mol) of **16** were obtained from thick-layer chromatography one minor and two major products. From the middle of the plate, 0.125 g (70%) of an orange solid, compound **17**, was isolated; mp 139–160 °C (softening at 55 °C). From the base of the plate was isolated 0.063 g of a yellow solid, which appeared by IR to be a mixture of compound **18** and *p*-chlorobenzoic acid **19**. Between the two previously discussed bands, 0.023 g of a red-orange oily substance was obtained, which had a broad carbonyl absorption at 1739–1668 cm^{-1} in the IR spectrum.

Compound **17** upon recrystallization (EtOH) yielded 0.054 g of fluffy orange crystals: mp 169–172 °C; mixture melting point with an authentic sample (mp 173–174 °C, see below) melted at 173–174 °C. Its IR spectrum was identical with that of the authentic sample.

The products from the base of the plate were fractionally crystallized (EtOH). Their IR spectrum was identical, peak for peak, with that obtained by superimposing those of authentic samples of **18** and **19**; mass spectrum, *m/e* calcd for $C_{22}H_{15}O_3Cl$ (**18**) 362.0708, found 362.0713; *m/e* calcd for $C_7H_5O_2Cl$ (**21**) 155.9978, found 155.9964. [This is outside the standard error limits. The large deviation (9.03 ppm) of the measured mass may have been due to an unresolved doublet.]

3-(*p*-Chlorobenzoyloxy)-2-phenyl-1-indenone (17). Compound **17** was prepared by a modification of the procedure for the preparation of the authentic sample of compound **6**. In a round-bottomed flask equipped with a condenser and drying tube, 3.959 g (1.78 × 10^{-2} mol) of 2-benzoyl-2-phenyl-1*H*-indene-1,3-(2*H*)-dione was heated to reflux with 6.8 mL (5.35 × 10^{-2} mol) of *p*-chlorobenzoyl chloride for 30 min. The reaction mixture was cooled, and an orange precipitate formed. The precipitate was collected by filtration and the excess acid chloride rinsed off with chilled pentane, yielding 7.276 g of orange product, mp 109–238 °C. The product was recrystallized (EtOH) and yielded 3.519 g (53%) of fluffy orange product, mp 170–171 °C (softening at 160 °C). A sample was prepared for analysis (EtOH) and melted at 173–174 °C: IR (KBr) 1741 (C=O), 1719 (C=O), 1617 cm^{-1} (C=C); mass spectrum, *m/e* calcd for $C_{22}H_{13}O_3Cl$ 360.0549, found 360.0544.

Anal. Calcd for $C_{22}H_{13}O_3Cl$: C, 73.24; H, 3.63; Cl, 9.83. Found: C, 73.02; H, 3.84; C, 10.22.

Acknowledgment. We wish to thank the University of Connecticut Research Foundation and the American Cyanamid Co. for stipends to J.S.W.

Registry No. **1**, 71627-60-6; **5**, 30336-09-5; **6**, 25098-00-4; **7**, 31590-00-8; **8**, 83-12-5; **16**, 71749-99-0; **17**, 71785-22-3; **18**, 71750-00-0; **19**, 74-11-3; **20**, 71750-01-1; diphenylmaleic anhydride, 4808-48-4; *α*-bromo-*α*-phenylacetonitrile, 5798-79-8; bromobenzene, 108-86-1; *tert*-butyl hydroperoxide, 75-91-2; *p*-bromochlorobenzene, 106-39-8; 2-benzyl-2-phenyl-1*H*-indene-1,3(2*H*)-dione, 69808-15-7; *p*-chlorobenzoyl chloride, 122-01-0.

Hindered Bis(*cis*-alkenyl)durene and Bis(*cis*-alkenyl)mesitylene: Preparation by Selective Photosensitized Isomerization and Hindered Rotation by Dynamic Nuclear Magnetic Resonance

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Received May 30, 1979

Recently we demonstrated that selective photosensitization is a useful method for preparation of hindered cis olefins, particularly those with a chromophore in a much more skewed conformation than the corresponding trans olefin.[1] In many cases, the conversion from trans to cis can be forced into one direction, thus giving quantitatively the cis isomer.

