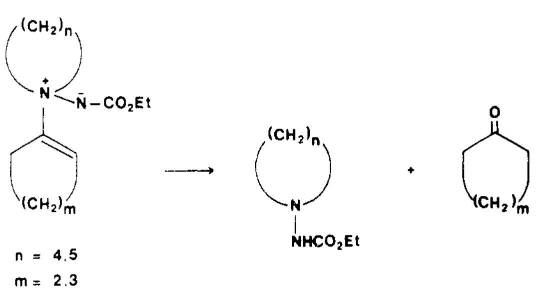
Scheme II. Degradation of Aminimides



23), 169 (23), 165 (46), 140 (46), 96 (100), 70 (69), 69 (46), 55 (23), 41 (38).

N-Cyclohexylidenepyrrolidinium perchlorate (14) was obtained as white crystals by treating **12** with 70% $HClO_4$: mp 228–229 °C (lit.[7] mp 228–229 °C); IR (Nujol) 1670 cm^{-1} (lit.[7] IR 1669 cm^{-1}).

Reaction of NBSU (1) with 14. The general procedure described for the enamines was followed, and the crude reaction mixture was analyzed by GC/MS; after a first peak identified as cyclohexanone, two further peaks were identified as **8** and **11**.

Reaction of NBSU (1) with Cyclohexanone. The general procedure described for the enamines was followed, and the only product recovered other than starting ketone was identified as N,N'-bis(ethoxycarbonyl)hydrazine.[12]

Reaction of NBSU (1) with Pyrrolidine. The general procedure described for the enamines was followed, and the crude reaction mixture was analyzed by GC. Three peaks were found, the latter of which was coincident with **11**. GC/MS confirmed the identity. No further investigation of the structures of the other two products was carried out.

Reaction of NBSU (1) with Cyclohexanone and Pyrrolidine in an Equimolar Ratio. The general procedure described for the enamines was followed, and the crude reaction mixture was analyzed by GC, showing the presence of either N,N'-bis(ethoxycarbonyl)hydrazine or the three products obtained from pyrrolidine alone.

Degradation of Aminimides. Small aliquots (0.1–0.5 mmol) of the aminimide (**7** or **13**) and 0.5 mL of 2 N HCl were placed in a sealed tube and were heated overnight at 105 °C (see Scheme II). The solution was made alkaline and was extracted with chloroform. The products (**5** or **11**) and cyclohexanone were recognized by GC, IR, ^1H NMR, and mass spectra.

Acknowledgment. This work has been financially supported by National Research Council (CNR), Rome; Progetto finalizzato "Chimica fine e secondaria".

Registry No. **1**, 2955-74-0; **2**, 1614-92-2; **3**, 83487-75-6; **4**, 83487-76-7; **5**, 4663-84-7; **6**, 2981-10-4; **7**, 83487-77-8; **8**, 13640-77-2; **9**, 7148-07-4; **10**, 83487-78-9; **11**, 83487-79-0; **12**, 1125-99-1; **13**, 83487-80-3; **14**, 18448-30-1; EtOCON, 2655-26-7; cyclohexanone, 108-94-1; pyrrolidine, 123-75-1.

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(+)- and (−)-1,1,2,2-Tetrakis(2,6-dimethyl-4-methoxy- and 4-hydroxyphenyl)ethane. First Examples of Optically Active *sym*-Tetraarylethanes: Syntheses, Chiroptical Properties, and Racemization

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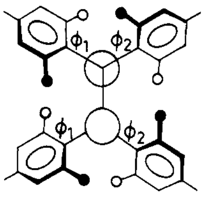
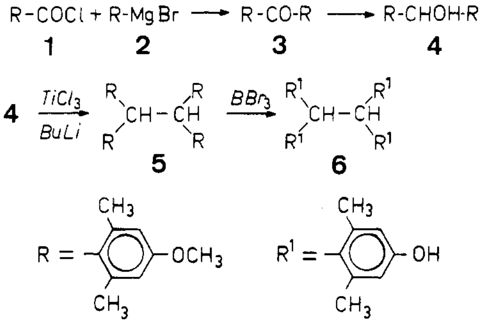


Figure 1. Propeller-shaped conformation of tetraarylethanes.

