was recrystallized from ethanol–water (10:1, v/v), leading to 80% recovery of 1 without racemization.

Registry No. 1, 78603-95-9; $CH_3(CH_2)_3COCH_3$, 591-78-6; $CH_3(CH_2)_4COCH_3$, 110-43-0; $CH_3(CH_2)_5COCH_3$, 111-13-7; $(CH_3)_2CHCOCH_3$, 563-80-4; $(CH_3)_2CHCH_2COCH_3$, 108-10-1; $(CH_3)_3CCOCH_3$, 75-97-8; (*R*)-$CH_3(CH_2)_3CH(OH)CH_3$, 26549-24-6; (*R*)-$CH_3(CH_2)_4CH(OH)CH_3$, 6033-24-5; (*R*)-$CH_3(CH_2)_5CH(OH)CH_3$, 5978-70-1; (*R*)-$(CH_3)_2CHCH(OH)CH_3$, 1572-93-6; (*R*)-$(CH_3)_2CHCH_2CH(OH)CH_3$, 16404-54-9; (*R*)-$(CH_3)_3CCH(OH)CH_3$, 1572-96-9; (*S*)-valine methyl ester hydrochloride, 6306-52-1; bromo benzene, 108-86-1; borane, 13283-31-3.

Chromatographic Resolution of Perchlorotriphenylamine on (+)-Poly(triphenylmethyl methacrylate)

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Perchlorotriphenylamine (1) is the first example of an optically active compound of the type Ar_3Z in which Z is not a chiral center.[2] Optical resolution of 1 has been achieved by liquid chromatography on microcrystalline cellulose triacetate.[2] However, because this method provided only partially resolved enantiomers and resolution by other methods proved fruitless, the optical properties of the pure enantiomers remained unknown. We report here the complete resolution of 1 by high-performance liquid chromatography (HPLC) on optically active (+)-poly(triphenylmethyl methacrylate) (**2**)[3] and the optical rotation and circular dichroism of the pure enantiomers obtained.

Results and Discussion

A typical chromatogram of the resolution of 1 on the (+)-**2** column is shown in Figure 1. The amine was completely resolved and the (+)-isomer was first eluted, followed by the (−)-isomer. The separation factor α[4] was found to be 2.9 under the experimental conditions given in Figure 1. When 6 mg of (±)-1 was injected on the column, the peaks became broader and partial overlap between the enantiomers was observed. In all about 18 mg of (±)-1 was resolved on this column. Recrystallization of the resolved enantiomeric components from hexane afforded the amine of low optical rotation and the impurities eluted from the column as precipitates. The recrystallization was therefore repeated until the precipitated amine and the amine in the mother liquor showed the same optical rotations. The UV spectral pattern of the purified enantiomers is in agreement with that of (±)-1, and the HPLC analysis on the (+)-**2** column showed that these were enantiomerically pure. The specific rotations are

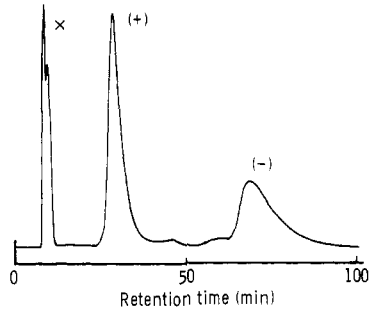

Figure 1. Chromatogram of the resolution of (±)-1 on a (+)-**2** column (30 × 2.2 (i.d.) cm). Flow rate of methanol 12 mL/min, temperature 10 °C, sample 0.6 mg. X: peaks due to CCl_4, which was used to dissolve (±)-1.

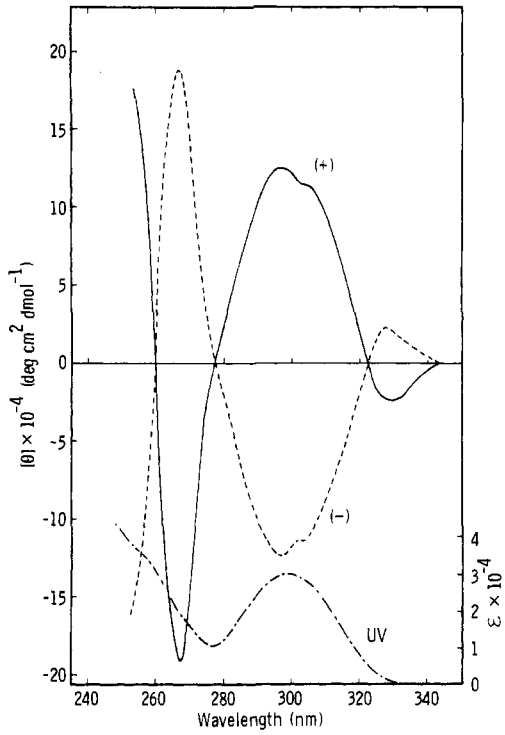

Figure 2. UV and CD spectra of (+)- and (−)-1 in CCl_4.

