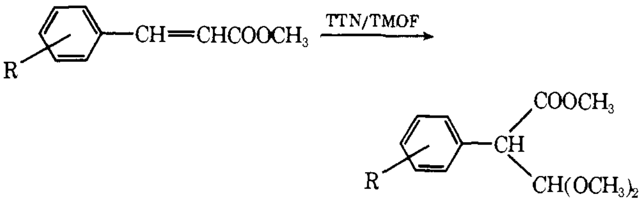
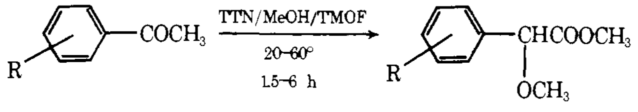
Scheme II. Conversion of Methyl Cinnamates to Methyl α-(Dimethoxymethyl)arylacetates



(a) R = H, 96%[a]
(b) R = 4-CH_3, 96%[a]
(c) R = 4-CH_3O, 90%[b]
(d) R = 2-F, 83%[a]
(e) R = 4-Cl, 96%[a]

[a] Reaction run under reflux. [b] Reaction run at 20°.

Scheme III. Conversion of Acetophenones to Methyl α-Methoxyarylacetates



(a) R = H, 70%
(b) R = 4-CH_3O, 81%
(c) R = 4-O_2N, 87%
(d) R = 3-C_6H_5O, 97%

involves two successive methoxythallation reactions. The first utilizes α-methoxystyrene as substrate, and involves an aryl migration; the second utilizes phenylketene dimethylketal as substrate, and terminates with oxidative displacement of thallium by methanol. This synthesis of methyl α-methoxyarylacetates is general; some representative conversions are summarized in Scheme III.

We have observed α-methoxylation of other carbonyl compounds under the same reaction conditions. For example, cyclohexanone and cyclopentanone are converted to their respective α-methoxyketals, phenylacetaldehyde is converted to α-methoxyphenylacetaldehyde dimethylacetal, and methoxyacetophenone is converted to phenylglyoxal dimethylacetal dimethylketal.

Although propiophenone was reported to rearrange to methyl α-methylphenylacetate in very low yield with TTN/MeOH,[10] we have now found that the rearrangement is essentially quantitative in MeOH/TMOF. In an analogous oxidative rearrangement, butyrophenone is converted to methyl α-ethylphenylacetate (93%). No α-methoxylation is observed in the latter two cases, apparently for steric reasons.

The full role of TMOF in the above oxidations is not yet clear. With some carbonyl compounds, initial conversion to acetals, ketals, or vinyl ethers (catalyzed by TTN, and more rapid with TMOF than with MeOH alone) occurs prior to oxidation. In addition, however, an apparently important role of TMOF is to lower the dielectric constant of the reaction medium, thus favoring S_N2 as opposed to S_N1 reactions of the methoxythallated intermediates. Thus, we have been able to effect the cinnamaldehyde rearrangements reported above by using a solvent combination whose dielectric constant is similar to MeOH/TMOF (e.g., MeOH/hexane, MeOH/*p*-dioxane, MeOH/CCl_4), although they proceed more slowly.[14] In marked contrast, the use of solvent mixtures of high dielectric constant (i.e., MeOH/CH_3CN) led to complex mixtures of products.

References and Notes

(1) (a) Thallium in Organic Synthesis. Part 43. For the previous paper in this series, see A. McKillop, D. H. Perry, M. Edwards, S. Antus, L. Farkas, M. Nogradi, and E. C. Taylor, *J. Org. Chem.*, **41**, 282 (1976). (b) We are deeply indebted to the National Science Foundation, (Grant No. MPS72-00427) and to Eli Lilly and Co., Indianapolis, Ind., for support of this work.
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(13) E. C. Taylor, H. Bozimo, and A. Litsky, unpublished observations.
(14) We assume that this slower rate is due to a slower rate of acetal formation, which can be demonstrated independently.