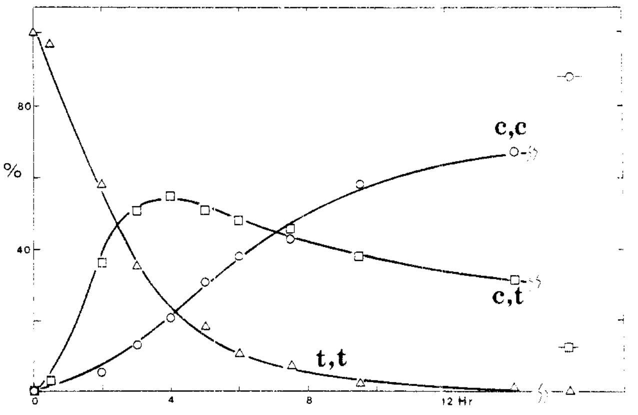
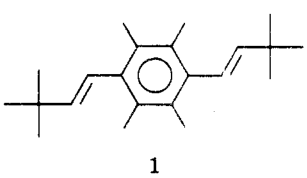


Figure 1. Time plot of triphenylene-photosensitized isomerization of the t,t isomer (Δ) of compound 1. The point corresponding to the longest period of irradiation was obtained after 23 h of exposure.

When applied to the aromatic series we showed that the method is useful for preparation of a series of homologous hindered styrenes.[2] As demonstrated by Adams and coworkers many years ago,[3] steric hindrance in such styrenes results in slow interconversion of enantiomeric conformers which we were also able to demonstrate with the aid of a chiral shift reagent. We now would like to report results of studies on two hindered bis(alkenyl) aromatic compounds, both on their photochemical and conformational properties.

Results and Discussion

Two compounds were prepared in this study: bis(3,3-dimethyl-1-butenyl)durene (**1**) and bis(3,3-dimethyl-1-butenyl)mesitylene (**2**). The trans,trans (t,t) isomers of both compounds were obtained via identical reaction sequences of bis acylation of the parent aromatic hydrocarbons and reduction by $LiAlH_4$ followed by acid-catalyzed dehydration. The only step that presented some difficulties was the reduction step. Due to severe steric crowding, the reaction proceeded very slowly. Only after rather long reaction times were good yields of diols possible.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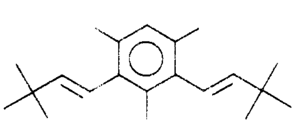
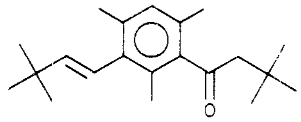

2


3

Photosensitized Isomerization. Upon sensitized irradiation of either **1** or **2**, the formation of two products, one dominant during early stages of irradiation, was detected by GLC analyses of the reaction mixtures. In the case of triphenylene-sensitized reactions, the processes during early stages were followed closely. The resultant time plots are shown in Figures 1 and 2. The buildup of the first photoproduct is particularly evident in the case of **2**. But, in both cases, this early product as well as the

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[1] Ramamurthy, V.; Butt, Y.; Yang, C.; Yang, P.; Liu, R. S. H. *J. Org. Chem.* **1973**, *38*, 1247–1249.

[2] Yang, C. S. C.; Liu, R. S. H. *Tetrahedron Lett.* **1973**, 4811–4814.

[3] Adams, R.; Mecorney, J. W. *J. Am. Chem. Soc.* **1945**, *67*, 798–802 and previous papers in the series.

