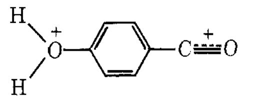
carboxyl (and protonated carboxyl group) no ring protonation occurs, as is the case with phenol itself.[3f]

We have also obtained the pmr spectra of *m*- and *p*-hydroxybenzoic acids in excess FSO_3H-SbF_5 solution at low temperature. Unlike the ortho isomer (salicylic acid) the meta and para isomers are diprotonated. At −70° the spectrum of protonated *m*-hydroxybenzoic acid consists of singlets at δ 13.36 (2 H, $CO_2H_2^+$) and 12.50 (2 H, OH_2^+) and a complex pattern between δ 8.3 and 9.1 (4 H). The pmr spectrum of the para isomer at −110° consists of broad singlets at δ 13.97 (2 H, $CO_2H_2^+$) and 12.34 (2 H, OH_2^+) and a multiplet between δ 7.8 and 9.1. (Assignments were made based on comparison with data on protonated substituted benzoic acids and phenols.) At comparable acid concentrations, it therefore requires a lower temperature to freeze out the proton-exchange processes of the para isomer. The reason for this is not yet clearly understood. The proton resonances of the phenolic hydroxyls in the *m*- and *p*-hydroxybenzoic acids are considerably deshielded from that of the ortho isomer. This is probably the result of greater positive charge on the phenolic oxygen atom in these isomers, compared with the ortho isomer.

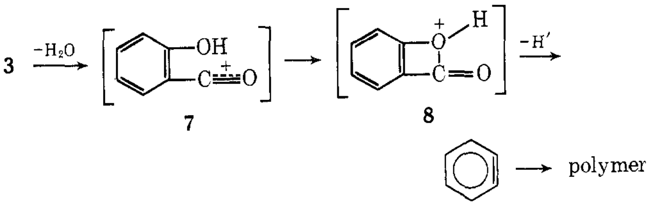
Protonated *m*- and *p*-hydroxybenzoic acids also react differently from the ortho isomer on heating. On warming a solution of *p*-hydroxybenzoic acid in HSO_3F-SbF_5 at 20°, the appearance of a multiplet with the characteristic pattern of an AA′BB′ spin system is observed in the nmr spectrum between δ 8.1 and 9.3. This spectral data and quenching experiments (H_2O), which yield *p*-hydroxybenzoic acid quantitatively, indicate the formation of dication **6**.



6

Similar results are observed for protonated *m*-hydroxybenzoic acid, which cleaves to the meta isomer of ion 6 on warming in FSO_3H-SbF_5 at room temperature. In the nmr spectrum of this dication a multiplet between δ 8.6 and 9.4 is found.

Similar experiments for protonated *o*-hydroxybenzoic acid gave only polymeric material, most likely *via* intermediates **7** and **8**, leading subsequently to benzyne and its polymeric products. Our studies directed to the generation of benzyne from salicylic acid derivatives will be reported separately.



Experimental Section

Materials. All compounds were reagent-grade commercial chemicals and were used without further purification.

Nmr Spectra. A Varian A56/60A nmr spectrometer with variable-temperature probe was used for all spectra. Solutions were prepared at −80° using a 1:1 *M* solution of HSO_3F-SbF_5 and SO_2ClF as a diluent according to procedures described previously.[3,4,6] Chemical shifts were referred to external TMS.

Acknowledgment. Support of our work by a grant of the National Institutes of Health is gratefully acknowledged.

Registry No.—**1**, 50-78-2; **2**, 50977-96-3; **3**, 51016-05-8; **4**, 50977-97-4; **6**, 50977-98-5; *m*-**6**, 50977-99-6; Magic Acid, 37204-12-9; salicylic acid, 69-72-7; *m*-hydroxybenzoic acid, 99-06-9; *p*-hydroxybenzoic acid, 99-96-7; protonated *m*-hydroxybenzoic acid, 51016-03-6; protonated *p*-hydroxybenzoic acid, 51016-04-7.