Scheme I



1,1,2,2-Tetraarylethanes adopt propeller-shaped ground-state conformations as first had been predicted by force field calculations[1,2] and may therefore be regarded as four-bladed molecular propellers.[3] In these conformations (Figure 1) (a) the ethane hydrogens are in antiperiplanar (ap) positions. (b) the signs of all dihedral angles ϕ (H–C_{ethane}–C_{aryl}–C_{ortho}) are the same (but the geminal aryls are not symmetry equivalent), and (c) tetraarylethanes with four equal aryls have C_2 symmetry and are therefore chiral. For one example (with aryl = phenyl[4]) this special type of chirality has been established in the solid state by X-ray crystal analysis.[5] By NMR spectroscopy the ap conformation in solution can be deduced from an analysis of the ^{13}C satellites of the ^1H NMR signal.[4] The feasible symmetries of *sym*-tetraarylethanes with an ap conformation correspond to the point groups C_{2h}, C_2, C_i, C_s, and C_1. A tetraarylethane with eight ortho methyls should display two (C_{2h}), four (C_2, C_i or C_s), or eight (C_1) methyl signals. Since four signals were found for tetraxylylethane[1] and the title compounds **5** and **6**, ground-state conformations C_{2h} and C_1 could be excluded in solution and the ap conformation confirmed by $^3J_{HH}$ measurements (see Experimental Section).

Results and Discussion

We have now succeeded in resolving the title compounds **5** and **6** thereby obtaining the first examples of optically active *sym*-tetraarylethanes and have therefore furnished the experimental proof for their C_2 symmetry in solution. Moreover, racemization experiments with **5** allowed the determination of $\Delta G^{\ddagger}$ for the racemization process, $\Delta G^{\ddagger}_{20}$ (93 ± 0.5 kJ mol^{-1}), being in good agreement with the value obtained for tetramesitylethane from NMR experiments.[6]

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[3] For a stereochemical discussion on molecular propellers see K. Mislow, *Acc. Chem. Res.* **9**, 26 (1976). Examples for two- and three-bladed molecular propellers are as follows: (a) optically active diarylacetic acids, O. S. Akkerman and J. Coops, *Recl. Trav. Chim. Pays-Bas*, **86**, 755 (1967); (b) perchlorotriphenylamine, K. S. Hayes, M. Nagumo, J. F. Blount, and K. Mislow, *J. Am. Chem. Soc.*, **102**, 2773 (1980).

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The method of choice for the optical resolution of a tetraarylethane with a relatively low inversion barrier seemed to be chromatography on triacetyl cellulose (at low temperature) which recently gave excellent results for resolving chiral aromatic compounds of various types[7] (see also[3b]). For this purpose a minimum solubility in ethanol or ether is required. As the above-mentioned tetraarylethanes are too insoluble, we have prepared the title compound **5** via a recently developed version of the titanium-induced reductive coupling of arylcarbinols[8] and the tetraphenol **6** by ether cleavage from **5** (Scheme I).

Optical resolutions of **5** and **6** were accomplished on triacetylcellulose in ether at 10 °C whereby (+)-**5** and (−)-**6** were eluted first (see Experimental Section).

The circular dichroism curves of (+)- and (−)-**5** are shown in Figure 2. The curves of (+)- and (−)-**6** are very similar in their shape to those of the corresponding enantiomers of **5**. It should be noted that for **5** and **6**, enantiomers of opposite rotations (and very probably of opposite chiralities) are eluted first.

At present no statements as to the optical purities and absolute configurations of the tetraarylethanes **5** and **6** can be made. Studies on these problems are being planned.

Racemization of (−)-**5** for the CD band at 242 nm at four temperatures show first-order kinetics with a half-life of 38.3 min at 21 °C and an inversion barrier $\Delta G^{\ddagger}_{20}$ of 93 ± 0.5 kJ (22.2 ± 0.1 kcal) mol^{-1}. For tetramesitylethane a $\Delta G^{\ddagger}_{134}$ of 95.5 kJ (22.8 kcal) mol^{-1} was found from NMR coalescence studies.[6]

Experimental Section

Melting points were determined on a Kofler microscope and are uncorrected. NMR spectra were obtained on a Bruker WM 250 instrument and mass spectra on a Varian MAT CH-7. Optical rotations were measured on a Perkin-Elmer 141 instrument in a 1-dm tube at 18 °C, and CD spectra were recorded on a Jobin Yvon Mark III dichrograph.

