lized from 2-propanol, was found by tlc (SiO_2, MeOH in $CHCl_3$), ir, nmr and analysis to be nearly pure, and on standing in an open dish for 8 months showed little change, but on standing for 2 yr in a sealed bottle crystals had sublimed into the upper part of the bottle. These crystals were found to be methylamine *N*-methylcarbamate salt ($CH_3NH_3^+$ CH_3NHCOO^-) by ir comparison with an authentic sample. The solid remaining in the bottom of the bottle was found by tlc (SiO_2, 60% EtOAc in cyclohexane or 20% MeOH in PhH) to be essentially all **4**. This was kept under vacuum (<0.1 mm) overnight at room temperature to remove any remaining *N*-methylcarbamate salt and then a 3.14-g sample was recystallized from 2-propanol giving 3.09 g of white crystals, mp 204–208°. This is equivalent to an 80% overall yield from chlordiazepoxide. The assignment of structure **4** is based on ir, uv, nmr, mass spectrum, and analysis. The principal spectral bands are: ir (Nujol mull) 1750 (C═O), 1660, 1605 (C═N), 1325, 1220, 1040, 1010, 850, 835, 755, 705 cm^{-1} (arom and other); uv (EtOH) 218 mμ (ε 95.82) 240 (74.74), 260 (53.91), 285 (33.43), 332 (ε 6.30); nmr ($CDCl_3$) δ 3.21 and 3.27 (s, 6, CH_3), 4.87 (s, 1, CH), between 7.2 and 7.7 (m, 8, arom H's); mass spectrum M^+ 338 (1 Cl).

Anal. Calcd for $C_{18}H_{15}ClN_4O$: C, 63.81; H, 4.46; Cl, 10.46; N, 16.53. Found: C, 63.40; H, 4.38; Cl, 10.45; N, 16.51.

1-(7-Chloro-5-phenyl-3*H*-1,4-benzodiazepin-2-yl)-1,3-dimethylurea 4-Oxide (5) and 4. A solution of 3.0 g (0.01 mol) of chlordiazepoxide (base), 1.4 ml (0.01 mol) of Et_3N, and 5.9 ml (0.1 mol) of MeNCO in 50 ml of tetrahydrofuran was stirred, under N_2, at room temperature for 4.5 hr and allowed to stand at 0° for 11 days. Tlc (SiO_2, 60% EtOAc in cyclohexane) showed two spots, one moving the same as **4**. The mixture was evaporated *in vacuo*, dissolved in $CHCl_3$, washed with water, and again evaporated. The residue was crystallized first from EtOAc and then from EtOAc–$CHCl_3$ yielding 0.4 g (11%) of white crystalline **5**, mp 175–177° dec. This was shown to have the structure **5** by ir, uv, nmr, mass spectrum, and analysis. The principal spectral bands are: ir (Nujol mull) 3270 (NH), 1665 (C═O), 1610, 1545, 1510 (C═N/C═C or "amide II"), 1260, 1230, 1170, 1070, 850, 830, 765, 715, 695 cm^{-1} (arom and other); uv (EtOH) 243 mμ (ε 72.69), 277 (91.75), 320 (21.75); nmr ($CDCl_3$) δ 2.9 (d, 3, $NHCH_3$), 3.55 (s, 3, NCH_3), between 7.0 and 7.6 (m, 8, arom H's), 9.0 (br s, 1, NH); mass spectrum M^+ 356 (1 Cl).

Anal. Calcd for $C_{18}H_{17}ClN_4O_2$: C, 60.59; H, 4.80; Cl, 9.94; N, 15.70. Found: C, 60.39; H, 4.87; Cl, 10.09; N, 15.49.

The filtrate from the first crystallization of **5** was evaporated and crystallized from 2-propanol giving 0.93 g (27%) of yellow crystals whose ir was identical with that of **4** above.