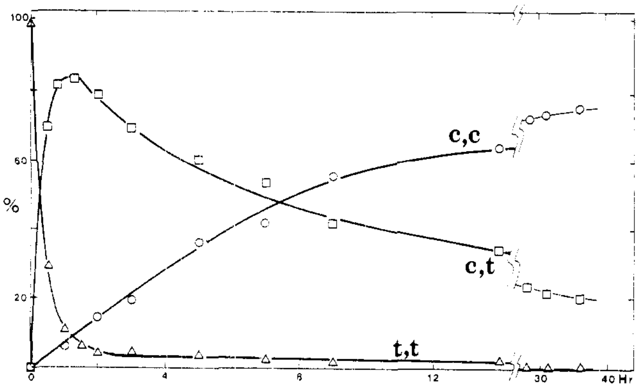


Figure 2. Time plot of triphenylene-photosensitized isomerization of the t,t isomer (Δ) of compound **2**.

Table I. Photostationary State Composition of Compounds 1 and 2 as a Function of Sensitizer Energy[a]

		% **1**			% **2**		
sensitizer	E_T	t,t	t,c	c,c	t,t	t,c	c,c
xanthone	74.2				0	30	70
benzophenone	68.5	0	14	86	0	5	95
triphenylene	66.6				0	5	95
β-naphthylphenyl ketone	59.6[b]	5	84	11	0	13	87
β-acetonaphthone	59.3[b]	0	21	79	0	37	63
fluorenone	53.3[b]				100	0	0

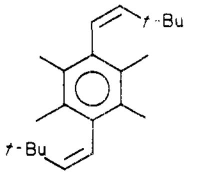
[a] Concentration of sensitizer = 0.05 M; concentration of t,t, the starting isomer = 0.005 M. [b] Reaction proceeded more slowly; photostationary state possibly not reached.

starting material gave way to predominantly one final product, which was isolated by preparative GLC. From the ^{1}H NMR spectra (see below) the compounds were characterized as the corresponding cis,cis (c,c) isomers. It is, therefore, reasonable to assume that the first major photoproduct is the cis,trans (c,t) isomer. This assignment was supported by ^{1}H NMR spectra of mixtures of products during early stages of reaction.

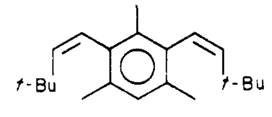
The difference in the extent of initial buildup of intermediate c,t isomer in the two cases is probably a reflection of possible through-ring resonance interaction of the two double bonds in **1**, but not in **2**. Such interaction leads to possible direct conversion from t,t to the c,c isomer.

The final stationary state compositions appear to depend on the nature of the sensitizer employed (Table I). It is interesting to note that in neither case did we accomplish quantitative conversion to the c,c isomer. On the other hand, benzophenone-sensitized isomerization of **3** gave quantitatively the corresponding cis isomer. The latter observation is consistent with our earlier observation on other styrene derivatives.[2]

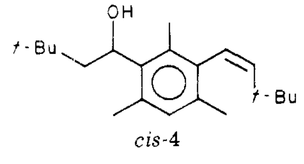
Restricted Rotation in the Hindered Cis Isomers. The ^{1}H NMR spectra of the c,c, isomer of **1** and **2** are temperature dependent. At room temperature, the high-field signals of *c,c*-**1** are two singlets (2:1) at 0.83 and 0.86 ppm. In contrast the high-field *tert*-butyl signal of *t,t*-**1** appears at 1.17 ppm. The shift toward high field is consistent with a change of the geometry of the olefinic linkage. The *tert*-butyl groups of *t,t*-**1** are now in the shielding region of aromatic ring current. The same observation was noted in a closely related homologous series of styryl derivatives.[2] Similarly for compound **2**, the chemical shift of the *tert*-butyl group shifted from 1.12 ppm for the t,t, isomer to 0.90 and 0.94 ppm (1:1.3) for the c,c isomer.