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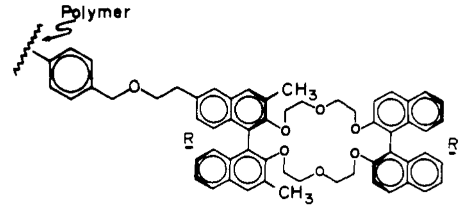
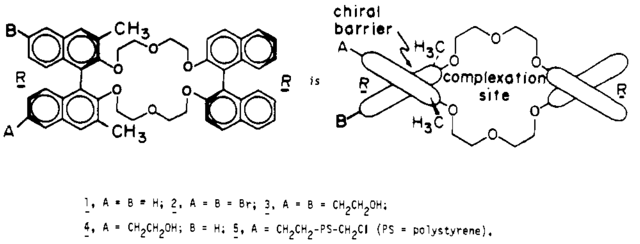
Total Chromatographic Optical Resolutions of α-Amino Acid and Ester Salts through Chiral Recognition by a Host Covalently Bound to Polystyrene Resin[1]

Sir:

We report here the covalent attachment of host (*RR*)-**1** to macroreticular cross-linked polystyrene *p*-divinylbenzene resin, and the use of the resin for total optical resolutions (both preparative and analytical) of amino acids and ester salts.[2]



(RR)-1



1, A = B = H; 2, A = B = Br; 3, A = B = CH_2CH_2OH;
4, A = CH_2CH_2OH; B = H; 5, A = CH_2CH_2-PS-CH_2Cl (PS = polystyrene),
B = H; 6, A = CH_2CH_2-PS-CH_2OCH_3, B = H

Optically pure (*R*)-2,2′-dihydroxy-3,3′-dimethyl-1,1′-binaphthyl[3] was brominated in dichloromethane (−78° to 25°) to give (90%) (*R*)-6,6′-dibromo-3,3′-dimethyl-2,2′-dihydroxy-1,1′-binaphthyl,[4] mp 115–119° ($CHCl_3$ solvate), $[\alpha]^{25}_{578}$ −68°.[5] This dibromide when refluxed for 17 h in $(CH_2)_4O$–KOH with mole for mole optically pure (*R*)-2,2′-bis-(1,4-dioxa-6-tosyloxyhexyl)-1,1′-binaphthyl[3] gave cycle (*RR*)-**2**[4] (69%), mp 135–143° (solvate from benzene-

Table I. Optical Resolution of $RC^*H(NH_3)CO_2R'^+\ ClO_4^-$ Guest (G) by Solid-Liquid Chromatography on a 9.5-g Column of Resin Containing 0.694 mmol of Host (H) Sites[a]

	Guest					Separation				
	Structure									
Run no.	R	R′	Wt (mg)	H/G[b]	% (v) CH_3CN in $CHCl_3$	Factor[c] (α)	Kind[d]	$\Delta(\Delta G)$[e] (cal/mol)	Resol factor,[f] R_s	Config more bound guest
1	C_6H_5	H	0.013	14 000	10	5.5	B.I.	926	1.99	*R*
2	C_6H_5	H	0.32	550	10	11	B.I.	1303	2.90	*R*
3	C_6H_5	H	5.0	35	10	15	B.I.	1471	1.13	*R*
4	C_6H_5	H	10.1	17	10	24	B.I.	1726	0.74	*R*
5	C_6H_5	H	15.2	11	10	12	B.I.	1350	0.76	*R*
6	C_6H_5	H	84	2	10	11	Min.	1303	0.21	*R*
7	p-HOC_6H_4	H	6.6	28	10	6.1	B.I.	982	2.31	*R*
8	p-$HOC_6H_4CH_2$	H	5.8	36	10	1.9	Min.	349	0.42	*R*
9	$C_6H_5CH_2$	H	4.6	40	4	2.3	B.I.	453	0.97	*S*
10	$C_8H_6NCH_2$[g]	H	2.0	104	20	6.1	B.I.	982	1.61	*R*
11	$(CH_3)_2CH$	H	1.6	97	10	2.3	Min.	452	0.45	*R*
12	$C_2H_5(CH_3)CH$	H	2.3	69	5	1.9	Min.	349	0.24	*R*
13	$(CH_3)_3C$	H	2.0	79	5	1.9	Min.	349	0.37	*R*
14	CH_3	H	1.6	82	4	1.5	Min.	220	0.21	*R*
15	$CH_3SCH_2CH_2$	H	6.6	26	4	1.4	Min.	183	0.25	*R*
16	p-HOC_6H_4	CH_3	9.5	50	10	26	B.I.	1770	3.0	*R*
17	C_6H_5	CH_3	9.5	48	10	18.5	B.I.	1585	4.5	*R*
18	p-$CH_3O_2CC_6H_4$	CH_3	9.5	50	10	12.6	B.I.	1376	2.3	*R*
19	p-ClC_6H_4	CH_3	9.5	47	10	8.5	B.I.	1163	2.2	*R*
20	p-$FC_6H_4CH_2$	CH_3	9.5	50	10	8.5	B.I.	1163	2.7	*S*
21	$C_6H_5CH_2$	CH_3	9.5	50	10	6.4	B.I.	1008	1.9	*S*
22	p-$HOC_6H_4CH_2$	CH_3	9.5	47	10	4.7	B.I.	841	1.7	*R*