$[\alpha]^{25}_{435}$ +2385°, $[\alpha]^{25}_{546}$ +1193°, and $[\alpha]^{25}_{589}$ +985° (*c* 0.041, CCl_4) for the first-eluted enantiomer and $[\alpha]^{25}_{435}$ −2344°, $[\alpha]^{25}_{546}$ −1200°, and $[\alpha]^{25}_{589}$ −967° (*c* 0.018, CCl_4) for the second-eluted enantiomer. Accordingly, the optical purities of the partially resolved enantiomers[2] are only ca. 0.4% for (+)-1 and 1% for (−)-1.

The UV and circular dichroism (CD) spectra of the enantiomers of 1 are shown in Figure 2. The enantiomers exhibit the CD pattern of complete mirror images.

Experimental Section

The preparations of (±)-1,[2] (+)-poly(triphenylmethyl methacrylate)[5] and the packing material for HPLC[3] have been reported. The material was packed by the slurry method in a column (30 × 2.2 (i.d.) cm).

The chromatography was accomplished on a JASCO TRI ROTAR II chromatograph equipped with a UV detector. The temperature of the chiral column was controlled at 10 °C and methanol was used as an eluent.

The optical rotation was measured on a JASCO DIP-181 polarimeter at 25 °C. The CD spectrum was obtained with a JASCO J40 CD apparatus at room temperature. The concentrations of

(1) (a) Osaka University. (b) Princeton University.
(2) Hayes, K. S.; Nagumo, M.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2773.
(3) Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, H.; Murata, S.; Noyori, R.; Takaya, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971.
(4) α = (retention volume of more retained enantiomer − void volume)/(retention volume of less retained enantiomer − void volume). The void volume of the column was estimated to be 84 mL.
(5) Okamoto, Y.; Shohi, H.; Yuki, H. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 601.

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samples were estimated spectrophotometrically on the basis of ϵ 29 870 at 300 nm for (±)-1 in CCl_4.[2]

Registry No. (±)-1, 88130-94-3; (+)-1, 74443-33-7; (−)-1, 74453-39-7; poly(triphenylmethyl methacrylate), 27497-74-1.

The Identity of 4-Bromo-3-phenylisocoumarin.[1] A Facile Preparation by Bromolactonization of Alkyl 2-(2-Phenylethynyl)benzoates

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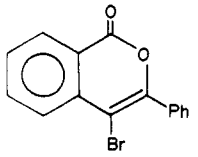
In a recent report[2] on syntheses of halo enol lactones, the title compound 1 was suggested as the product (A) of



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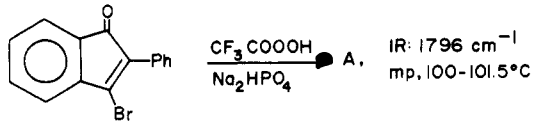
the reaction of 3-bromo-2-phenylinden-1-one (**2**) and trifluoroperacetic acid in the presence of sodium diphosphate.



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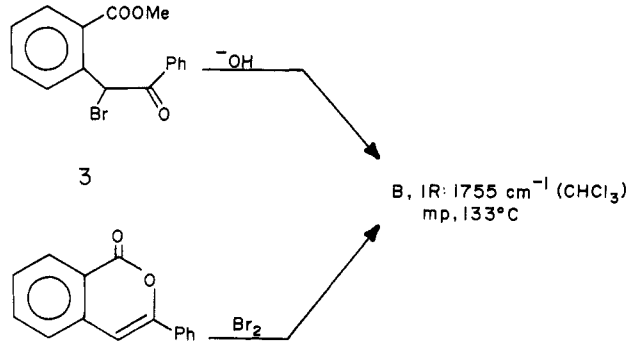
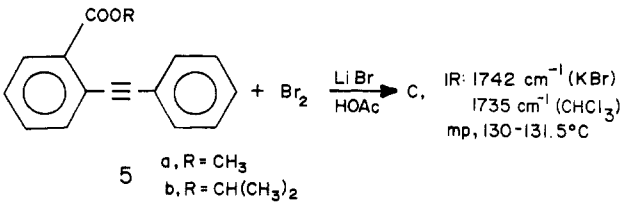
Compound 1 had been previously suggested[3] as the product (B) in the base-catalyzed cyclization of methyl 2-(1-bromo-2-oxo-2-phenylethyl)benzoate (**3**). The latter claim