Bis(2,6-dimethyl-4-methoxyphenyl) Ketone (3). A solution of 11.5 g (53.5 mmol) of 2,6-dimethyl-4-methoxy-1-bromobenzene[9] in dry ether (50 mL) was added to 1.3 g (53.5 mmol) of Mg in 20 mL of dry ether. After the mixture was refluxed for 2 h, 6.7 g (33.7 mmol) of 2,6-dimethyl-4-methoxybenzoyl chloride (1)[10] was added, refluxing was continued for 1 h, and the mixture was poured onto crushed ice (100 g) and acidified with 6 N HCl. The ketone was collected, washed with water, dried, and crystallized from toluene–heptane: yield 4.8 g (48%); mp 155–157 °C. ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 12 H), 3.83 (s, 6 H), 6.63 (s, 4 H); mol wt $C_{19}H_{22}O_3$ 298.4; mass spectrum, *m/e* 298 (M^+).

The corresponding **diarylmethanol (4)** was obtained from the ketone **3** (4.8 g) by reduction with $LiAlH_4$ (0.92 g) in 120 mL of dry ether (2 h, room temperature). The usual workup gave 4.1 g (85%) of **4**: mp (from toluene–heptane) 122–123 °C; ^{1}H NMR ($CDCl_3$) δ 1.9 (d, 1 H, *J* = 3 Hz), 2.23 (s, 12 H), 3.82 (s, 6 H), 6.37 (d, 1 H, *J* = 3 Hz), 6.63 (s, 4 H); mol wt $C_{19}H_{24}O_3$ 300.4; mass spectrum, *m/e* 300 (M^+).

1,1,2,2-Tetrakis(2,6-dimethyl-4-methoxyphenyl)ethane (5). The reductive coupling of the Li salt of 3.0 g of **4** with $TiCl_3$ (and triethylamine) in dimethoxyethane was performed as described in ref 8. For **5**: yield 2.4 g (85%); mp 226–227 °C (from toluene–heptane); ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 6 H), 1.93 (s, 6 H), 1.98 (s, 6 H), 2.12 (s, 6 H), 3.69 (s, 6 H), 3.72 (s, 6 H), 5.35 (s, 2 H), 6.22, 6.26, 6.31, 6.46 (d, 2 H each, *J* = 3 Hz); analysis of the ^{13}C satellites of the ethane signal gave $^3J_{HH}$ = 12.2 Hz and $^2J_{^1H^{13}C}$ = 111.2 Hz; therefore, the ethane protons adopt the ap position; UV (ether) λ_{max} 212 nm (log ε 5.0), 230 (4.67), 236 (4.61), 241 (4.58), 280 (3.83), 289 (3.89); mol wt $C_{38}H_{46}O_4$ 566.8; mass spectrum, *m/e* 283 ($M^+/2$). Anal. Calcd: C, 80.53; H, 8.18. Found: C, 80.52; H, 8.22.

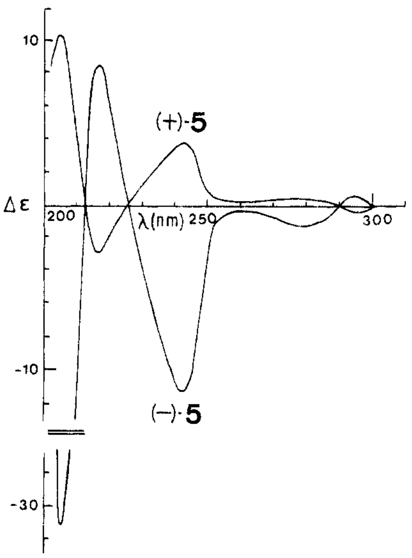

Figure 2. Circular dichroism of (+)- and (−)-tetrakis(2,6-dimethyl-4-methoxyphenyl)ethane (**5**) in ether.