[a] Average host site ~14 000 mass units, or 0.073 mmol of host per gram. [b] Ratio of total moles of host to total moles of guest. [c] Separation factor (α) = (retention volume of less mobile component minus total dead volume)/(retention volume of more mobile component minus total dead volume). [d] B.I. means baseline separation and Min., minimum between fractions. [e] $\Delta(\Delta G) = RT \ln \alpha$ (ref 10) and measures the free energy differences of the diastereomeric complexes. [f] R_s = 2(retention volume of less mobile component minus that of more mobile component)/(sum of bandwidths of two peaks). [g] Tryptophane side chain.

cyclohexane), $[\alpha]^{25}{}_{578}$ +172°.[5] In dry glyme under nitrogen, (*RR*)-**2** was metalated at −75° with 2 equiv of BuLi, and 4 equiv of dry ethylene oxide was added (−75°) to give after chromatography on alumina: optically pure (*RR*)-**1**[3] (25%), $[\alpha]^{25}{}_{578}$ +152° (*c* 1.0, $CHCl_3$); (*RR*)-**3**[4b] (6%, glass); and (*RR*)-**4**[4] (60%, glass), $[\alpha]^{25}{}_{578}$ +164° (*c* 1.7, CH_2Cl_2). Host (*RR*)-**4** was covalently attached to chloromethylated and highly cross-linked polystyrene-divinylbenzene resin[6] to give first (*RR*)-**5** and (*RR*)-**6**[7] after CH_3ONa treatment, which was packed into a chromatographic column.[8] The resin volume did not change observably with solvent changes.

Runs were made[9] at 0° and monitored by passing the column eluate ($CHCl_3$-CH_3CN) through a conductivity detector.[2a,b] Plots of relative conductance vs. volume of column eluate were made from which the parameters of Table I were calculated.[10] The peaks were Gaussian (little tailing). The configurational identities and optical purities of the less complexed and faster moving, and more complexed and slower moving enantiomers were identified by isolation and characterization of the pure antipodes in runs 5, 7, 9, 15, and 18–20 (or runs that simulated them). In the other runs the enantiomers were identified either by comparisons of their retention volumes with those of authentic enantiomers or from signs of rotations of eluate fractions. Runs 18–20 involved esters[11] not previously resolved. Their optically pure enantiomers were obtained by preparative chromatography.[12] Comparisons of the CD curves of the more and less bound enantiomers in these runs with those of runs 5, 7, 8, and 9 (configurations known) provided the needed configurational assignments.[13] In the many runs with baseline separation of enantiomers, the areas under the two peaks were equal within experimental error.