c,c-**1**

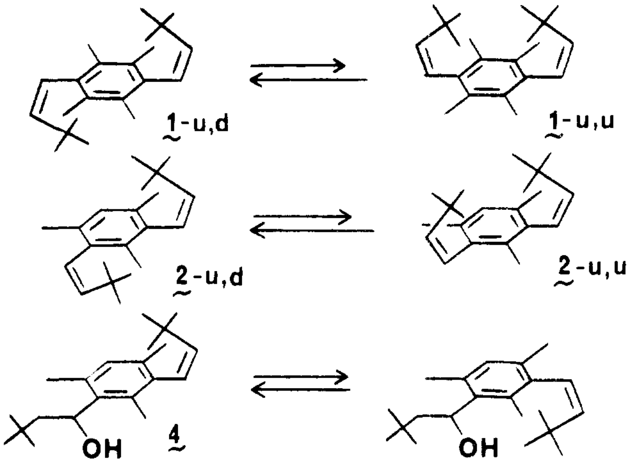


c,c-**2**



cis-**4**

Scheme I



Upon warming samples of compound *c,c*-**1** and *c,c*-**2** to temperatures above 100 °C their spectra exhibit features characteristic of activated two-site exchange: the high-field singlets first broadened, coalesced, and then sharpened to an averaged singlet. The coalescence temperatures for the two compounds were 125 (**1**) and 112 °C (**2**). The approximate free energies of activation for the two processes were calculated to be 21.5 and 20.0 kcal/mol for *c,c*-**1** and *c,c*-**2**.[4]

Similarly, compound **4** exhibits identical dynamic NMR behavior (for details see Experimental Section) with a similar free energy of activation ($\Delta G^{\ddagger}$ = 21.5 kcal/mol). On the other hand, the mono- or ditrans isomers of **1**, **2**, and **4** did not show temperature dependence in their ^{1}H NMR spectra.

Considering the known properties of hindered styrenes, it appears reasonable to assume that the observed dynamic behavior is due to a slow rate of interconversion of the rotational isomers created by the considerable steric interaction between the *tert*-butyl and the ring methyl groups. The room temperature spectra of *c,c*-**1** *c,c*-**2**, and *cis*-**4** are therefore those of the diastereomeric mixtures (Scheme I). We have not succeeded in isolating any of these conformers, even though the height of the barriers suggests this possibility. Perhaps some additional modifications of the molecule will facilitate isolation of the diastereomers.

The direction of the equilibria appears intuitively reasonable. However, if one invokes the idea of steric attraction,[5] the opposite direction will be predicted. In an attempt to clarify the situation we conducted an experiment to force the equilibrium of the diastereomers of *c,c*-**1**

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(4) The coalescence temperature approximation was used for calculation of the activation parameters. Because of unequal site population, the calculated numbers are only qualitatively meaningful. The approach is perhaps partially justified by the more equal population of the two sites at elevated temperatures.

(5) See, e.g., Carter, R. E.; Stilbs, P. *J. Am. Chem. Soc.* **1976**, *98*, 7515–7521.

to the u,u conformer by adding a π-acid such as tetracyanoethylene, benzoquinone, or dinitrobenzene to the NMR samples. Although an immediate coloration was noticed (particularly in the case of tetracyanoethylene), we did not, unfortunately, detect a significant change of the ratio of the high-field singlets.

Experimental Section

General Procedure. All ^{1}H NMR spectra were recorded on a Varian HA-100 spectrometer. VPC analyses were conducted on a Varian 2800 chromatograph equipped with a flame ionization detector using either a SE-30 or a QF-1 column ($^1/_8$ in. × 8 ft). Preparative runs were conducted on a Varian 90-P instrument. All irradiation was carried out on a "merry-go-round" apparatus[6] with irradiation samples degassed and sealed in the usual manner.[7]

Bis(3,3-dimethylbutyroyl)durene (7). The Friedel-Crafts reaction was conducted in the usual manner. A mixture of 40 g (0.3 mol) of anhydrous $AlCl_3$, 200 mL of CS_2, 28 mL (0.2 mol) of dimethylbutyroyl chloride, and 6.78 g (0.05 mol) of durene after refluxing for 10 h and usual workup yielded 12.5 g of a white crystalline solid (78%), mp 221–222 °C, after recrystallization from benzene. The spectral data are consistent with the expected bis acylated product: ^{1}H NMR ($CDCl_3$) δ 1.24, 2.19, 2.86 (3 s, relative intensity 9:6:2); MS M^+ 330; IR (Nujol) 1680 cm^{-1}.