References and Notes

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(2) Postdoctoral Research Fellow, 1971–1973.
(3) (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 7072 (1967); (b) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967); (c) G. A. Olah and T. E. Kiovsky, *ibid.*, **90**, 6461 (1968); (d) G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3908, 3925 (1970); (e) N. C. Deno, R. W. Gaugler, and M. J. Wisotsky, *ibid.*, **31**, 1967 (1966); (f) T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Can. J. Chem.*, **42**, 1433 (1964); (g) T. Birchall and R. J. Gillespie, *ibid.*, **43**, 1045 (1965); (h) M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1735 (1967).
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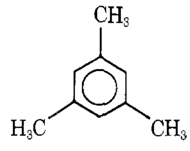
Photoelectron Spectra of Mesitylene Derivatives. Electronic Interactions Between Arene Ion Groups

T. Koenig* and M. Tuttle

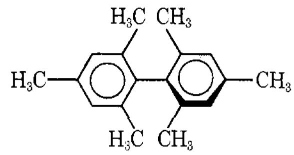
Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Received October 24, 1973

We wish to report the results of our investigation of the He(I) photoelectron spectra of mesitylene (**1**), bimesityl (**2**), 2,7-dimethyl-4,5,9,10-tetrahydropyrene (**3**), *anti*-6,13-dimethyl[2.2]metacyclophane (**4**), and [2.2.2](1,3,5)cyclophane (**5**). These compounds were chosen for study because of their relationship with mesitylene. The symmetry of this parent system dictates a degeneracy among the Π ionic states. All of the derivatives (**2**–**5**) are substituted in such a way that this degeneracy should be approximately preserved in the absence of interring interaction. With this approximation the observed splittings, which remove these degeneracies, can be simply interpreted in terms of interring interactions.



1



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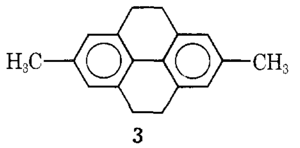

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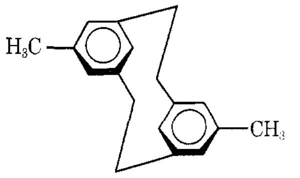

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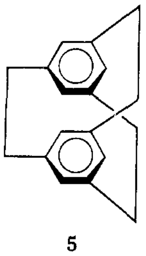

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The spectra are shown as Figures 1 and 2. The first band in the spectrum of mesitylene (IP_{vert} = 8.42 eV)[1]

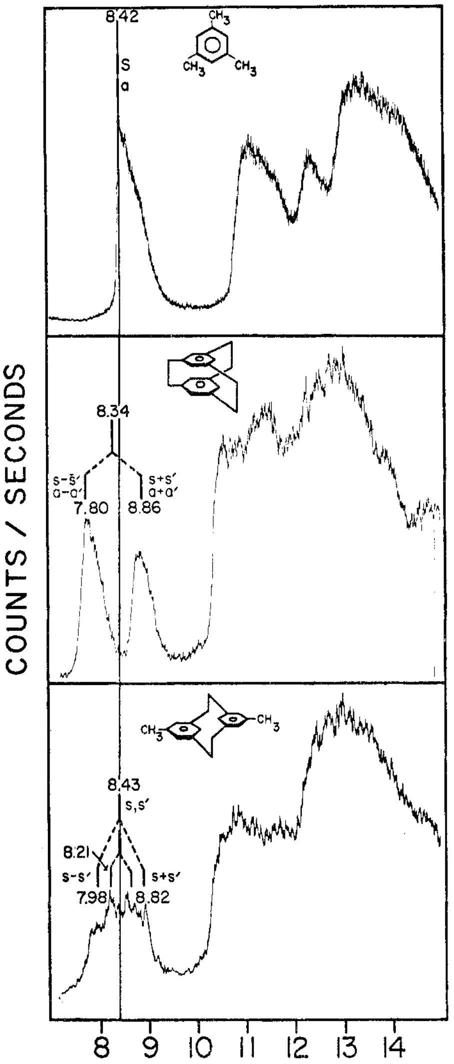


Figure 1. He(I) photoelectron spectra of **1**, **5**, and **4** (top to bottom).