Conclusions are as follows. (1) Resin-bound host **6** provides effective chromatographic material for both analytical and preparative resolution of amino acid and ester perchlorate (or hexafluorophosphate)[14] salts. Separation factors (α)[10] ranged from 26 (run 16) to 1.4 (run 15), and $\Delta(\Delta G)$[10] values for the diastereomeric complexes ranged from 1770 to 183 cal/mol. Resolution factors R_s[10] ranged from 4.5 (run 17) to 0.21 (run 14). Figures 1 and 2 are plots that represent extremes in resolution factors for the amino acids (runs 2 and 14). Minima or baseline separations were observed when the amount of amino acid salt was varied by a factor of ~6500 (runs 1 and 6). Even with methionine (run 5, lowest α), proper cutting of fractions provided substantial amounts of pure enantiomers. Qualitatively, each acid salt gave results similar to those of its ester salt. (2) Unlike conventional optical resolutions, these are rational in the sense that the more bound enantiomer was predicted in advance of experiment based on complementary steric compatibility between host and guest in Corey, Pauling, Koltun (CPK) molecular models of the diastereomeric complexes (runs 9, 20, and 21 involving phenylalanine, its ester, and its *p*-fluoro ester provide exceptions). The changes in $\Delta(\Delta G)$ between the diastereomeric complexes correlate roughly with the steric requirements of the R groups of the guest compounds (larger R groups generally provide larger $\Delta(\Delta G)$ values). (3) The directions and extents of chiral recognition toward a variety of guests exercised by host bound to resin (**6**) are similar to those observed for the same host (**1**) in solution. At the resin-solvent interface and in chloroform or

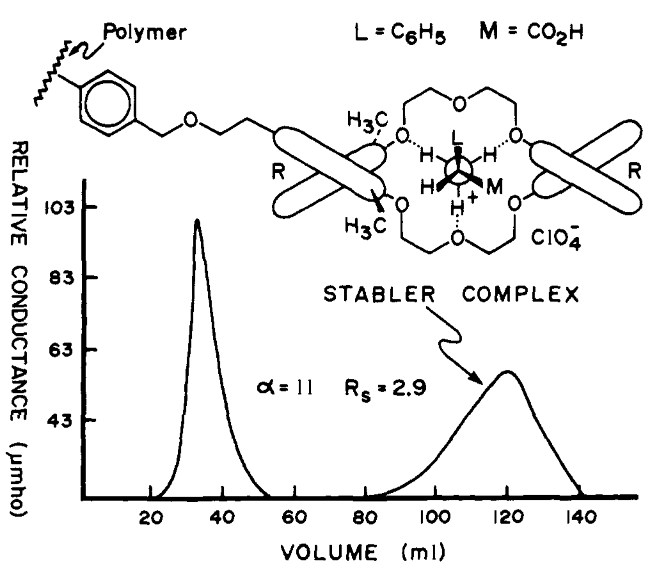


Figure 1. Plot of relative conductance vs. volume of column eluate for phenylglycine perchlorate (run 2).