Bis(1-hydroxy-3,3-dimethyl-1-butyl)durene (8). Diketone 7 (9.9 g, 0.03 mol) was reacted with 8.48 g (0.3 mol) of $LiAlH_4$ at refluxing THF (250 mL) for 2 days giving 6.11 g of the diol: ^{1}H NMR ($CDCl_3$) δ 5.3 (diastereotopic AB signals). Without further purification the crude product was used for the next step.

Bis(3,3-dimethyl-1-butenyl)durene (1). Dehydration of the diol 8 (5.0 g) was accomplished with the aid of a Dean-Stark trap with 250 mL of benzene and catalytic amounts of β-naphthalenesulfonic acid. The hydrocarbon was purified by chromatography on a silica gel column, giving 1.68 g of a white solid (12.5% yield from 8). Spectral data are consistent with the expected product with the t,t geometry: ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 18 H), 2.20 (s, 12 H), 5.58 (d, 2 H, J = 17 Hz), 6.30 (d, 2 H, J = 17 Hz); MS M^+ 298; IR (neat) 968, 1360, 1460 cm^{-1}.

***cis,cis*-1.** A solution of 0.2 g of *t,t*-1, 0.5 g of benzophenone, and 25 mL of hexane was deoxygenated with a stream of N_2 and irradiated with light ≥320 nm. The end mixture contained approximately 85% *c,c*-1 and 15% *c,t*-1. The dicis isomer, a viscous oil, was purified by preparative GLC: ^{1}H NMR ($CDCl_3$, room temperature) δ 0.83, 0.86 (*tert*-butyl, 2:1), 2.18, 2.20 (benzylic CH_3's, 1:2), 5.55 (d), 6.18 (2 d, coupled vinylic H's, J = 12.5 Hz).

Bis(3,3-dimethylbutyroyl)mesitylene (9) was obtained in the same manner as 7: 62% yield; mp 108–109 °C; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 18 H), 2.08 (s, 3 H), 2.16 (s, 6 H), and 2.58 (s, 4 H); MS M^+ 316.

Bis(3,3-dimethyl-1-butenyl)mesitylene (2) was obtained by $LiAlH_4$ reduction of 9 followed by acid-catalyzed dehydration following the procedure described for 8 and 1. The reduction reaction apparently failed to reach completion because, from the final product mixture, the expected product 2, mp 34.6–36 °C (44%), was isolated along with small amounts (13%) of the ketostyrene 3. The spectral data for 2 are: ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 18 H), 2.21 (3, 9 H), 5.60 (d, 2 H, J = 17 Hz), 6.18 (d, 2 H, J = 17 Hz); MS M^+ 284; IR (Nujol) 955, 1250, 1346, 1445 cm^{-1}. And those for 3 are: ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 18 H), 2.12, 2.18 (6 s, 9 H), 2.58 (s, 2 H), 5.65 (d, 1 H, J = 17 Hz), 6.13 (d, 1 H, J = 17 Hz); IR 960, 1350, 1450, 1695 cm^{-1}.

***cis,cis*-2** was obtained in the same manner as *cis,cis*-1: ^{1}H NMR ($CDCl_3$, room temperature) δ 0.90, 0.94 (s, 1:1.3, *tert*-butyl), 2.16 (br s, benzylic CH_3's), 5.48 (d, J = 12.5 Hz), 5.95, 6.03 (two sets of d, J = 12.5 Hz). See text for high-temperature spectra.

***cis*-3** was obtained by irradiation in the presence of benzophenone. The conversion was complete within 3 h. The product was isolated by column chromatography on silica gel (petroleum ether 30–60 °C): ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 9 H), 1.15 (s, 9 H), 2.15–2.2 (3 s, 9 H), 2.60 (s, 2 H), 5.62 (d, 1 H, J = 13 Hz), 6.00 (d, 1 H, J = 13 Hz), 6.84 (br s, 1 H).