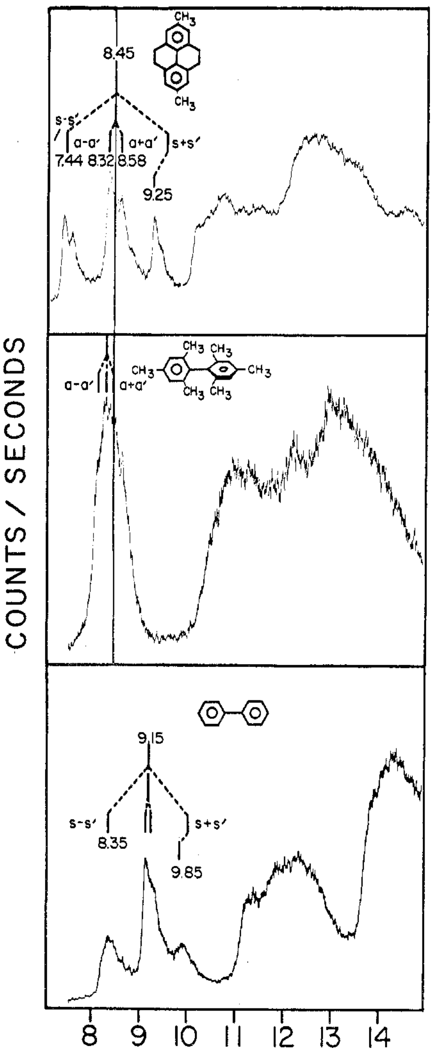
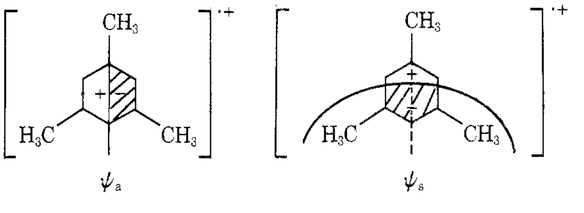


Figure 2. He(I) photoelectron spectra of **3**, **2**, and biphenyl (top to bottom).

shows the expected shape for degenerate ionic states (Jahn–Teller vibronic coupling as in benzene). The importance of this spectrum is in setting the value about which the corresponding bands in **2**–**5** should be split. The most striking feature of Figures 1 and 2 is the close adherence of the experimental spectra to this expectation.

Our method of analysis of these spectra is derived from Simpson's[2] structure representation formalism. The observed spectra of **2**–**5** can be very simply analyzed by considering the basis functions associated with the degenerate lowest Π state of **1** to be symmetric (Ψ_s) or antisymmetric (Ψ_a) with respect to a perpendicular plane.



The tris-bridged compound **5**[3] and the metacyclophane **4** should show splittings derived from the direct (through space) interaction of the two ionic structures (Ψ_a, Ψ_s) in each of the two rings. Compound **5** shows only two bands for the four possible linear combinations [($\Psi_a + \Psi_{a'}$), ($\Psi_a - \Psi_{a'}$), ($\Psi_s + \Psi_{s'}$), ($\Psi_s - \Psi_{s'}$)] since the interaction constant between Ψ_a, $\Psi_{a'}$ and Ψ_s, $\Psi_{s'}$ (0.52 eV) must be the same. For the metacyclophane **4**, the splitting parameter between Ψ_a and $\Psi_{a'}$ will not be the same as that between Ψ_s and $\Psi_{s'}$. Four bands are thus predicted by the model. From simple geometrical consideration, the largest interaction constant is expected from the s, s′, combination and a value of 0.45 eV is derived from the spectrum by inspection. The splitting parameter for the a, a′ interaction is 0.22 eV. These are examples of a lattiresonant[4] interaction.