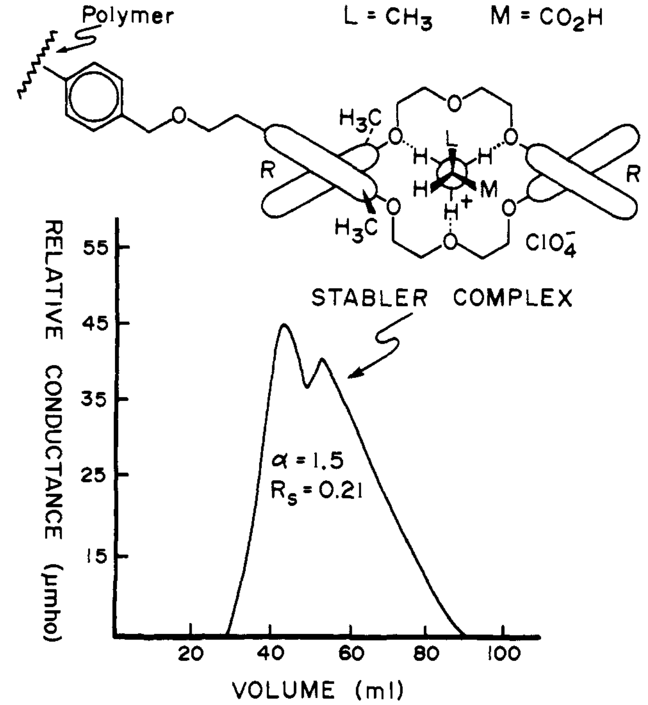
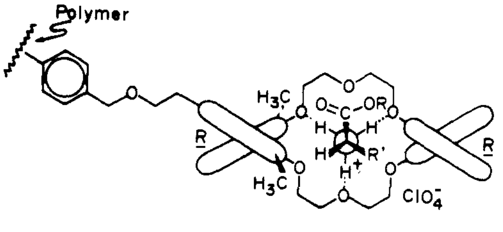
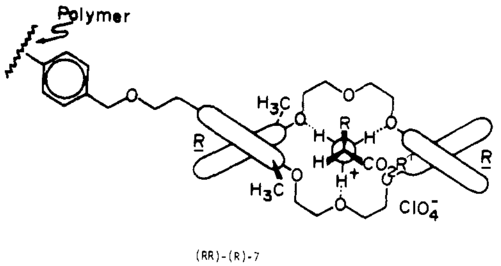


Figure 2. Plot of relative conductance vs. volume of column eluate for alanine perchlorate (run 14).

chloroform-acetonitrile solution,[15] the (*RR*)-(*R*) diastereomers are the more stable for all of the amino acids and esters except for phenylalanine and its ester whose (*RR*)-(*S*) diastereomers are the more stable (the *p*-fluorophenylalanine ester (run 20) resembles its para hydrogen analogue at the resin-solvent interface and has not been examined in solution experiments). At both the interface and in solution, the differences in free energies of the diastereomeric complexes are close to one another for any given guest.[15] The chiral recognition decreases with increases in temperature both at the interface[14] and in solution,[3,15] and with the absence of the two methyl groups that extend the chiral barrier of the host.[3,14,15] (4) The nontypical preferences of (*RR*)-**6** for the (*S*)-phenylalanine isomer (run 9), its ester (run 21), and *p*-fluorophenylalanine ester (run 20) but not for tyrosine (run 8) or its ester (run 22) indicate that remote substituents affect the chiral bias in complexation. The *p*-hydroxy, *p*-hydrogen, *p*-carboxymethyl, and *p*-chlorophenyl glycine esters of runs 16–19 provide a series of decreasing α values that range from 26 to 8.5 whose logarithms are correlated by σ_p (coefficient of 0.84)[16] with $\rho = -0.54$. In CPK molecular models of the diastereomeric complexes of the (*RR*)-(*S*)-diastereomers of the phenylglycine and phenylalanine ester series, an oxynaphthalene (π-base) is face-to-face with the aryl group of the guests,[3] whose π-character is determined by its attached 1,4-substituents. The $CHNH_3CO_2CH_3^+$ and $CH_2CHNH_3CO_2CH_3^+$ groups are strongly electron withdrawing, and the para substituents vary. The para-hydroxy group decreases relative to para hydrogen or para fluoro the π acidity by electron delocalization and destabilizes (*RR*)-(*S*)-**7**. The para-chloro and para-carbomethoxy groups relative to para hydrogen increase the π acidity by electron withdrawal, an effect that stabilizes (*RR*)-(*S*)-**7** somewhat. The stability of (*RR*)-(*R*)-**7** is free of these effects (models) and is sterically the more stable. The directions of chiral recognition in the more delicately balanced and less hindered complexes of the phenylalanine series were inverted by changes in the para substituent, probably due to similar π-π interactions.[17]



(RR)-(S)-7



(RR)-(R)-7

References and Notes

(1) This work was supported by the U.S. Public Health Service, Research Grant No. GM12640-12 from the Department of Health, Education and Welfare, and by a grant from the National Science Foundation, GP 33533X-1.