3 4

was bolstered by the fact that B was isolated[3] in the bromination of 3-phenylisocoumarin (3-phenyl-1*H*-benzo-2-pyran-1-one, **4**).

This discrepancy was noticed in this laboratory as a result of an unsuccessful attempt to prepare some 1,2-dibromo-1,2-diphenylethene derivatives. Product C was isolated in 78% yield from the bromination of the substituted ethyne methyl 2-(2-phenylethynyl)benzoate (**5a**)



5 a, R = CH_3; b, R = $CH(CH_3)_2$

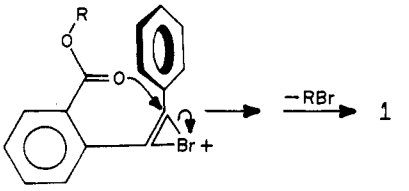
in acetic acid containing lithium bromide. The reaction was also conducted in ether and CCl_4 at temperatures ranging from −40 to 25 °C; C was the only product isolated. Bromination of the isopropyl ester **5b** at −40 °C in ether afforded C in 92% crude yield. Numerous attempts to grow a single crystal for X-ray analysis failed.

When C was treated with tributyltin hydride, **4** was the only product isolated other than starting material. The ^1H NMR spectrum and MS data of C matched those reported for B.

Based on these data, it is proposed that B and C are the same compound, viz., **1**. The carbonyl stretch for **1** lies in the reported[4] range, 1670–1755 cm^{-1}, for a series of isocoumarins. Product A is outside this range and the range reported for coumarins.[4] In the absence of data other than the IR data, a speculation is that A is the epoxide of **2**. The carbonyl stretch for A suggests a five-membered ring.

It is of interest to contrast the bromination of **5** with an ethene analogue,[5] 2-(2-phenylethenyl)benzoic acid. In the case of the latter, lactonization occurs in acetic acid or chloroform but dibromide is formed in carbon tetrachloride. No such solvent effect is observed with **5**. Whether this difference is due to the triple bond or the ester group remains to be explored.

The regioselectivity seen in the bromolactonization of **5** is predictable. Baldwin's rules[6] for cyclization permit both 6-Endo-Dig and 5-Exo-Dig, although many lactonizations of acetylenic compounds[2,7] give the exo product. In this reaction, cyclization likely occurs after formation of a bridged bromonium ion. Cyclization can then occur as a 6-Endo-Trig or 5-Exo-Trig process; both are permitted by Baldwin's rules. The factor that dominates the regioselectivity in these cyclizations is the relative charge density on the two carbons of the putative bridged cationic intermediate. For **5**, the electron-donating phenyl group stabilizes its side of the bromonium ion intermediate more so than does the (alkoxycarbonyl)phenyl group. The



(alkoxycarbonyl)phenyl group is also less effective in stabilizing positive charge on its end of the bridged ion because the cyclic transition structure constrains the π system of this aryl group to be orthogonal to the π orbitals involved in the complexing of the bromonium ion. The phenyl group, being free to rotate, can provide stabilization.[8] This stabilization likely produces the observed regiospecificity.

(1) Chemical Abstracts name: 4-bromo-3-phenyl-1*H*-benzo-2-pyran-1-one.
(2) Krafft, G. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5459–5466.
(3) Buckley, D. G.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.* **1969**, *22*, 577–95.
(4) Mallabaev, A.; Sidyakin, G. P. *Chem. Nat. Compd. (Engl. Transl.)* **1972**, 276–277 and references cited therein.
(5) Berti, G. *Tetrahedron* **1958**, *4*, 393–402.
(6) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736.
(7) Struve, G.; Seltzer, S. *J. Org. Chem.* **1982**, *47*, 2109–2113. For a recent review, see: Dowle, M. D.; Davies, D. I. *Chem. Soc. Rev.* **1979**, *8*, 171–196.
(8) We thank referee I for this suggestion.

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