10-Chloro-7,11b-dihydro-1-methyl-11b-phenyl[1,2,4]oxadiazolo[2,3-*d*][1,4]benzodiazepine-2,6(1*H*,5*H*)-dione (8) and 10-Chloro-7,11b-dihydro-1-methyl-7-(methylcarbamoyl)-11b-phenyl[1,2,4]oxadiazolo[2,3-*d*][1,4]benzodiazepine-2,6(1*H*,5*H*)-dione (9). A solution of 2.87 g (0.01 mol) of 7-chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepin-2-one 4-oxide (**6**) and 20 ml of MeNCO in 70 ml of tetrahydrofuran was stirred under N_2 at room temperature for 22 hr. The resulting solid was collected, yielding 1.4 g (41%) of white crystals, mp 213.5–214.5° dec. Recrystallization from 2-methoxyethanol gave white crystals with the same melting point. Ir, nmr, mass spectrum, and analysis showed this to have the structure **8**. The principal spectral bands are: ir (Nujol mull) 3220 (NH), 1740, 1690 (C═O), 1485, 1240, 1215, 815, 755, 700 cm^{-1} (arom and other); nmr (at 100° in DMF-d_7) δ 2.8 (s, 3, CH_3), 5.2 (br s, 2, CH_2), 8.2 (s, 1, NH), between 6.6 and 8.1 (m, 8, arom H's); mass spectrum M^+ 5343 (1 Cl).

Anal. Calcd for $C_{17}H_{14}ClN_3O_3$: C, 59.40; H, 4.10; Cl, 10.31; N, 12.22. Found: C, 59.37; H, 3.97; Cl, 10.42; N, 12.57.

To the filtrate from **8** was added 10 ml more of CH_3NCO and the solution was allowed to stand at room temperature for 6 days. Evaporation *in vacuo* gave a residue showing only one spot on tlc (SiO_2, 60% EtOAc in cyclohexane) moving differently from **8** and starting material. Crystallization from 2-propanol yielded 2.0 g (50%) of white crystals, mp 158–161° dec, which was found by ir, nmr, mass spectrum, and analysis to have the structure **9**. The principal spectral bands are: ir (Nujol mull) 3340 (NH), 1775, 1730, 1690 (C═O), 1505, 1190, 745, 700 cm^{-1} (arom and other); nmr ($CDCl_3$) δ 2.5 (d, 3, $NHCH_3$), 2.7 (s, 3, NCH_3), ab centered at 3.4 and 4.1 (s, *J* = −10 Hz, CH_2), between 7.2 and 7.75 (m, 8, arom H's); mass spectrum M^+ 400 (1 Cl).

Anal. Calcd for $C_{19}H_{17}ClN_4O_4$: C, 56.93; H, 4.28; Cl, 8.84; N, 13.98. Found: C, 56.98; H, 4.67; Cl, 8.90; N, 14.32.

10-Chloro-7,11b-dihydro-1,7-dimethyl-11b-phenyl[1,2,4]oxadiazolo[2,3-*d*][1,4]benzodiazepine-2,6(1*H*,5*H*)-dione (10). A solution of 6.0 g (0.02 mol) of 7-chloro-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one (**7**) and 25 ml of MeNCO in 100 ml of tetrahydrofuran under N_2 was stirred under reflux for 25 hr. Evaporation *in vacuo* gave a gum which crystallized from 2-propanol yielding 6.97 g (97.5%) of white crystals, mp 166–168° dec. Ir, nmr, mass spectrum, and analysis confirm the structure **10**. The principal spectral bands are: ir (Nujol mull) 1770, 1675 (C═O), 1595, 1485, 1120, 1075, 830, 760, 745, 705 cm^{-1} (arom and other); nmr ($CDCl_3$) δ 2.58 (s, 3, NCH_3), 2.70 (s, 3, NCH_3), ab centered at 3.5 and 4.55 (2, *J* = −10 Hz, CH_2), between 7.15 and 7.75 (m, 8, arom H's); mass spectrum M^+ 357 (1 Cl).

Anal. Calcd for $C_{18}H_{16}ClN_3O_3$: C, 60.43; H, 4.51; Cl, 9.91; N, 11.74. Found: C, 60.63; H, 4.90; Cl, 9.74; N, 11.34.