The tetrahydropyrene derivative **3** was chosen to reveal the strength of the longiresonant (classical conjugation) interaction. The two bridging groups, in this case, bring about near coplanarity of the two rings.[5] Again four bands split about 8.4 eV are predicted from the symmetry and geometrical relationship of the basis structures. The observed spectrum shows a pair of bands with a small coupling (S = 0.14 eV) centered at 8.45 eV which we assign to the a, a′ combinations. The small coupling is expected because of the long distance (*ca.* 3 Å) between nearest charge-bearing atoms involved in the ionization. The first band (maximum at 7.44 eV) is assigned to the antisymmetric combination of s and s′ and this gives the longiresonant splitting parameter the value of +1.01 eV.[6]

In bimesityl the two rings are oriented at 90° to one another.[7] This arrangement produces an orthogonality between the basis functions associated with the two s ionic structures and suggests that the interaction between these structures should be zero. Interaction between the a and a′ basis functions is not so restricted and would constitute an example of spiroresonant[4] interaction. The magnitude (but not the sign) of this interaction should be similar to that between the same structures in the tetrahydropyrene because the distance between interacting groups is the same. The observed spectrum of bimesityl shows characteristics consistent with this reasoning. The magnitude of the spiroresonance interaction parameter is ≤ 0.2 eV.

The principal variables in this analysis are the interaction parameters. The results are all in qualitative accord with expectations of the structure representation model. However, the small magnitude of the reduction in the interaction between s and s′ on going from the [2.2.2]cyclophane (**5**, $S_{s,s'} = 0.52$ eV) to the metacyclophane (**4**, $S_{s,s'} = 0.44$ eV) deserves comment. The through-bond interactions of the bridging groups were used, in our model, in shifting the s and a basis functions from 9.25 eV (benzene) to 8.42 eV. There is a contribution from the totally symmetric Π states for **4** (which is absent in **5**) which we have neglected but this does not appear to be a good explanation of the similarity of the two S values. A more important consideration is the quantitative nature of the atomic density distribution in the Ψ_s basis function. The effect of the three electron-donating substituents in a 1,3,5 relationship is to shift vacancy density toward the 4 position in this structure.[8] The metacyclophane **4** places two such high-density centers (4 and 4′) in close proximity. The third bridge brings the 1 and 1′ centers near to one another but the increment in interaction is not additive since the density in these regions is relatively low in the basis function itself. The magnitude of the interaction parameter is responding to the placement of the nodal surface represented in Ψ_s. Our interpretation of the 0.08-eV displacement of the center of the two first bands in **5** is strain, *i.e.*, the deviation from planarity of the two rings,[3] caused by the three bridging groups though other effects could also give rise to such shifts.

The suggested change in the nature of the a, a′ interaction from longiresonant in **3** to spiroresonant in **2** means that the corresponding splitting parameter ($S^{\theta}_{a,a'}$) should have a cos 2θ dihedral angle dependence, where θ is the angle between the planes of the two arene moieties. Using 20° for an estimate of θ in **3** and the observed splitting parameter (0.14 eV, Figure 2), one obtains eq 1.

$$S^{\theta}_{a,a'} = 0.2 \cos 2\theta \tag{1}$$

For the s, s′ interaction a cos θ dependence is suggested and a similar parameterization from the spectrum of **3** gives eq. 2.[5a]

$$S^{\theta}_{s,s'} = 1.08 \cos \theta \tag{2}$$

These equations predict that the splitting of the s, s′ states of bimesityl ($\theta \simeq 90°$) should be zero while that for the a, a′ states should be 0.4 eV ($2S^{90}_{a,a'}$). For biphenyl itself with $\theta \simeq 40°$,[9] the splitting parameter for the s, s′ interaction is estimated at 0.83 eV while that for the a, a′ interaction is 0.03 eV. The observed splittings in the spectrum of biphenyl give $S_{s,s'} = 0.8$ and $S_{a,a'} \leq 0.05$ eV. The observed spectrum of bimesityl is also consistent with these predictions, though the fit is not unambiguous.