Tetrakis(2,6-dimethyl-4-hydroxyphenyl)ethane (6). A solution of 2 mL (20 mmol) of BBr_3 in 50 mL of CH_2Cl_2 was added at −76 °C to a solution of 0.7 g (1.2 mmol) of **5** in 100 mL of dry CH_2Cl_2 and the mixture stirred for 12 h at room temperature. Water (100 mL) and ether (500 mL) were added at 0 °C, the organic layer was extracted with three 50-mL portions of 2 N NaOH, and the phenol **6** was precipitated by addition of 2 N HCl (pH 5–6). After being collected, washed with water, dried, and chromatographed on silica gel (5 bar, toluene–ethylacetate, 85/15) **5** was obtained: 0.5 g (82%); mp 254 °C; ^{1}H NMR (acetone-d_6) δ 1.81 (s, 6 H), 1.93 (s, 6 H), 2.00 (s, 6 H), 2.12 (s, 6 H), 5.37 (s, 2 H), 6.21, 6.27, 6.29, 6.44 (d, 2 H each, *J* = 3 Hz), 7.81 (s, 2 H), 7.86 (s, 2 H); UV (ether) λ_{max} 214 nm (log ε 4.82), 230 (4.52), 241 (4.40), 283 (3.78), 291 (3.83); mol wt $C_{34}H_{38}O_4$ 510.6, mass spectrum, *m/e* 255 and 254 ($M^+/2$), 211, 134. Anal. Calcd C, 79.95; H, 7.50. Found: C, 79.56; H, 7.53.

Chromatographic resolutions of **5** and **6** (10 mg in dioxane–ether, 1:1) were performed on a column of triacetylcellulose (1.5 × 74 cm; particle size 30–60 μm) in ether at 10 °C and 1.5 bar (97 mL/h) with UV detection (254 nm) as described in detail in ref 7. With no apparent peak separation and a very broad peak for **6**, two fractions were taken: **5**, (1) 80–100 mL and (2) 120–125 mL; **6**, (1) 250–300 mL and (2) 310–400 mL. The cold solutions were used immediately for the measurement of the optical rotations and circular dichroism (Figure 2) after dilution; concentrations were determined by UV spectrometry at 289 nm. **5** (part 1): $[\alpha]_D$ +180 ± 50° (*c* 0.009); CD Δε (λ, nm) +10.4 (205), −2.8 (217), +3.8 (242), +0.4 (279), −0.21 (292). **5** (part 2): $[\alpha]_D$ −525 ± 50° (*c* 0.009); CD Δε (λ, nm) −31.0 (205), +8.4 (217), −11.3 (242), −1.2 (279), +0.62 (292). **6** (part 1): $[\alpha]_D$ −112 ± 60° (*c* 0.007). **6** (part 2) $[\alpha]_D$ + 280 ± 90° (*c* 0.007). The CD curves of (−)- and (+)-**6** are very similar in their shape to those of (−)- and (+)-**5**, respectively (cf. Figure 2).

Kinetics. Racemization of (−)-**5** was measured by observing the decrease of the CD band at 242 nm. The measurement was carried out with the original solution from the column which was stored in an ethanol–dry ice bath to prevent racemization prior to measurement. Before being placed into the dichrograph the cuvettes were thermostated for a short period in a bath of the temperature given below. During the measurements the actual temperature in the sample compartment was determined by a thermocouple digital thermometer (±0.2 °C) [temperature (°C), τ (min), $\Delta G^{\ddagger}$ (kJ mol^{-1})]: 19.0, 45.5, 93.1 ± 0.5; 21.0, 38.3, 93.2 ± 0.5; 24.5, 25.3, 93.4 ± 0.5; 28.0, 15.0, 93.2 ± 0.5.

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Acknowledgment. This work was supported in part by the Hochschuljubiläumsstiftung der Stadt Wien and by the Fonds zur Förderung der wissenschaftlichen Forschung (under project 4009). We are indebted to Drs. E. Haslinger and A. Nikiforov for recording the NMR and mass spectra, respectively.