(2) Amino esters as a family have been previously resolved by: (a) solid–liquid chromatography, G. Dotsevi Y. Sogah and D. J. Cram, *J. Am. Chem. Soc.*, **97**, 1259 (1975) (the first author's name appeared as if he were two rather than one person in the original reference); (b) liquid–liquid chromatography, L. R. Sousa, D. H. Hoffman, L. Kaplan, and D. J. Cram, *J. Am. Chem. Soc.*, **96**, 7367 (1974); (c) gas–liquid chromatography, α's as high as 1.3, R. Charles, U. Beitler, B. Feibush, and E. Gil-Av, *J. Chromatogr.*, in press. The covalent attachment of L-arginine to Sephadex G-25 provided a liquid–solid column that gave α = 1.60 in the resolution of racemic Dopa, 1.19 for racemic tyrosine, and 1.00 for phenylalanine; (d) R. J. Baczuk, G. K. Landram, R. J. Dubois, and H. C. Dehm, *J. Chromatogr.*, **60**, 351 (1971). No chromatographic resolution of amino acids as a class have been reported prior to our paper.

(3) R. C. Helgeson, J. M. Timko, P. Moreau, S. C. Peacock, J. M. Mayer, and D. J. Cram, *J. Am. Chem. Soc.*, **96**, 6762 (1974).

(4) (a) Carbon and hydrogen analyses were within 0.30% of theory; (b) ^1H NMR spectra in $CDCl_3$ were as expected; (c) 70 eV mass spectra gave parent ion.

(5) Solvent free, *c* 1.0–1.4, CH_2Cl_2.

(6) We warmly thank Rohm and Haas for this material and a description of its properties.

(7) Amberlite XAD-2 ground through a 150 mesh sieve was chloromethylated with 3 mol of chloromethyl methyl ether–aluminum chloride in 1,2-dichloroethane at 25° for 4 h, washed, and dried under vacuum at 90° for 20 h. Anal. Found: C, 86.58, H, 7.98; Cl, 3.97 (1.12 mequiv of Cl per g, or 15% of aromatic rings chloromethylated based on 130 for equivalent weight of polymer). To 2.63 g of (*RR*)-**4** and 2.5 g of NaH in refluxing $(CH_2)_4O$ under nitrogen was added 29.0 g of dry chloromethylated resin. The mixture was refluxed for 7 days and filtered, and the solids were washed with CH_3OH, H_2O, CH_2Cl_2, and CH_3OH and dried at

90° for 12 h under vacuum to give 30.3 g of (*RR*)-**5**, analysis for chlorine, 3.71%. Recovered from the filtrates was 1.8 g of crude and 1.3 g of chromatographed (*RR*)-**4**. The resin was refluxed 15 h with excess CH_3ONa in CH_3OH, washed, and dried to give 30.0 g of (*RR*)-**6**, 0.65% Cl, or 0.18 mequiv/g of Cl, 0.87 mequiv/g of CH_3O, and 0.073 mmol of host/g (based on the difference between (*RR*)-**4** used and recovered, and consistent with the difference in percent Cl of chlorinated resin and (*RR*)-**5**). Almost one in every hundred benzene rings of the polymer carries a host, and the remaining polymer provides structural support, channels, and environment.

(8) A 60 by 0.75 cm (i.d.) stainless steel jacketed (insulated) column was packed by a balanced-density slurry method in 50% (v) $CH_3CN–CHCl_3$ at 3 ml/min (800–900 psi) and was washed with methanol and then chloroform. It contained 9.5 g of 250–325 mesh (*RR*)-**6**, and possessed a dead volume of 18.4 ml.

(9) Samples dissolved in a minimum of mobile phase solvent were injected on the column through an injection loop. Corrections (less than one-third of dead volume) were made for loop, detector, and tubing volumes. Chromatograms were run at constant flow rates of 0.36–2.0 ml/min with pressure drops of 350–700 psi. After runs, the columns were washed and stored under methanol.

(10) L. R. Snyder and J. J. Kirkland, "Introduction to Modern Liquid Chromatography", Wiley, New York, N.Y., 1974, pp 25–29, 35–37.