Ethyl 10-Chloro-1,2,5,6,7-11b-hexahydro-7-methyl-2,6-dioxo-11b-phenyl[1,2,4]oxadiazolo[2,3-*d*][1,4]benzodiazepineacetate (11). Similarly 6.0 g (0.02 mol) of **7** in 100 ml of tetrahydrofuran was treated under N_2 with 12.9 g (0.01 mol) of ethyl isocyanatoacetate, stirred under reflux for 7 hr, and allowed to stand at room temperature for 18 hr. The solution was filtered, evaporated at 50° (0.1 mm), mixed with xylene, and again evaporated. The resulting gum crystallized on triturating with ether and was recrystallized from 2-propanol yielding 7.67 g (95%) of white crystals, mp 160.5–162°. Ir, nmr, mass spectrum and analysis confirm the structure **11**. The principal spectral bands are: ir (Nujol mull) 1775, 1745, 1680 (C═O), 1485, 1310, 1225, 1185, 1170, 1145, 830, 790, 700 cm^{-1} (arom and other); nmr ($CDCl_3$) δ 1.05 (t, 3, CH_2CH_3), 2.53 (s, 3, NCH_3), between 3.4 and 4.5 (m, 6, CH_2's), between 7.15 and 7.75 (m, 8, arom H's); mass spectrum M^+ 429 (1 Cl).

Anal. Calcd for $C_{21}H_{20}ClN_3O_5$: C, 58.68; H, 4.69; Cl, 8.25; N, 9.78. Found: C, 58.33; H, 4.64; Cl, 8.54; N, 9.77.

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Registry No. 1, 58-25-3; **2,** 49626-75-7; **3,** 49626-76-8; **4,** 49626-77-9; **5,** 49626-78-0; **6,** 963-39-3; **7,** 2888-64-4; **8,** 49626-81-5; **9,** 49626-82-6; **10,** 49626-83-7; **11,** 49626-84-8.

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Preferential Complexation of One of the Diastereomers of 1,2-Diazido-1,2-di-*tert*-butylethane with an Europium Nuclear Magnetic Resonance Shift Reagent[1]

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The reaction of olefins, ceric ammonium nitrate (CAN), and azide ion usually gives α-azido-β-nitratoalkanes;[2] however, α,β-diazidoalkanes have been obtained from sterically hindered olefins.[3] The reaction of 1 mol of *trans*-1,2-di-*tert*-butylethene with 2 mol of CAN and 1 mol of sodium azide in 10% aqueous acetonitrile at 0° gives a *ca.* 5% yield of comparable amounts of *meso*- and *dl*-1,2-diazido-1,2-di-*tert*-butylethane.[4] These diastereo-

Table I
Chemical Shifts of Hydrogens of Di-*tert*-butylethene and the Diastereomers of 1,2-Diazido-1,2-di-*tert*-butylethane in the Presence of Increasing Amounts of $Eu(fod)_3$[a]

	Chemical shifts, δ					
	Olefin		Isomer A		Isomer B	
$Eu(fod)_3$, mmol	$-CH=$	$-CH_3$	$>CHN_3$	$-CH_3$	$>CHN_3$	$-CH_3$
	5.15	0.94	2.90	1.03	2.98	1.01
0.003	5.15	0.93	2.90	1.06	3.04	1.06
0.005	5.16	0.93	2.91	1.05	3.20	1.11
0.007	5.17	0.96	2.90	1.05	3.41	1.18

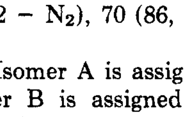
[a] Spectra were obtained on a Varian A-60 spectrometer using 0.3 ml of CCl_4 as solvent at ambient temperatures with 0.015 mmol of isomer A, 0.023 mmol of isomer B, and 0.184 mmol of starting material. $Eu(fod)_3$ was dried for at least 24 hr over P_2O_5 before use.

mers were separated by chromatography on silica gel using pentane as the eluent.

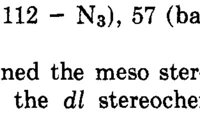
Isomer A (eluted first) had nmr ($CDCl_3$) δ 2.98 (s, 1) and 1.05 (s, 9); ir ($CHCl_3$) 2970 (s), 2940 (s), 2880 (s), 2100 (s), 1470 (m), and 1380 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity, fragment) 126 (67, $P^+ - C_4H_8N_3$), 112 (33, HCN_3Bu-*t*), 84 (83, 112 − N_2), 70 (100, 112 − N_3), 57 (base, very intense, Bu-*t*).