This analysis is superficially similar to that given by Maier and Turner[10] for a series of unsymmetrically substituted biphenyls. The principal difference is in the interpretation of spectra of compounds with $90° > \theta > 45°$. The positive intercept of the regression line of that analysis[10] ignores the probable change in the assignment of the lowest ionization potential in this conformation space ($\theta > 45°$) from s, s′ to a, a′ combinations. The recently reported[11] photoelectron spectra of spiroconjugated cations adds weight to the present suggestion.

Experimental Section

The photoelectron spectra were obtained using a Perkin-Elmer PS-18 spectrometer and He(I) source. The peak positions were determined by calibration with an argon (15.76 eV)–xenon (12.13 eV) mixture. (A referee has pointed out that the PS-18 spectra should be calibrated with a low ionization potential calibrant.) Mesitylene was obtained from Matheson Chemical Co. and was purified by distillation. Bimesityl was prepared by the ferric chloride oxidation of mesitylene.[12] The [2.2.2]cyclophane **5** was prepared from the corresponding triene[13] by hydrogenation.

***anti*-6,13-Dimethyl[2.2]metacyclophane (4).** This metacyclophane was prepared by photolysis of the corresponding bis(sulfide) in the presence of trimethyl phosphite.[14]

A solution of 3,5-bis(bromomethyl)toluene[15] (33 g, 0.118 mol) in benzene (800 ml) was added by Hershburg dropping funnel at the same rate as $Na_2S \cdot 9H_2O$ (34 g, 0.142 mol) in water (200 ml), and ethanol (600 ml) was added dropwise from a second Hershburg funnel into a 5-l. Morton flask containing 95% ethanol (1 l.) with vigorous stirring, under nitrogen, at room temperature for 29 hr. The solvent was evaporated and the residue was chromatographed on silica gel using hexane to elute the bis(sulfide) 2,11-dithia[3.3]metacyclophane (**4a**). The yield was 8 g (23%), mp 100–101°, nmr ($CDCl_3$, Varian XL-100) singlet, δ 2.17 (6 H); singlet, δ 3.71 (8 H); singlet, δ 6.62 (2 H); singlet, δ 6.72 (4 H).

Anal. Calcd for $C_{18}H_{20}S_2$: C, 71.95; H, 6.71. Found: C, 71.95; H, 6.80.

This bis(sulfide) **4a** (2.0 g, 6.7 mmol) was dissolved in freshly distilled trimethyl phosphite (17 ml) and degassed by freeze–thaw. The solution, in a Vycor reaction tube, was placed in a water-cooled photolysis apparatus under nitrogen and was irradiated with a Hanovia 450-W high-pressure mercury lamp for 40 hr. The bulk of the trimethyl phosphite was removed by evaporation and the residue was chromatographed after preadsorbing on silica gel using hexane eluent. The column chromatography yielded 200 mg of **4**, mp 144–145° (lit.[15] mp 147–149°), along with unreacted bis(sulfide) (major) and the corresponding monosulfide (minor).

The tetrahydropyrene **3** was obtained by the ferric chloride oxidation of the dimethyl metacyclophane, 98% yield, mp 144–145° (lit. mp 146.5–148°).

Acknowledgment. We are grateful to the National Science Foundation and the Du Pont Co. for financial support of this work.

Registry No.—**1**, 108-67-8; **2**, 4482-03-5; **3**, 10549-25-4; **4**, 10549-23-2; **4a**, 42082-65-5; **5**, 27165-88-4; 3,5-bis(bromomethyl)toluene, 19294-043.