***cis*-4** was obtained by $LiAlH_4$ reduction of *cis*-3 in a manner similar to that described for 8. The product was isolated by chromatography over silica gel (benzene): ^{1}H NMR ($CDCl_3$) δ 0.89, 0.92 (2 s, 9 H), 1.06 (s, 9 H), 1.36 (d, 1 H), 1.47 (s, 1 H), 2.02 (dd, 1 H), 2.16 (s, 3 H), 2.36 (br s, 6 H), 5.20 (d, 1 H), 5.55, 5.98 (d and d, 1 H, 1 H, J = 13 Hz), 6.66 (s, 1 H). At temperatures above 130 °C the two high-field singlets coalesce into an averaged singlet. At room temperature in the presence of Eu(fod)$_3$ shift reagent, the singlet at δ 1.06 also split into two singlets. IR (neat) 735, 1360, 1470, 3480 cm^{-1}.

Acknowledgment. The work was partially supported by a grant from the National Science Foundation (CHE-15233).

Registry No. *t,t*-1, 71734-33-3; *c,c*-1, 71734-34-4; *c,t*-1, 71734-35-5; *t,t*-2, 71766-68-2; *c,c*-2, 71734-36-6; *trans*-3, 71734-37-7; *cis*-3, 71734-38-8; *cis*-4, 71734-39-9; 7, 71734-40-2; 8, 71734-41-3; 9, 71734-42-4; dimethylbutyroyl chloride, 7065-76-5; davene, 95-93-2.

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[6] Moses, F. G.; Liu, R. S. H.; Monroe, B. *Mol. Photochem.* **1969**, *1*, 245–249.

[7] See e.g., Liu, R. S. H.; Turro, N. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 3406–3412.

Conversion of Nitriles to Amides and Esters to Acids by the Action of Sodium Superoxide

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Received June 18, 1979

To our surprise, we have found that sodium superoxide smoothly converts nitriles to amides at room temperature. The utility of this transformation is apparent from Table I, in which yields refer to pure isolated products.

Our surprise derives from the fact that the cyano group is reported to be stable to superoxides.[1-3] It well may be that our choice of solvent is responsible for the discrepancy; whereas previous workers used benzene,[1] pyridine,[2] and acetonitrile,[2] we employ Me_2SO. Another, probably less significant, difference is that the previous workers used potassium superoxide and 18-crown-6 ether (to enhance the solubility of the superoxide), while we employ the sodium salt without a crown ether.

Our understanding of the mechanism of this conversion of a nitrile to an amide by sodium superoxide is meager. The fact that benzonitrile on treatment with potassium superoxide in dry benzene containing 18-crown-6 ether fails to react after 2 days at ambient temperature[1] and that cinnamonitrile is stable to superoxide in pyridine[2] does not rule out the possibility that superoxide in Me_2SO is capable of directly attacking a cyano group. But it certainly encourages one to consider alternate mechanisms.

Thus, although we employed dry reagents and reasonable precautions, we made no effort rigorously to exclude moisture. Adventitious water would react with superoxide as shown in eq 1,[4] and this would likely be followed by a

$$H_2O + 2O_2^{-}\cdot \rightarrow HO^- + HOO^- + O_2 \qquad (1)$$

$$HOO^- + Me_2SO \rightarrow HO^- + Me_2SO_2 \qquad (2)$$

second reaction–that of eq 2.[5] The sodium hydroxide so

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[1] J. San Filippo, Jr., L. J. Romano, C. Chern, and J. S. Valentine, *J. Org. Chem.*, **41**, 586 (1976).

[2] M. J. Gibian, D. T. Sawyer, T. Ungermann, R. Tangpoonpholvivat, and M. M. Morrison, *J. Am. Chem. Soc.*, **101**, 640 (1979).

[3] E. Lee-Ruff, *Chem. Soc. Rev.*, **6**, 195 (1977).

[4] J. Wilshire and D. T. Sawyer, *Acc. Chem. Res.*, 105 (1979).