Absence of a Special Salt Effect in the Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Norbornene[1]

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The addition of arene and alkanesulfenyl chlorides to alkenes is known to occur in an anti stereospecific manner[2,3] and usually does not involve skeletal rearrangement or formation of large amounts of solvent-incorporated products. A major exception is the report that added $LiClO_4$ forms substantial amounts of both rearranged and solvent-incorporated products in the addition of 2,4-dinitrobenzenesulfenyl chloride to norbornene in acetic acid.[4] This effect of added salt has been attributed to the same type of special salt effect observed in solvolysis reactions.[4] However, the special salt effect is kinetic in nature[5] while added $LiClO_4$ is reported to affect only the product composition. To determine if added $LiClO_4$ also affects the rate as well as the products, we have measured the rate of addition of 2,4-dinitrobenzenesulfenyl chloride to norbornene in acetic acid at various concentrations of $LiClO_4$.

Results and Discussion

The rates of addition of 2,4-dinitrobenzenesulfenyl chloride to norbornene were measured in acetic acid at 25 °C in the presence and absence of added $LiClO_4$ by a titrimetric method.[6] The additions were found to exhibit normal second-order kinetics, first order in both alkene and sulfenyl chloride to 80% completion of the reaction. The rate data are presented in Table I.

The addition of low concentrations (10^{-5}–10^{-3}M) of $LiClO_4$ in acetic acid has no effect upon the rate of addition. This is the concentration range where $LiClO_4$ causes a special salt effect in solvolysis reactions.[5] As the $LiClO_4$ concentration is further increased, the rate begins to increase. At a $LiClO_4$ concentration of 0.536 M, the reaction occurs too fast for accurate determination of the rate constant by our technique. However, the rate increases caused by $LiClO_4$ concentrations of 0.0815 and 0.536M are about that expected from the work of Kharasch.[6]

Table I. Second-Order Rate Constants for the Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Norbornene in Acetic Acid at 25 °C in the Presence of Varying Amounts of $LiClO_4$

10^{-3}[norbornene], M	10^{-3} × [ArSCl], M	[$LiClO_4$], M	k, M^{-1} s^{-1}
5.38	4.02	0	0.107 ± 0.007
5.96	7.94	0	0.10 ± 0.01
5.38	8.06	0	0.0980 ± 0.008
8.98	6.92	0	0.114 ± 0.008
8.98	6.92	4.29 × 10^{-5}	0.113 ± 0.005
5.96	7.94	5.64 × 10^{-5}	0.103 ± 0.008
6.68	7.94	1.13 × 10^{-4}	0.10 ± 0.01
8.00	6.92	4.29 × 10^{-4}	0.10 ± 0.01
8.00	6.92	8.58 × 10^{-4}	0.100 ± 0.008
8.98	6.92	8.58 × 10^{-4}	0.103 ± 0.008
8.00	6.92	4.29 × 10^{-3}	0.092 ± 0.005
8.98	6.92	4.29 × 10^{-3}	0.101 ± 0.008
8.98	6.92	8.15 × 10^{-2}	0.126 ± 0.003
6.27	7.94	5.36 × 10^{-1}	0.5 ± 0.1

The first conclusion reached from the data in Table I is that the effect of added $LiClO_4$ is not a special salt effect. The lack of such an effect indicates that added $LiClO_4$ does not increase the electrophilicity of the arenesulfenyl chloride in this addition reaction as claimed by Zefirov.[4] From the data in Table I, further conclusions can be reached about specific details of the mechanism of arenesulfenyl chloride additions to alkenes.

The two-step mechanism originally proposed by Kharasch[7] has been expanded to include a number of ion-pair intermediates as shown in the Scheme I.[3] The existence of ion-pair intermediates in electrophilic additions has been proposed by a number of investigators.[8-11]

Structures **1** and **2** are intimate ion pairs while **3** and **4** are solvent-separated ion pairs.[12] The difference between **1** and **3** and **2** and **4** is the location of the counterion. In **1** and **3**, the chloride ion is near sulfur while in **2** and **4**, the chloride ion is near carbon. The pathway involving ions **2**, **4**, and **5** is the general solvolysis scheme proposed by Winstein.[5] The solvolysis of β-chloroalkyl aryl sulfides meets the requirements for solvolysis by means of any or all of the ions **2**, **4**, and **5**.[13] The pathway involving ions **1**, **3**, and **5** is based on a similar scheme proposed for the chlorination of alkenes.[14] The experimental data that

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