References and Notes

(1) (a) A previous report[1b] of the photoelectron spectrum of mesitylene gave the value of the first ionization potential as 8.65 eV. We have rechecked our measurements very carefully and found them to be quite reproducible, giving the first band maximum at 8.43 ± 0.03 eV. This value is near that reported by Watanabe[1c] from photoionization measurements. (b) M. Klessinger, *Angew. Chem., Int. Ed. Engl.*, **11**, 525 (1972). (c) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

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(3) A more complete discussion of the photoelectron spectrum of this particular compound is given by V. Boekelheide and W. Schmidt, *Chem. Phys. Lett.*, **17**, 410 (1972).

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(5) (a) The dihedral angle of 9,10-dihydrophenanthrene has been estimated at 20°. The additional two-carbon bridge in **3** would not be expected to change this value because of its geometrical equivalence with the original bridging unit. (b) A. Unanue and P. Botherel, *Bull. Soc. Chim. Fr.*, 1640 (1966).

(6) The fourth band is at lower energy (9.25 eV) than this predicts (9.46 eV). This is as it should be because of the interaction of the totally symmetric Π ion structures which we have neglected here.

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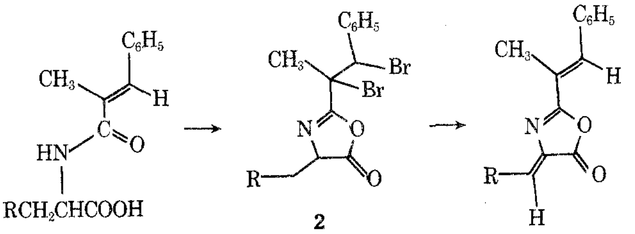
Stereoselective Formation of a Pseudo Oxazolone

Edward G. Breitholle and Charles H. Stammer*

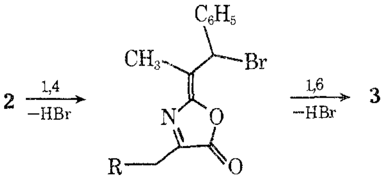
Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received December 18, 1973

It has recently been shown in our laboratories that unsaturated azlactones (**3**) can be prepared by treatment of *N*-cinnamoyl amino acids (**1**) with a pyridine perbromide–acetic anhydride–pyridine mixture.[1] This reaction most likely proceeds through a dibromo saturated azlactone (**2**), since we have shown[1] that dibromodihydrocinnamoyl amino acids also afford **3** under these reaction conditions. The halogenated intermediate, **2**, apparently undergoes a 1,4-dehydrobromination, giving a pseudo oxazolone, **4**, which again dehydrobrominates giving **3**. It was shown that the configuration of the 1-methylstyryl group was unchanged during the **1** → **3** conversion. If we assume trans bromination to give **2**, then knowledge of the steric course of the 1,4-dehydrobromination step would allow us to infer the stereochemistry of the 1,6-dehydrobromination and, consequently, the configuration of the new double bond at the 4 position. We chose to examine the stereochemistry of the 1,4 elimination by using the two diastereomers of an *N*-mandeloylphenylglycine derivative (**5**), since the required chiral starting materials are readily available. If the reaction occurs stereospecifically, the DD,LL racemate should afford one stereoisomer of the pseudo oxazolone, **6**, while its diastereomer, the DL,LD isomer, should give the other geometric isomer. Formation of the same isomer of **6** from both diastereomers of **5** would indicate that the reaction is stereoselective.



1 **2** **3**



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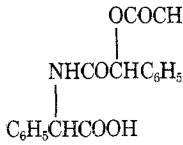
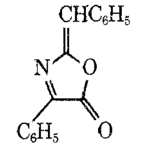
Racemic mandelic acid was O-acetylated and coupled to racemic phenylglycine to give the mandeloyl derivative **5**, which consisted of a diastereomeric mixture. When **5** was treated with an acetic anhydride–pyridine mixture the crystalline pseudo oxazolone **6** was formed. Recrystallization of crude **6** gave the pure compound having physical properties in agreement with those previously reported by Adembri.[2] Liquid chromatography of crude **6** failed to show the presence of a second oxazolone and ^{13}C nmr spectroscopy showed clearly that only one stereoisomer was present. This indicated strongly that the reaction was stereoselective, giving only the more stable product.