(11) The authors warmly thank Ms. Linda A. Domeier for preparing these compounds, which were characterized for the first time (ref 4a): *p*-$ClC_6H_4CHNH_3Cl(CO_2CH_3)$, mp 194–197°; *p*-$CH_3O_2CC_6H_4CHNH_3Cl(CO_2CH_3)$, mp 200–201°. The corresponding acids are known, e.g., A. H. Neims, D. C. DeLuca, and L. Hellerman, *Biochemistry*, **5**, 203 (1966).

(12) The methyl ester perchlorate salts of the phenylglycines gave: for the para chloro derivative, mp 82.5° for the less retained enantiomer, $[\alpha]^{25}{}_{578}$ +73.7° (*c* 0.83, MeOH), mp 82° for the more retained, $[\alpha]^{25}{}_{578}$ −69.5° (*c* 0.77, MeOH); for the para carbomethoxy derivative, less retained, mp 53.5°, $[\alpha]^{25}{}_{578}$ +75.9° (*c* 0.80, MeOH), more retained, mp 53°, $[\alpha]^{25}{}_{578}$ −76.0° (*c* 0.80, MeOH). The methyl ester perchlorate salts of *p*-fluorophenylalanine gave: mp 79° for the less retained, $[\alpha]^{25}{}_{578}$ +35.5° (*c* 0.80, MeOH); mp 79.5° for the more retained, $[\alpha]^{25}{}_{578}$ −33.8° (*c* 0.80, MeOH).

(13) The CD spectrum of all four phenylglycine and three phenylalanine methyl ester salts in MeOH (*c* 0.8 ± 0.1) gave Cotton effects at 215–220 nm ($\pi \rightarrow \pi^*$) whose sign was configuration dependent, and at 250–260 nm whose sign was configuration independent and negative. The ester salts of known configuration correlated as follows: (*S*)-phenylglycine, ~220 nm, $[\theta] = +1260°$; (*R*)-*p*-hydroxyphenylglycine, ~215 nm, $[\theta] = -950°$; (*S*)-phenylalanine, ~220 nm, $[\theta] = +800°$; (*S*)-tyrosine, ~220 nm, $[\theta] = +1100°$; (+)-*p*-chlorophenylglycine, less bound, ~215 nm, $[\theta] = +240°$ thus *S* configuration and (−)-*p*-chlorophenylglycine, more bound, ~215 nm, $[\theta] = -240°$, thus *R* configuration; (+)-*p*-carbomethoxyphenylglycine, less bound, ~220 nm, $[\theta] = +300°$, thus *S* configuration, and (−)-*p*-carbomethoxyphenylglycine, more bound, ~220 nm, $[\theta] = -310°$, thus *R* configuration;(+)-*p*-fluorophenylalanine, less bound, ~220 nm, $[\theta] = -275°$, thus *R* configuration, and (−)-*p*-fluorophenylalanine, more bound, ~220 nm, $[\theta] = +280°$, thus *S* configuration.

(14) G. D. Y. Sogah and D. J. Cram, unpublished results.

(15) S. C. Peacock and D. J. Cram, *J. Chem. Soc., Chem. Commun.*, in press.

(16) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(17) F. Suzuki and M. Oki, *Bull. Chem. Soc.*, **48**, 596 (1975), observed that intramolecular attractive forces of the π–π variety between differently substituted benzene rings accounted for the dominant conformation of 9-benzyltriptycenes.

(18) African–American Institute, AFGRAD Fellow.

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Enhanced Dimol Emission of Singlet Oxygen by Cyclic Tertiary Diamines

Sir:

One criterion for the presence of singlet oxygen ($^1O_2$) in chemical and biological systems is the inhibition of the process under investigation by specific quenchers of $^1O_2$.[1,2] Tertiary amines have been studied extensively in this regard, and have been shown to inhibit product formation in several systems,[3,4] as well as inhibiting $^1O_2$ dimol emission at 634 nm in the gas phase[3,4] produced in the following reaction:

$$O_2(^1\Delta_g) + O_2(^1\Delta_g) \rightarrow 2O_2(^3\Sigma_g^-) + h\nu$$

The proposed mechanism for amine quenching is through the formation of a charge-transfer complex.[3-9] We wish to report here a *stimulation* of $^1O_2$ dimol emission by certain cyclic tertiary diamines in aqueous solution.

