isomerization, and Two Reactive Triplet States

Sir:

It is remarkable that the valence isomers of benzene, although they store enormous potential energy in their highly strained aromatizable structures, are kinetically stable at room temperature.[1] To identify features controlling the storage and release of chemical energy in simple organic molecules, we studied the response of one of these valence isomers, benzvalene,[2] to the further energy enhancing processes of direct and sensitized excitation by light.

The photochemistry of benzene (**1**), the prototype aromatic molecule, has been studied extensively.[3] Several isomers (**2, 3, 4**) are known to result upon irradiation in solution,[3-5] but none of these result from benzene's fluorescent state, the lowest vibrational state of S_1. Apparently, **2** is formed from an upper vibrational state of S_1 (**1**) and **3** from



1 **2** **3** **4**