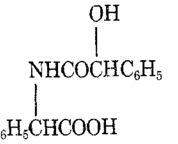
$$\begin{array}{c}\text{OCOCH}_3\\ |\\ \text{NHCOCHC}_6\text{H}_5\\ |\\ \text{C}_6\text{H}_5\text{CHCOOH}\end{array}$$

5



6

In order to check this result, the optically active mandeloylphenylglycines (**5**) were prepared. *N*-(*O*-Acetyl-D(−)-mandeloyl)-D-(−)-phenylglycine[3] and *N*-(*O*-acetyl-D(−)-mandeloyl)-L(+)-phenylglycine were prepared by the same method used to prepare the racemate. When these isomers were subjected to the acetic anhydride–pyridine treatment, the pseudo oxazolone obtained was identical in all respects with that obtained from the racemate. We were concerned that the results of these experiments might be invalidated by the possibility of racemization of the mandelic acid chiral center during the Schotten–Baumann coupling of the acid chloride with phenylglycine. In order to check this, *N*-(*O*-acetyl)-D(−)-mandelic acid was coupled with each of the enantiomers of phenylglycine methyl ester using carbodiimide, and the ester functions were saponified to give both diastereomers of *N*-mandeloylphenylglycine (**7**). The acetic anhydride–pyridine reagent converted these two compounds into the same pseudo oxazolone **6** in yields almost identical with those obtained before.



$$\begin{array}{c}\text{OH}\\ |\\ \text{NHCOCHC}_6\text{H}_5\\ |\\ \text{C}_6\text{H}_5\text{CHCOOH}\end{array}$$

7

We can conclude from these results that the 1,4 dehydrobromination of intermediate **2** is stereoselective rather than stereospecific. This means that the overall conversion of **1** → **3** is most probably stereoselective. In the six cases that we have investigated[1] so far, the *Z* isomer is formed predominantly when R is aliphatic and exclusively when R is aromatic.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer as Nujol mulls with polystyrene as a standard. The proton nuclear magnetic resonance spectra were recorded on a Varian HA-100 spectrometer with tetramethylsilane as the internal or external standard. All chemical shifts are reported in parts per million. The carbon-13 nuclear magnetic resonance spectrum was determined on a JEOL PFT-100 spectrometer. The ultraviolet–visible spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer. Melting points were uncorrected and determined on a Nagle Model Y6 hot stage. Elemental analyses were carried out by Atlantic Microlabs, Atlanta, Ga. Observed rotations were obtained on a Perkin-Elmer Model 141 polarimeter.

***O*-Acetyl-L(+)-mandelic Acid.** A mixture of 7.2 g (0.0475 mol) of L(+)-mandelic acid, $[\alpha]^{27}D$ +158° (c 1.0, H_2O) [lit.[4] $[\alpha]^{26}D$ +157° (c 1.07, H_2O)], and 20 ml (0.278 mol) of acetyl chloride was warmed on a water bath for 2 hr. The excess acetyl chloride was removed *in vacuo*, leaving a colorless oil which crystallized after 2 days. Recrystallization from benzene–*n*-hexane gave 59 g (69%) of the acid: mp 95–97.5° (lit.[5] mp 96.8°); $[\alpha]^{27}D$ +148° (c 1.87, acetone) [lit.[6] $[\alpha]^{25}D$ +153° (c 2.0, acetone)]; nmr ($CDCl_3$) δ 2.10 (s, 3 H, CH_3), 5.95 (s, 1 H, C_6H_5CHO), 7.18–7.48 (m, 5 H, C_6H_5), 11.70 ppm (s, 1 H, COOH); ir (Nujol) 1745 (C=O ester), 1700 cm^{-1} (C=O acid).