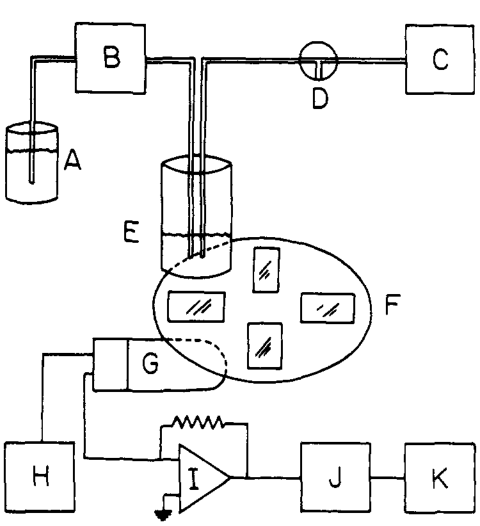
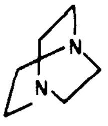


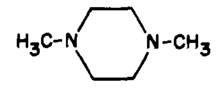
Figure 1. Experimental apparatus for detecting $^1O_2$ dimol emission and effects of added tertiary diamines. The production of $^1O_2$ in the peroxide/hypochlorite reaction is initiated by pumping 0.4 M NaOCl from reservoir (A) using a peristaltic pump (B) to the reaction flask (E) containing 5.0 ml of 1.2 M H_2O_2. The emitted light passes through a filter wheel (F) containing interchangeable interference filters and falls on a red-sensitive photomultiplier (G) powered by a high voltage supply (H). The resulting current is converted to voltage by operational amplifier (I), put through a low-pass filter (J) and displayed on a strip chart recorder (K). Air was bubbled through the reaction mixture by a pump (C). To test the effect of added tertiary amines, 1.0-ml solutions of these compounds were injected through a three-way stopcock (D) directly into the air line and carried to the reaction mixture.

$^1O_2$ was produced from the reaction of NaOCl and H_2O_2[1,2,10] in a scintillation vial above a red-sensitive photomultiplier tube RCA 4832 (formerly C31025C). Interchangeable interference filters, which transmitted light at 634, 670, and 703 nm, were placed between the reaction vial and the photomultiplier tube. $^1O_2$ specific dimol emission occurs at 634 and 703 nm with little light emitted at 670 nm. Thus a comparison of light transmitted by these three interference filters can be used to differentiate $^1O_2$ specific emission from other types of chemiluminescence. The current from the photomultiplier tube was converted to voltage by an operational amplifier (Model 310J, Analog Devices, Norwood, Mass.) and displayed on a strip chart recorder after passive attenuation and low-pass filtering. A schematic of the experimental set-up is shown in Figure 1. A preliminary report of this apparatus has appeared.[11]

NaOCl as Clorox (0.4 M) was added by an LKB peristaltic pump at a rate of 1.4 ml/min into 5 ml of 1.2 M H_2O_2 in a scintillation vial. An air bubbler was used to promote uniform mixing and by 45 s after the onset of $^1O_2$ generation a steady state light emission had been reached. At that time, 1.0-ml solutions of various nitrogen-containing compounds were injected through the air line and carried to the reaction vial. By 45 s after the addition of the tertiary amine or an equivalent amount of distilled water, a new steady state light emission was observed and data were expressed as percent change in light emission caused by the addition of amine. Among the tertiary amines tested were 1,4-diazabicyclo[2.2.2]octane (DABCO, I) its monocyclic analogue *N,N'*-dimethylpiperazine (II) and



I



II

$(CH_3)_2–NCH_2CH_2N(CH_3)_2$

III