Isomer B (eluted second) had nmr ($CDCl_3$) δ 3.14 (s, 1) and 1.05 (s, 9); ir ($CHCl_3$) 2970 (s), 2940 (s), 2880 (s), 2100 (s), 1470 (m), 1380 (m), and 1340 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity, fragment) 224 (9, P^+) 126 (23, $P^+ - C_4H_8N_3$), 112 (41, HCN_3Bu-*t*), 84 (100, 112 − N_2), 70 (86, 112 − N_3), 57 (base, very intense, Bu-*t*).

Isomer A is assigned the meso stereochemistry and isomer B is assigned the *dl* stereochemistry since europium(III) tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, $Eu(fod)_3$, did not affect the nmr spectrum of isomer A but did affect both nmr signals of isomer B. This preferential interaction of $Eu(fod)_3$ with isomer B is clearly shown by the results of an nmr study of a 8:~1:~1 mixture of starting olefin, isomer A, and isomer B. As shown in Table I, as the amount of $Eu(fod)_3$ was increased, the shifts of the signals for the protons on the carbon atoms bearing the azide groups and the protons of the *tert*-butyl groups increased for isomer B, but those for the starting olefin and isomer A were unchanged. We believe that this preferential interaction means that only one isomer can form a bidentate chelate to the europium which involves both azide groups. The steric interaction of the two bulky *tert*-butyl groups accounts for this difference in stability of the chelates from the *dl* and meso isomers since the two *tert*-butyl groups would be trans to each other on the chelate ring formed from the *dl* isomer (conformations 1 or 2) but would be cis to each other on the chelate ring formed from the meso isomer (3).[5] Evidently, a single azide group does not form strong complexes with the nmr shift reagents, which no doubt accounts for the lack of any report of shifts induced in alkyl azides by paramagnetic reagents.[6-9]



1



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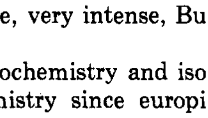

3

Unequal shifts of nmr signals of diastereomers by paramagnetic reagents have been reported[10-13] but in all cases both diastereomers, not just one, were affected.

The present results appear to be strong evidence for chelation of a substrate to an nmr shift reagent, a phenomenon which has received little or no support from previous reports.[6-9,14,15]

The effects on the nmr spectrum of a mixture of the starting olefins and isomers A and B by the chiral shift reagent, tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium,[13,16] were the same as those of $Eu(fod)_3$. No difference between the shifts of the enantiomers of the *dl* pair was noted, a finding which is not surprising since only small differences in shifts of the signals for other pairs of enantiomers induced by chiral reagents have been reported.[13,16]

Experimental Section

Methods and Materials. Most equipment and methods have been previously described.[17] *trans*-Di-*tert*-butylethene was obtained from Chemical Samples Co., $Eu(fod)_3$ as obtained from Norell Chemical Co., and tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium was obtained from Alfa Products of Ventron Corp.

***meso*- and *dl*-1,2-Diazido-1,2-di-*tert*-butylethanes.** A quantity of 0.49 g (3.5 mmol) of *trans*-di-*tert*-butylethene and 0.26 g (4.0 mmol) of sodium azide were dissolved in 6 ml of 50% aqueous acetonitrile in a flask immersed in an ice bath. To this mixture approximately 16 ml of an 0.5 *M* solution of CAN in acetonitrile was added slowly and dropwise. During the addition the orange color of the CAN changed to light yellow and gas evolution occurred. The reaction was complete when the addition was over. This mixture was poured into water and extracted twice with pentane and twice with methylene chloride. The methylene chloride extract yielded no organic compounds. The pentane extracts were combined, concentrated, and chromatographed as described above to give the two isomeric diazides whose spectral properties are given above.

Yields of the products were determined by adding mesitylene to the product mixture after work-up and analyzing the mixture by nmr spectroscopy (the signals for the aromatic protons of mesitylene, the protons α to the azido groups, and the olefinic protons of the starting material were integrated). For three runs, 2.6 ± 0.6% of the *dl* diazide, 2.0% of the meso diazide, and 71 ± 3% of the starting olefin was obtained. In all runs, a large amount of nitrogen was evolved.

Registry No. *meso*-1,2-Diazido-1,2-di-*tert*-butylethane, 42915-91-3; *dl*-1,2-diazido-1,2-di-*tert*-butylethane, 42915-92-4; *trans*-di-*tert*-butylethene, 692-48-8; $Eu(fod)_3$, 17631-68-4.

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